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Zechstein copper-bearing shales as a potential resource of rhenium in Poland

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Mineral raw materials are an essential component of the global economy for the development of new technologies. One such element is rhenium, whose unique properties have led to its numerous specialized applications, particularly in the aerospace industry. The Zechstein copper-bearing shale (Kupferschiefer) formation, which occurs in Germany and Poland, is a crucial rhenium resource. In the copper ore deposit exploited by KGHM Polska Miedź S.A., rhenium is concentrated significantly in the copper-bearing shales, with traces in the adjacent rocks. The maximum rhenium content in these shales reaches 15 ppm, with a mean content of 1.1 ppm. Rhenium resources in the mining areas have been estimated at 700 Mg, and similar values should be attributed to the prospective areas. In the long term, this means an effectively sustainable resource base for mining rhenium production by KGHM Polska Miedź S.A. The development of technology for the recovery of rhenium via acids flushing smelter gases has made it possible to set up appropriate installation units at the copper smelters of KGHM Polska Miedź S.A. and to produce ammonium perrhenate and metallic rhenium. Since 2006, Poland's share in global rhenium mine production has been increasing significantly, currently reaching 9.5 Mg/year. For many years, the main producer of rhenium, with mine production of 27–30 Mg Re/year, has been Chile. We provide comprehensive data on the concentration of rhenium in the deposits currently exploited by KGHM Polska Miedź S.A. and in prospective areas in a context of global resources. We discuss: the production of rhenium by Europe's only company extracting this metal from its own sources; its further prospects; the contemporary global market and its trends; and rhenium applications in the global economy.

Key words: rhenium, copper-bearing shales, Fore-Sudetic Monocline, mineral resources.

INTRODUCTION

The management and use of by-products of the main production process play an important role in the operations of global mining companies. Since the beginning of its participation in the metals market, KGHM Polska Miedź S.A. has taken active steps to manage a range of elements hosted in copper ore deposits. Given their diversity, some elements increase the value of the deposit, while others have a negative impact on the technological process flow and work or natural environment. Among recovered elements, Ag is of primary importance, which justifies the deposit's Cu-Ag designation. Other recovered elements include Pb, Ni, Se, Au, Pt and Pd and Re. In 2022, the output volumes of these elements were as follows: Ag – 1298 t, Pb – 28.77 kt, Se – 81.71 t, nickel sulphate – 3.24 kt, Au – 762 kg, and several tens of kilograms of platinum. Rhenium occupies a particular position within the recovered elements and its output of 9.5 t qualifies KGHM Polska Miedź S.A. as a significant player in the global economy of this metal.

Mineral raw materials are an important component of the global economy, especially for the development of new technologies. Hence the need to qualify them as strategic and critical to the economy. Since 2011, the European Commission (2020) has published such lists. The latest 2023 classification covers 27 elements including nine critical ones. The list of strategic elements for the US economy includes 50 elements. However, rhenium is not listed on any of these lists. In the Polish literature, the issue of strategic and critical elements has long been discussed (Smakowski, 2011; Radwanek-Bąk et al., 2018). Among the elements recovered by KGHM Polska Miedź S.A. from copper ores, only Ag and Pt-Pd are classified as critical. Regardless of the absence of rhenium from the formal designation, it is an important element with applications in highly specialised industries.

Rhenium is characterized by its unique chemical properties. Its particularly high melting point, hardness and abrasion resistance enable specialized high-tech applications. Rhenium-nickel or tungsten-molybdenum alloys known as superalloys have excellent mechanical properties at high temperatures and are resistant to corrosion under extreme conditions. They are mainly used in the aerospace (e.g., Boeing, Airbus), rocket and space industries, where ~80% of rhenium is consumed by the leading companies in this field: General Electric, Pratt & Whitney and Rolls-Royce.

Regrettably, there is also widespread use of rhenium for military purposes, where it is used as a core for anti-tank missiles

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and for combat aircraft (e.g., F-16, F-35). The second most popular rhenium application, accounting for ~15% of consumption, is for the production of high-octane unleaded petrol; Pt-Re-containing catalysts improve the efficiency of refineries producing high-quality gasoline. Rhenium compounds also play an important role in medicine, particularly in oncology at the treatment of radioisotope therapy, which relies on the interaction of beta radiation emitted by the radioactive rhenium isotope ^{186}Re. Superalloys used in the nuclear power industry form components of cladding in which the nuclear fuel is encased, and here an Nb-Re alloy is used. New-generation liquid lithium reactors containing a Mo-Re alloy are virtually corrosion-free in this environment. And, W-Re alloys with ThO_2 have been used in thermionic energy converters mounted on space probes and instruments.

RHENIUM, ITS RESERVES AND IMPORTANCE

Rhenium is one of the rarest elements in the Earth's crust; its abundance has been estimated at the very low level of 0.001 ppm. There are no known rhenium deposits. For economic purposes, it is mainly obtained as a by-product of by-products of the processing of molybdenum and copper ores. Until recently, many publications have reported global rhenium reserves in these Mo and Cu deposits as of 17 kt. Most of the ore deposits containing rhenium are located in the western Cordillera of North and South America, stretching from Alaska to Peru and Chile. The presence of rhenium is mainly associated with magmatic input into porphyry deposits of copper, molybdenum and copper, copper and gold, occasionally copper and nickel, and exceptionally molybdenite. The rhenium content of porphyry deposits is typically 0.1–0.6 ppm; the exceptionally rich Marlin molybdenite deposit in Australia contains 22 ppm Re (Brainard, 2023). The range of Re contents in particular mines and types of deposits and, in this context, the position of the ore deposit of KGHM Polska Miedź S.A. (marked as Lubin), is shown in Figure 1.

The main producer of rhenium from porphyry deposits is Chile, accounting for 55% of mine production. This type of mineralization also occurs in China, the USA, Peru, Mexico, Armenia, Australia, and elsewhere (Werner et al., 2023). The few stratified deposits are associated with a copper-bearing formation in Kazakhstan and uranium sediment-hosted deposits in

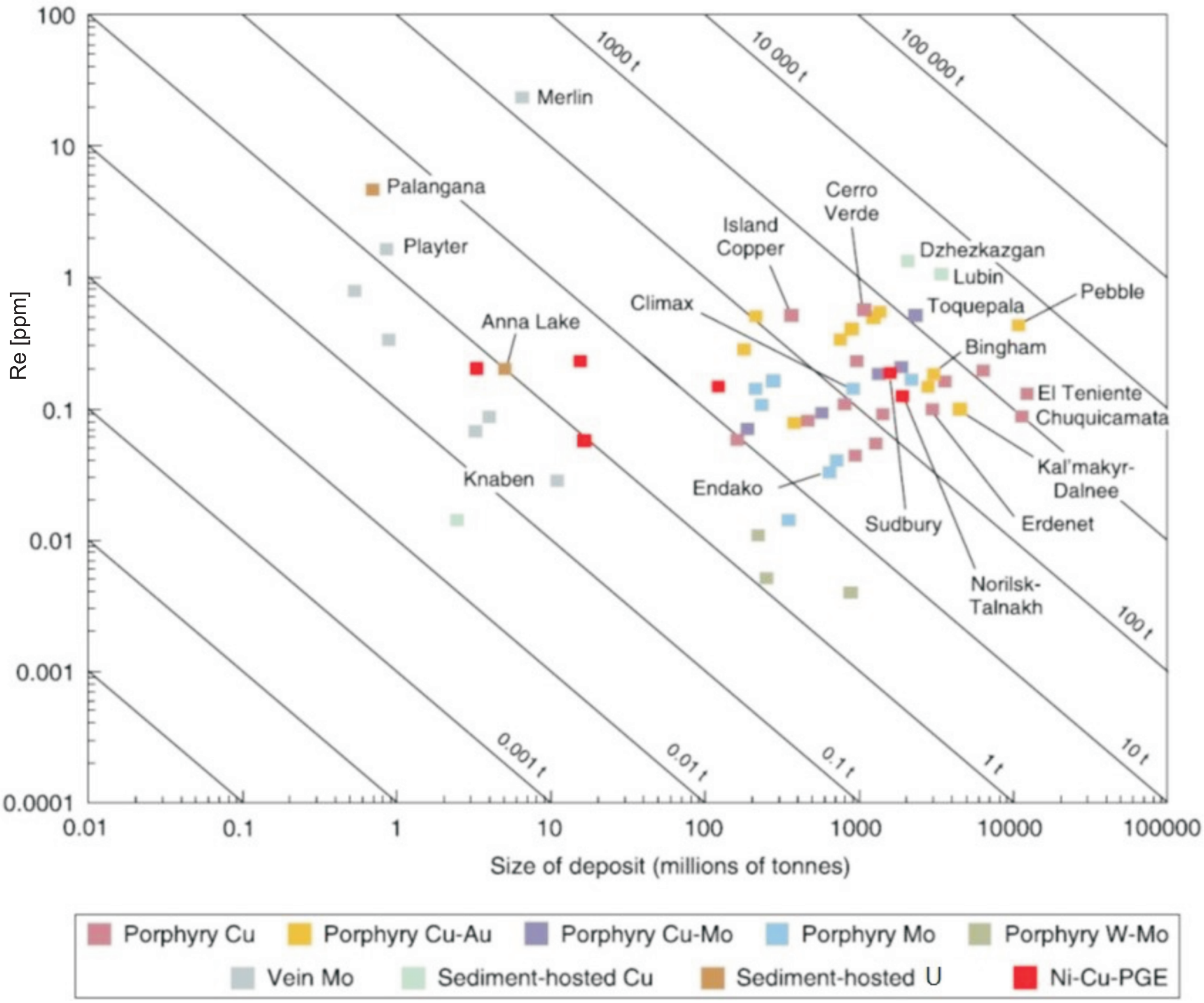

Fig. 1. Rhenium content relative to deposit size (Millensifer et al., 2014)

Kazakhstan and Uzbekistan. In Europe, the presence of rhenium has been found in the Zechstein Group, mainly in copper-bearing shales known as the Kupferschiefer in the Zechstein rocks of Germany and Poland. Yet, rhenium is recovered only from the Cu-Ag deposits of the Fore-Sudetic Monocline.

Rhenium has also been found in strata containing organic matter in bituminous shales, in bituminous and lignite coals, and in crude oil. The content of this element varies widely, typically between 0.3 and 1 ppm, reaching higher values with increased organic contents. The presence of rhenium in coals and crude oil is intermittent, with up to 1.3 ppm in coals and up to 0.2 ppm in oil (Kijewski and Wirth, 2011).

Estimates of rhenium reserves based on an analysis of metal ore deposits were made by Werner et al. (2023). The authors reviewed 618 known deposits hosting resources of Cu and Mo based on their exploration level. They estimated that these deposits host somewhere between ~55,000 and 140,000 t of Re. These authors carried out a more comprehensive and detailed analysis of 2018 deposits, listing these in the text, of which 181 were classified as porphyry-type deposits. They reported rhenium resources of 47 kt, of which 39 kt are hosted in porphyry deposits. With current global rhenium consumption of ~55 t Re/year, their estimate indicates sufficiency to meet global long-term demand.

Werner et al. (2023) also provided a useful summary of rhenium resources based on the main producers, taking into account the certainty of the sources (Fig. 2). This shows that Poland is a main contributor, ranking just after Chile, the USA and Canada. Yet, in their assessment, Polish rhenium resources were considered as of low certainty.

Based on current and previous data (Kijewski and Wirth, 2011), it appears that the amount of rhenium entering the technological cycle of KGHM Polska Miedź S.A. remains at a high and stable level in the range of 14–24 t in 1986–2010 and somewhat lower (8.6–14.2 t/year) in 2011–2022. Taking into account the balance resources of copper ore to a depth of 1200 m and the mean rhenium content in the deposit of 0.6 ppm (Kijewski and Jarosz, 1987), potential rhenium resources in the KGHM Polska Miedź S.A. concession areas have been estimated at over 700 t. If we consider deposits in the documented areas of Retków, Głogów and Bytom Odrzański, these resources can be estimated at a similar level of 700 t. The rhenium-bearing capacity in these areas is corroborated by the most recent research carried out on a copper deposit documented in the Nowa Sól area. This means that the Polish rhenium resources in the Zechstein of the Fore-Sudetic Monocline can be regarded as belonging to certain groups.

In their analysis of global rhenium resources, Werner et al. (2023) also drew attention to the correlation of rhenium production with copper and molybdenum production volumes. Figure 3 shows, over a significantly long and representative period since 1983, an increase in the production of rhenium and its correlation with the main carriers, the observed changes in this relationship being related to the mining production of the basic metals (Mo, Cu).

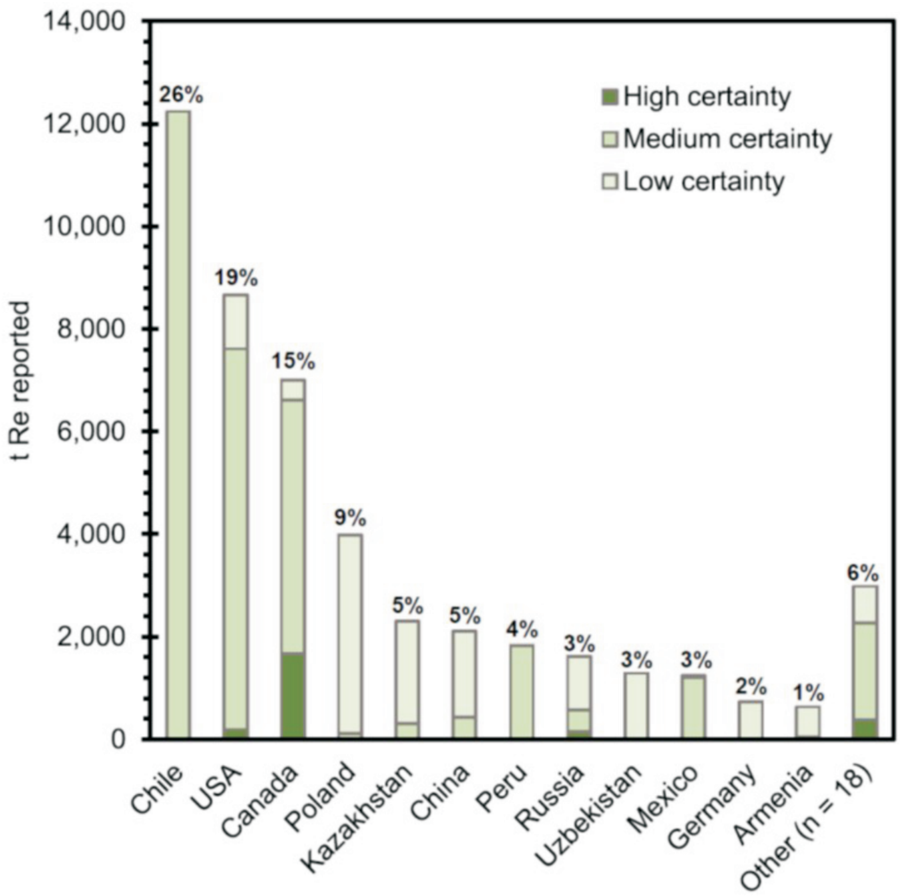

Fig. 2. Global rhenium resources classified according to the source quality scale (Werner et al., 2023)

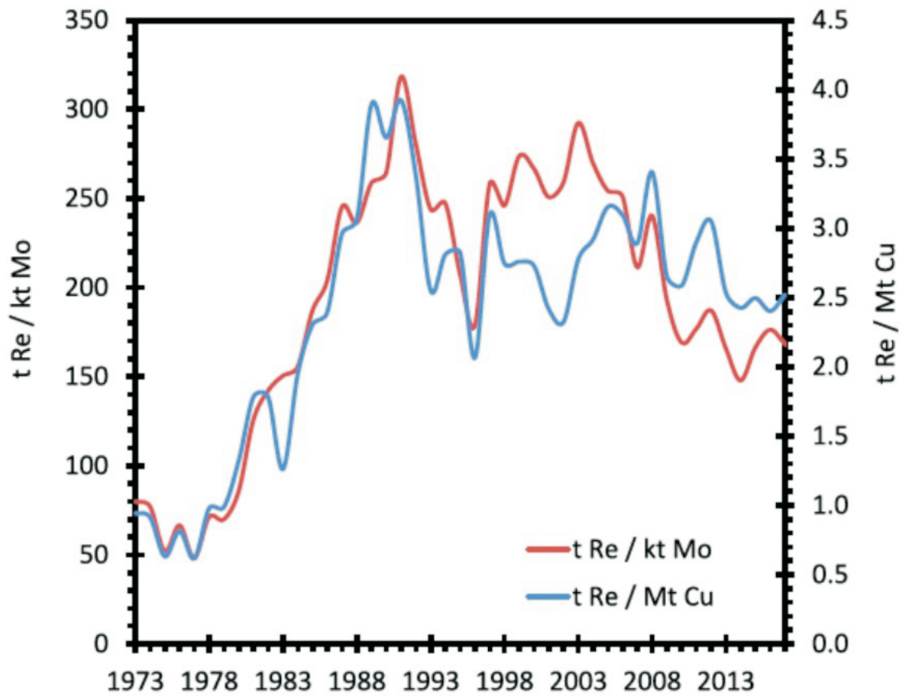

Fig. 3. Global rhenium production per unit of Cu and Mo production from 1973 to 2017 (Werner et al., 2023)

OCCURRENCE OF RHENIUM IN THE Cu-Ag DEPOSIT OF THE FORE-SUDETIC MONOCLINE

Rhenium is one many elements found in the copper ore deposit, with concentrations occurring mainly in the copper-bearing shale horizon. The basic exploration of the content and distribution of particular elements, including rhenium, is possible thanks to comprehensive analyses carried out at the deposit logging stage. Also, accessory elements have been characterized in mineralogical and geochemical studies, which constitute another more detailed source of information. These studies were conducted for scientific and practical purposes aimed at full exploitation of the deposit. They are mainly mineralogical in nature and were initiated at the Jagiellonian University, Kraków, by Prof. Cz. Harańczyk, then at the AGH University in Kraków by the team of Prof. M. Banaś. These studies involved the mechanical processing of ores, carried out at the Institute of Non-Ferrous Materials in Gliwice by Dr. Z. Grzebieluch, and mainly by mgr inż J. Jarosz at the Research and Experimental Department in Lubin. The work concludes with the recognition of a set of over 100 ore minerals (Piestrzyński, 2007) with no rhenium minerals being identified. The latest mineralogical and geochemical studies of rhenium are related to the work of the Polish Geological Institute – National Research Institute (PIG-PIB; Mikulski et al., 2018, 2020), a doctoral thesis (Raczyńska, 2017) and the Nowa Sól deposit documented by the Miedzi Copper Corporation (MCC; Speczik, 2023, pers. comm.).

According to existing studies (Serkies, 1972; Banaś et al., 1979; Kijewski and Jarosz, 1987; Kucha, 1990; Kucha et al., 1994; Piestrzyński, 2007; Kijewski and Wirth, 2011), high and varying rhenium contents are associated with the reduced zone of the copper-bearing formation. Rhenium at levels of 0.02–0.148 ppm was also found in the oxidized zone (Piestrzyński et al., 2002). However, there were discrepancies between the results of the comprehensive analyses performed during the deposit logging stage and the subsequent research based on samples taken from mining excavations. During the deposit logging stage, systematic rhenium estimates included the full copper-bearing shale profile as the primary deposit layer. In this case, the maximum rhenium content in a single shale profile was estimated at 15 ppm with a mean of 1.1 ppm for shales from the entire explored area and 0.06 ppm Re in the balance deposit (Kijewski and Jarosz, 1987). On the other hand, individual samples taken randomly from shales during mining excavation research at an early stage of mining operations were found to have a high rhenium content of up to 200 ppm, with the most common range being 1–30 ppm (Banaś et al., 1979). These results as well as those from later studies (Raczyńska, 2017; Mikulski et al., 2020), clearly deviate from the values that were obtained from the methodical sampling carried out during the deposit logging stage.

The analysis of the available results of determination of the rhenium content in the Fore-Sudetic Monocline copper ore deposit shows: the average rhenium content in the copper-bearing shale ore is 1.1 ppm; in the carbonate ore 0.5 ppm; in the sandstone ore 0.4 ppm; and in the balance sheet ore deposit 0.6 ppm (Kijewski and Jarosz, 1987). This means a 400–1100 fold enrichment in rhenium in the deposit and individual ore varieties compared to the average in the Earth's crust.

New results were reported by Raczyńska (2017) based on the study of samples taken from mine workings. She analysed 35 samples, of which 19 are Kupferschiefer ore samples, for rhenium, the basic elements of the deposit (Cu, Ag) and accompanying elements (Mo, Ni, Co, Zn, Mn, V, Fe and Corg). The rhenium-related results obtained in the Kupferschiefer ore are at 0.98–18.78 ppm in the area defined as Polkowice and 2.33–20.28 ppm in the Rudna area. In other ore varieties, rhenium was found in individual samples at 0.97–5.97 ppm in the sandstone ore and 1.47 ppm in the carbonate ore. Based on these results, Raczyńska (2017) determined the correlation of individual elements with rhenium: Mo-Re – 0.84; Ag-Re – 0.60; Ni-Re – 0.54 and Fe-Re – 0.48.

Using archival borehole core samples, as part of the work of the PIG-PIB, Mikulski et al. (2018, 2020) carried out mineralogical and geochemical tests on 71 samples from the Polkowice, Sieroszowice and Rudna mining areas. The results confirmed the rhenium content in the range between 0.05 to 68.7 ppm and an arithmetic mean of 5.8 ppm. Unfortunately, these chemical analyses were mainly concerned with Kupferschiefer ore and did not include rhenium determination in the base ore minerals (chalcocite, digenite, djurleite, chalcopyrite, bornite), which does not bring us any closer to identifying the sources of this element. The most intensely mineralized intervals usually occur above the roof part of the Weissliegend sandstone within the layer defined as copper-bearing clay-organic shale. According to these authors, the results showed no correlation with molybdenum (Mo-Re – 0.36) and a much stronger correlation with copper (Cu-Re – 0.55) and bismuth (Bi-Re – 0.76). Cu-Re correlations of 0.70 were also reported in an earlier paper by Serkies (1972).

A separate and poorly explored issue is the presence of rhenium in ore minerals including the molybdenum minerals molybdenite and castaingite. The first studies of this relationship (Banaś et al., 1979) identified rhenium in molybdenite at up to 115 ppm, as well as in the other minerals: chalcopyrite (up to 0.6 ppm) and pyrite (up to 0.3 ppm). Later studies by Kucha (1990; Kucha et al., 1994) indicated that molybdenum phases, mainly castaingite, are the main rhenium carrier in the deposit with a mean Mo/Re ratio of 70:1. Other mineral phases, (K, Cu)Mo_2S_4 and (Pb, Cu)Mo_2S_2), appeared to contain 0.18–0.43% Re (Kucha, 2007). An original line of research is the search for sources of rhenium in ore minerals using MLA microscopy. Focusing on molybdenum minerals, Raczyńska (2017) identified only one mineral with a high Mo content (62.95 ppm), 2.83 um in size with a rhenium content of 1.47 ppm.

The most recent mineralogical and geochemical work, which also deals with rhenium from the copper ore mine area, was carried out by Fołtyn et al. (2022). This LA-ICP-MS research showed sulphides (chalcocite, djurleite, bornite, chalcopyrite, covellite, sphalerite, pyrite) in selected samples and a Re content below the detection limit. However, the authors found notable exceptions where Cu-S sulphides appear to be preferential for the presence of rhenium. Massive djurleite and chalcocite from the two carbonate rock samples showed a median of 0.67 μg/g Re (up to 3.86 μg/g Re), and in the sample where the djurleite from the shale was adjacent to the 'red spots', a median of 0.3 μg/g (up to 0.9 μg/g) was recorded. Fołtyn et al. (2022) concluded that either the structure of the djurleite may be favourable for re-incorporation, or the processes responsible for djurleite formation may also be related to Re enrichment.

A particularly valuable source of information for the assessment of rhenium prospects in new deposits located in the northern part of the Fore-Sudetic Monocline is the results obtained in the Nowa Sól deposit by the MCC group. In this area, rhenium was analysed for in 85 samples from 14 boreholes. In addition, four boreholes were drilled in other areas, giving a total of 110 samples with varying rhenium contents in the orebody: carbonate, shale and sandstone ores. In copper-bearing shales, rhenium presence is common and ranges from 0.18 to 8.70 ppm Re, with exceptionally higher contents exceeding 15 ppm. Carbonate rocks adjacent to the shale are characterized by rhenium contents with traces of up to 1.54 ppm in only a few samples. In the Weissliegend sandstones, rhenium was observed at levels of 0.04–0.4 ppm with individual cases reaching 1.83 and 2.23 ppm (S. Speczik, 2023, pers. comm.). These results corroborate the rhenium-bearing capacity of the shale layer of copper ore deposits in the Fore-Sudetic Monocline.

RHENIUM RECOVERY IN TECHNOLOGICAL PROCESSES

The beginnings of rhenium exploration in metallurgical processes date back to 1983 when specialists from the Institute of Non-Ferrous Metals in Gliwice embarked on the development of a technology for the recovery of rhenium in the form of ammonium perrhenate through precipitation from wash acids (Godycki-Ćwirko and Pluciński, 1987). Production of this compound was low and in 1985 amounted to a maximum of 100 kg. In the following years (until 1995), a total of several hundred kilograms of ammonium perrhenate were produced. The low efficiency of this process caused production to stop. There was renewed interest in rhenium between 2002 and 2005 when KGHM Metale and the Institute of Non-Ferrous Metals (Chamer et al., 2004) launched a targeted project: 'Implementation of a technology for the recovery of rhenium from wash acids of flash smelting furnace gases", which was completed with the development of a new, original technology. In brief, the process is as follows: first, acidic industrial wastes from Głogów II Copper Smelter are filtered and then passed through a special unit, that is an ion exchange column filled with ion exchange resin. The resulting solution is transferred to another unit where the final product, ammonium perrhenate with 69.4% rhenium content, is produced. The recrystallisation process makes it possible to obtain a high-quality product of metallic rhenium (Fig. 4).

Metallic rhenium is obtained by reducing ammonium perrhenate with hydrogen gas. The resulting rhenium powder is pressed and then sintered in a hydrogen atmosphere to achieve a density of 10 g/dm^3.

The implemention of this technology, which began in 2005, took place in several stages that led to the establishment of production units at the Głogów II, Głogów I and Legnica Copper Smelters. The implementation of this effective method for rhenium recovery from wash acid allowed a significant amount of ammonium perrhenate (1690 kg) to be obtained in 2005. There was an exponential increase in the output to the level of 4048 kg of ammonium perrhenate and in 2010, to 4500 kg, of which metallic rhenium was just over 600 kg. At present, the rhenium production stands at 9,000 kg/year (Table 1) and includes the following products: ammonium perrhenate, metallic rhenium powder and metallic rhenium pellets.

Ammonium perrhenate contains 69.4% Re and trace admixtures of other elements including Cu, Co, Mg, Mo, Ni, and Fe at 5 ppm and others such as Ag, Au, Pt, Pd, Si, and Ca at 10 ppm, as well as Hg at 1 ppm.

RHENIUM MARKET

Rhenium production and trade are mainly linked to the U.S. economy (consumption, imports), which uses up around 80% of the world's consumption of this element. The data provided by the U.S. Geological Survey show that, over the period 2007 to 2019, the US imported between 31.5 and 44.3 t/year while using between 33.0 and 52.6 t Re/year for production. There have been substantial quantitative changes over recent years involving a reduction in both imports to 19.0 t and consumption in production to 29.0 t in 2022 (U.S. Geological Survey, 2011–2022).

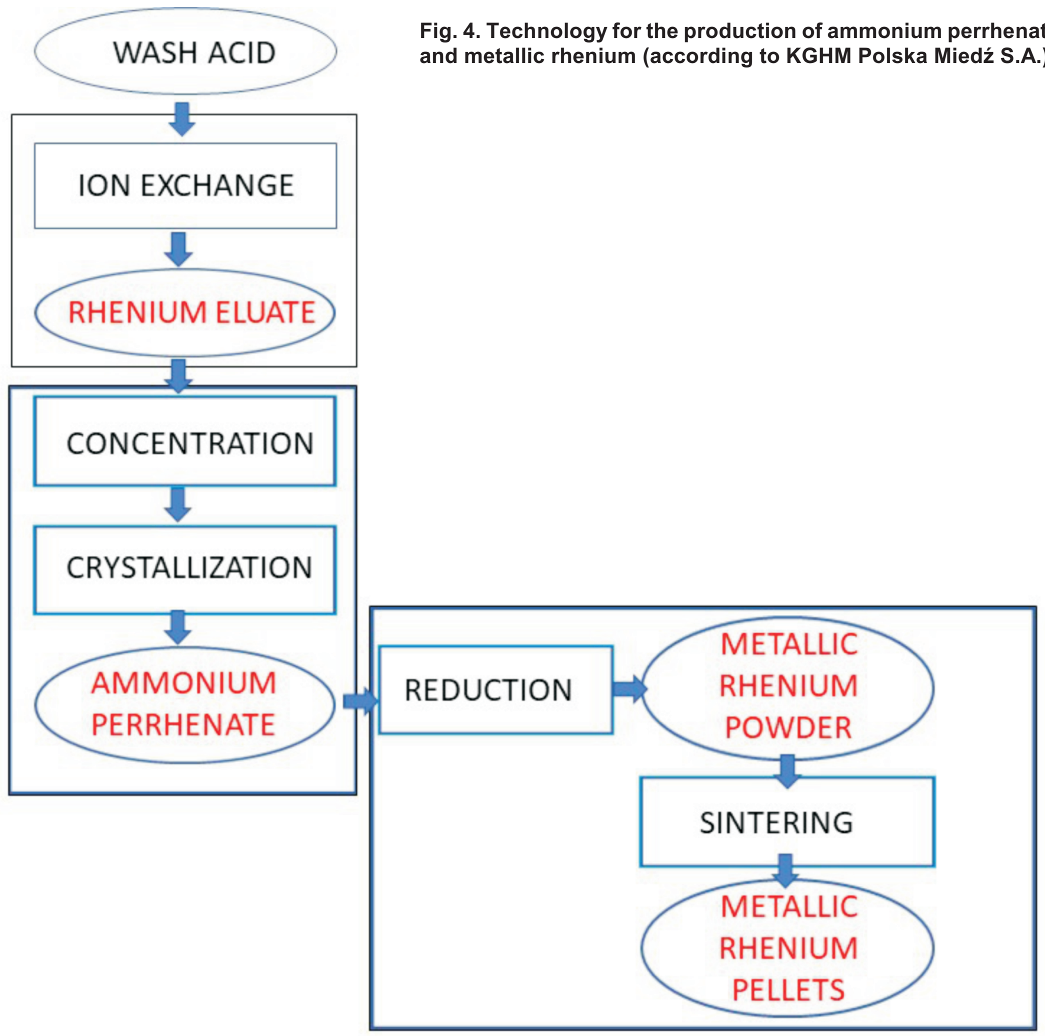

Fig. 4. Technology for the production of ammonium perrhenate and metallic rhenium (according to KGHM Polska Miedź S.A.)

Table 1

Amount in kilograms of rhenium from mine production; years: 2012–2021 (according to the U.S. Geological Survey, 2011–2022)

Country	Year						
	2012	2015	2017	2019	2020	2021	2022
Chile	27 000	26 000	27 000	30 000	30 000	30 000	29 000
USA	7 910	7 900	8 200	8 360	8 830	9 290	9 000
Poland	6 000	8 900	9 300	8 340	9 510	9 290	9 500
Uzbekistan	5 400	1 000	460	460	4 900	4 900	4 900
Kazakhstan	3 000	1 000	1 000	500	500	500	500
South Korea	–	–	–	2 800	2 800	2 800	2 800
China	–	2 400	2 500	2 500	2 500	2 500	2 500
Armenia	600	350	300	280	260	260	260
Total	52 600	49 400	48 800	53 200	59 300	59 500	58 000

For many years now, the main producer of rhenium from mine production of 27–30 t Re/year has been Chile (Table 1). Other participants in the rhenium market are changing, and so is the amount of rhenium they are bringing into the global economy. Examples include Canada, Russia and Peru, which are not included in the lists after 2010, while China's presence in rhenium mining has been noticeable since 2015. According to Brainard (2023), 26–35% of available rhenium is currently recovered from the mining production of Cu and Mo ores. Poland has been a participant in the rhenium market since 2006 and has increased its market share to its current level of 9.5 t.

Werner et al. (2023) demonstrated the changes among the rhenium producers that took place between 1963 and 2021 (Fig. 5). In that period, Chile is shown as a major source of Re supply, followed by Poland and the USA, with Uzbekistan, China and South Korea lower in the ranking.

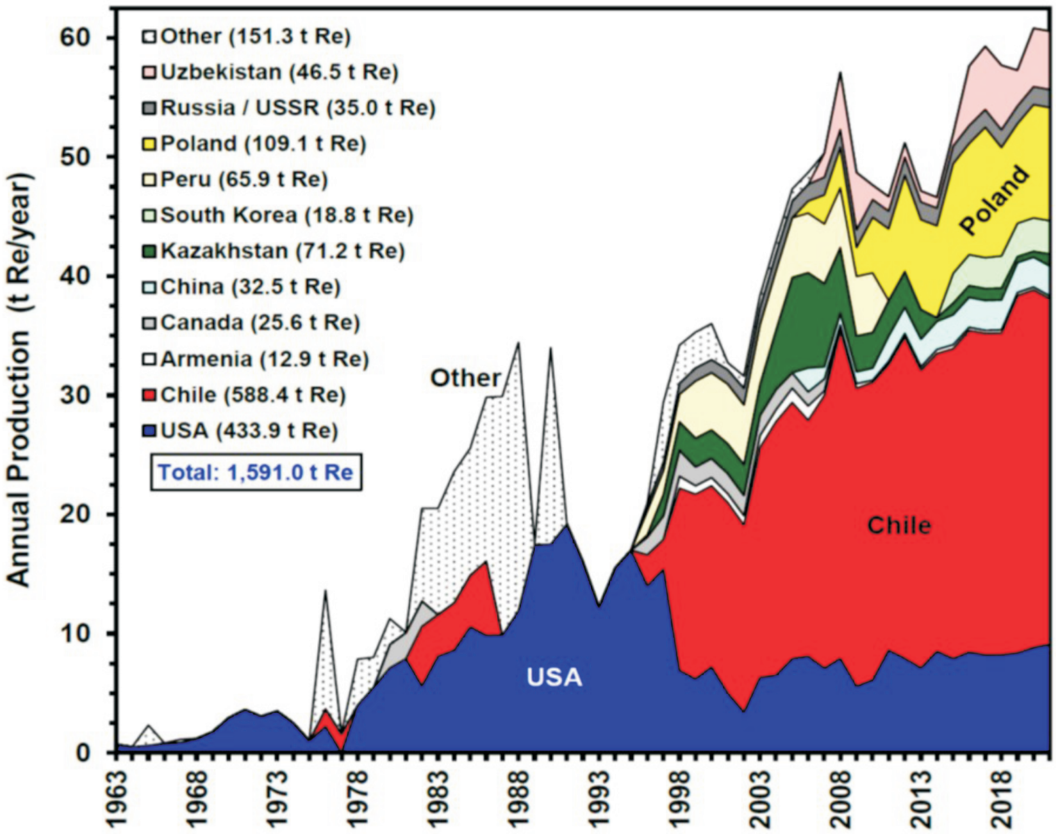

Fig. 5. Global production of primary Re by country, 1963–2021 (Werner et al., 2023)

Recycled sources should also be considered in the trading of rhenium (Fig. 6). It is estimated that ~25% of rhenium is recovered from this process. Recycling is growing mainly in the USA, which in 2020 accounted for as much as 72% of the rhenium recovered, compared to 13% in Germany, 8% in France and 7% in United Kingdom. Recovery of rhenium from Pt-Re catalysts takes place directly in a closed cycle and is estimated to be in the range of 4–15 t.

An analysis of rhenium prices over the period 1993–2022 showed their sharp rise between 2007 and 2010, peaking at USD 11500/kg (Fig. 7). This was followed by a sharp decline to USD 4400/kg in 2010 and a gradual reduction in prices to USD 1750/kg in 2020. The price increase was particularly associated with the use of superalloys in growing aerospace production and the limited supply of the metal. The economy's response to rising price levels has been the development of rhenium recov-

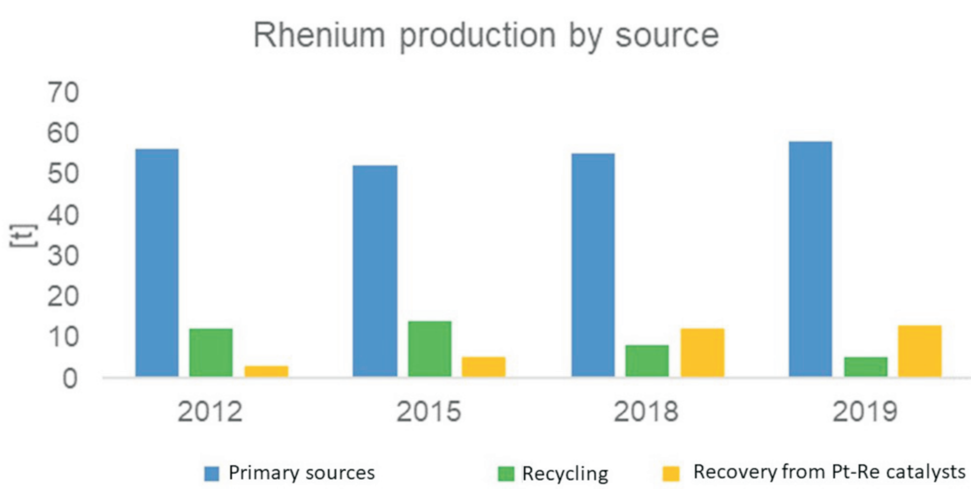

Fig. 6. Rhenium production by source (developed by Roskill)

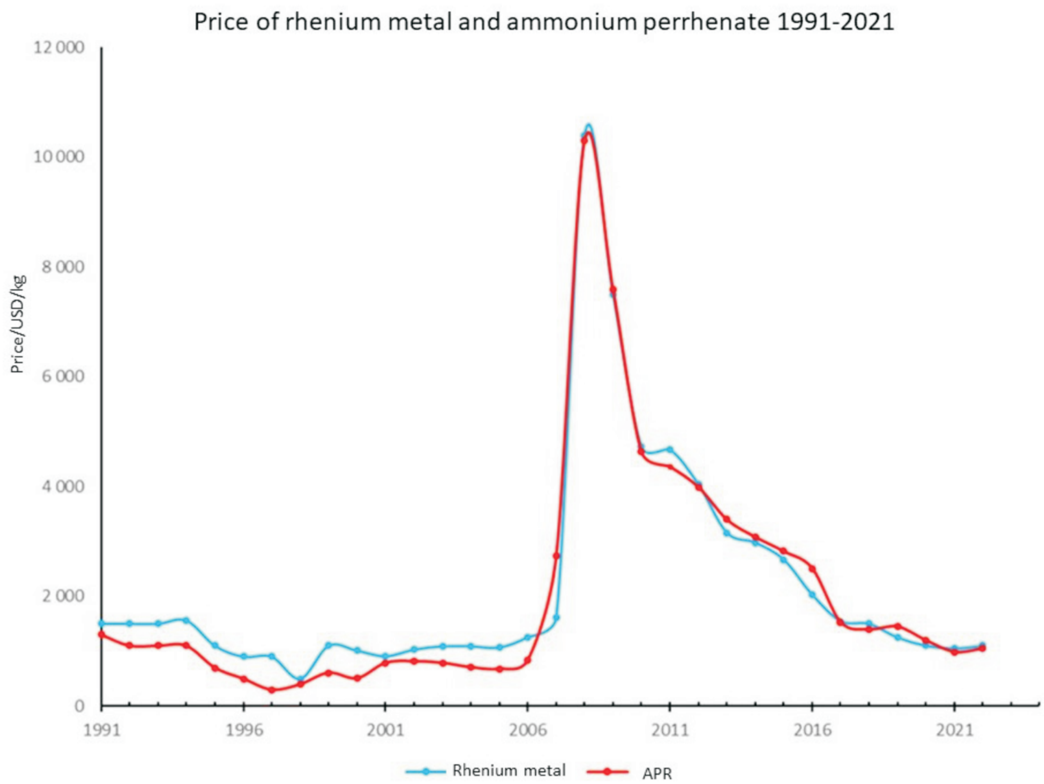

Fig. 7. Price of rhenium metal and ammonium perrhenate (source Roskill)

ery through recycling, which has mainly taken place in the USA, and new technologies in the production of superalloys. While the first generation of superalloys contained 3–6% rhenium, its successors only contained 1.5%. These processes, combined with the recessionary phase at the time, led to relatively stable rhenium prices.

In the analysis of factors impacting rhenium prices, special attention should be paid to the growing production potential of the arms industry (combat aircraft, anti-tank missiles). This is linked to the numerous current armed conflicts, especially the war in Ukraine, and the general increase in militarisation and how this process will affect price forecasts. Another factor in the potential growth of rhenium consumption is the health sector and the progress made in recent years in this area (Global Rhenium Market – Forecasts from 2023–2028). In the biomedical sector, the development of radiotherapy technologies is forecast to have an increased impact on rhenium demand. The current price of this element is just above US$ 2,000/kg and is on an upward trend.

RHENIUM IN COPPER CONCENTRATE AND PRODUCTION PROSPECTS

To date, the basic study on the occurrence and distribution of rhenium in the copper ore deposit documented dates from 1979 to 1985. It can be found in archival studies of ZBiPM Cuprum, which includes maps of the distribution of individual elements in the deposit and individual lithological ore varieties (Romanowska et al., 1984). One map covers the distribution of rhenium content in the Kupferschiefer. Analysis of the distribution of rhenium in the shale ore indicates the presence of two clearly marked zones of varying rhenium content, which will not fail to affect the development prospects for its production in the long term.

The first zone, where enrichment in rhenium is clearly visible, comprises the Polkowice mining area and the central and southern parts of the Lubin and Małomice mining areas, the Rudna and the Sieroszowice mining areas. The extent of this zone is defined by the mean rhenium content of the deposit at 1.0 ppm Re (Fig. 8). As the main resource of rhenium is the Kupferschiefer, and its concentration determines the amount of rhenium entering the technological circuit, the main focus should be on the distribution of rhenium in this layer. The highest mean rhenium content in the shale (2.67 ppm) for the entire mining area was found in the Polkowice mining area; it was much lower (1.99 ppm) in the Lubin mining area and lowest – at 1.20 ppm – in the Rudna and Sieroszowice mining areas.

The clearly rhenium-poorer second zone includes areas of deep deposits located in the northern part: the Sieroszowice, Rudna and Głogów Głęboki Przemysłowy mining areas, as well as the documented deposit areas of Bytom Odrzański, Głogów and Retków. In this zone, the presence of elevated rhenium contents in the shales is locally revealed in separate patches. The partial exploration carried out to date shows extraction results in these parts of the deposit with variously enriched contents of rhenium in the ores explored. This is indicated by a trend towards lower rhenium contents in the concentrate over the period 2003–2022. However, this does not affect the basis for assessing the rhenium-bearing capacity of these areas. This is corroborated by the most recent studies of a deep copper ore deposit in the Nowa Sól area (MCC works) from 2023.

While core sample analysis indicates mineral-enriched zones, the technological samples (feed, concentrate) data characterize the mean values for the extracted ore produced in particular years and at particular ore enrichment plants. The 1986 results reported in the official publication (Czajowski, 1987) pro-

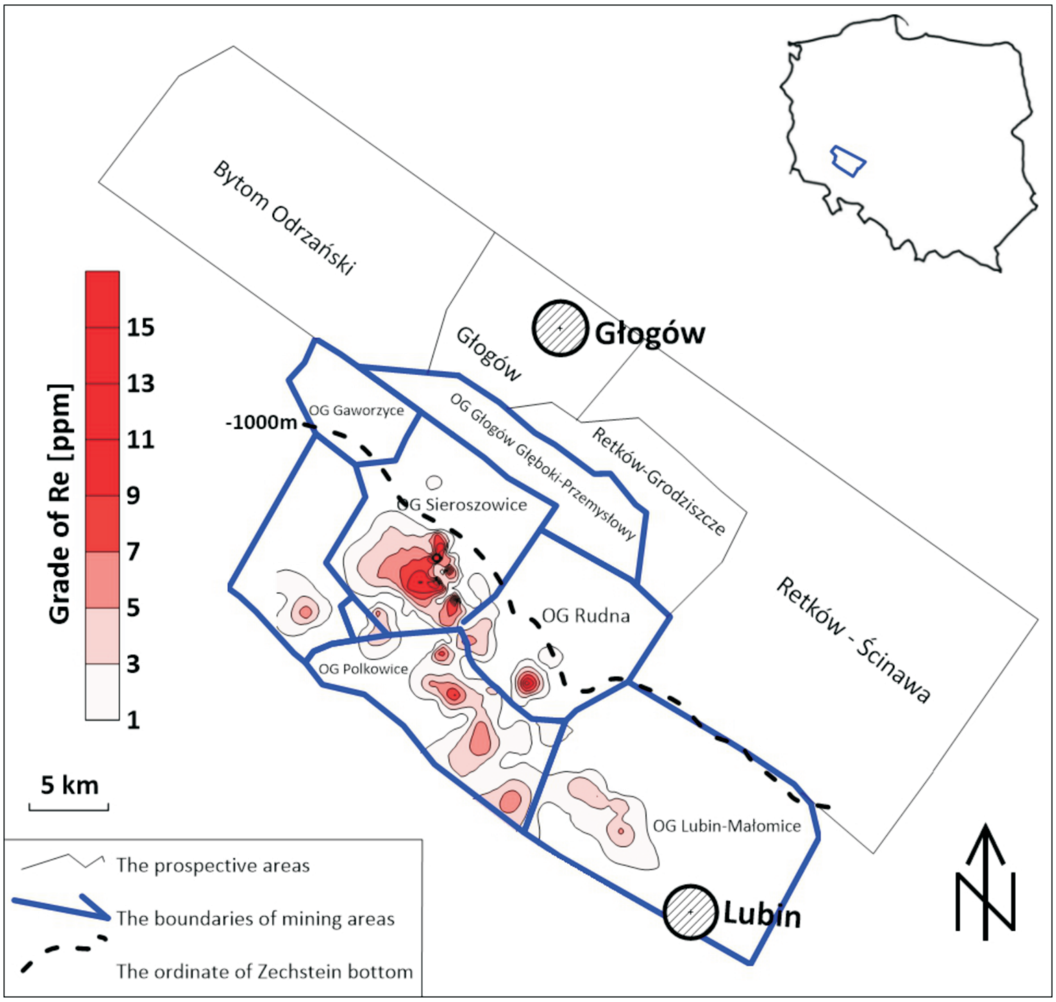

Fig. 8. Distribution of rhenium in copper-bearing shales in KGHM Polska Miedź S.A. mining areas

vided a reference point for assessing changes in the rhenium content of the feed (1.3–2.0 ppm) and concentrate (8.0–10 ppm). However, the information regarding the feed in the following years is very scarce and only concerns the years 1992–1996. At that time, the rhenium content of the feed was determined to be: 1.0–1.6 ppm at the ZWR ore enrichment plant, Lubin, 1.4–2.0 ppm at ZWR Polkowice and 1.2–1.8 ppm at ZWR Rudna.

Unfortunately, after 1996, rhenium determination in feeds was discontinued, which makes it difficult to explore rhenium contents introduced into the circuit in relation to ore varieties and mining regions, to assess the level of its enrichment and forecasting possibilities. Previous work (Sobierajski et al., 2007) showed that the processing of ores results in a significant (4.5–8 times) enrichment of the copper concentrate in rhenium relative to the feed. Rhenium estimates in the concentrate carried out since 1992 (Kijewski and Wirth, 2011) indicated its varying content, ranging from 7.1–17.5 ppm at ZWR Polkowice and 5.7–15.3 ppm at ZWR Rudna, while at ZWR Lubin it ranges from 2.8 to 12.3 ppm (Figs. 9 and 10).

Based on the rhenium content and the volume of concentrate produced, the amount of rhenium entering the technological circle at KGHM's copper smelters was determined as potential material for the production of ammonium perrhenate and metallic rhenium. This is clearly illustrated by the example of ZWR Lubin, where the concentrate is produced exclusively from ore from the Lubin and Małomice mining areas, where ore with similar characteristics is mined. The calculated amount of rhenium in the ZWR Lubin concentrate was stable between 1992 and 1996, remaining in the range of 3070–4880 kg/y. Since 2008, the amount of rhenium in the concentrate has decreased significantly (Table 2). In this case, a correlation can be observed between the amount of rhenium and the mining regions. In recent years, there has been an increase in mining activities from the northern part of the deposit with a definite predominance of rhenium-diluted and rhenium-low sandstone ore, resulting in a clear reduction in rhenium content (2.5–4.5 ppm) in the concentrate and consequently a reduction in its amount entering the smelting process (Table 3 and Fig. 9).

ZWR Polkowice processes mainly carbonate-shale ore from OG Sieroszowice with an increased rhenium content in the ore, which affects the quality of the concentrate. Following a period of processing the sandstone ore dominant in the feed and an increase in the exploration from the Głogów Głęboki Przemysłowy mining area, ZWR Rudna is approaching Re values characteristic of carbonate-shale ores (Fig. 9). The dependence of the rhenium grades in the concentrate on the quality of the ore is confirmed by the 20-year averaged Re value of, respectively: 9.6 ppm for ZWR Polkowice, 8.65 ppm for ZWR Rudna and 4.1 ppm for ZWR Lubin.

In total, the largest quantities of rhenium (between 18.7 and 24.4 mt/y) entered into the circuit with copper concentrates be-

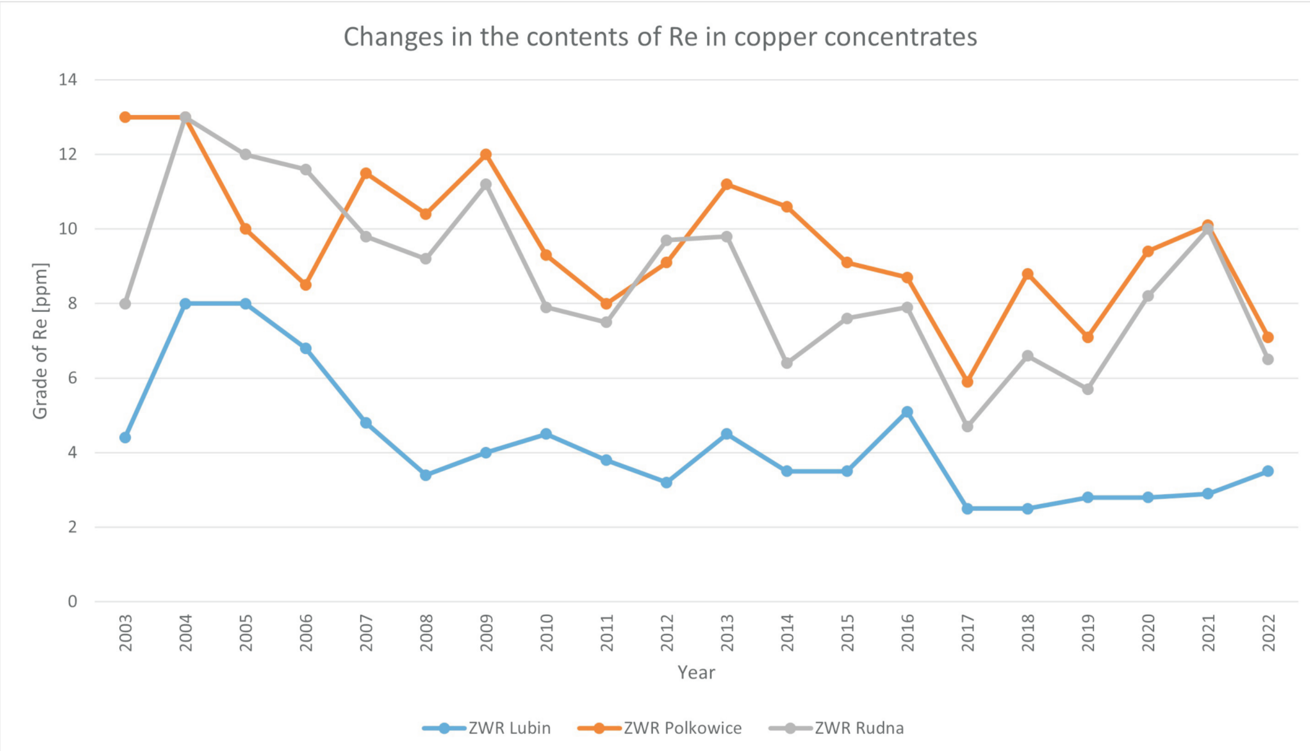

Fig. 9. Changes in rhenium content in copper concentrates in KGHM Polska Miedź S.A. ore enrichment plants in the years 2003–2022

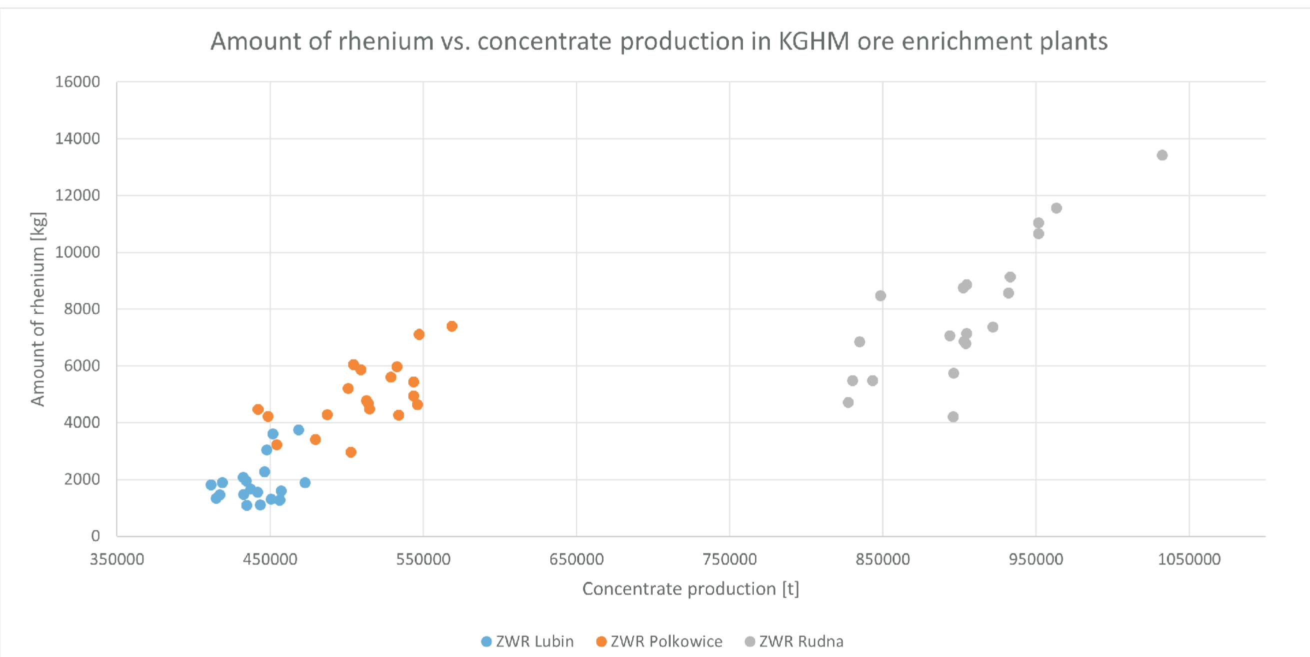

Fig. 10. Amount of rhenium *versus* concentrate production in the KGHM Polska Miedź S.A. ore enrichment plants

tween 1992 and 2006. In subsequent years, the level was lower and remained between 15.0 and 18.6 mt/y with a clear reduction to 13.79 mt in 2010. The latest results covering the period up to 2021 indicate a further reduction in the amount of rhenium in the copper concentrate (Table 2), particularly at ZWR Lubin. Moreover, rhenium grades are balanced off in the concentrate from ZWR Polkowice and ZWR Rudna. This is indicated by the transfer of a significant proportion of ore exploration from the Rudna mining area processed at ZWR Rudna to the Głogów Głęboki area with a significant proportion of shale ore as the main ore carrier.

The current state of knowledge about the rhenium in the deposit, especially from the northern part of the Sieroszowice and Głogów Głęboki, raises the question of how mining of low exploration confidence rhenium content areas can impact the quality of the ore (Fig. 1) and whether it may cause changes in the rhenium content of the concentrate. The results of studies of deep deposits from the Nowa Sól area partially answer this

Table 2

Contents and quantities of rhenium in copper concentrates

Year	ZWR Lubin concentrate		ZWR Polkowice concentrate		ZWR Rudna concentrate	
	Content of Re [ppm]	Amount of Re [kg]	Content of Re [ppm]	Amount of Re [kg]	Content of Re [ppm]	Amount of Re [kg]
2003	4.4	1811	13	7113	8	7374
2004	8	3614	13	7394	13	13422
2005	8	3748	10	5437	12	11559
2006	6.8	3045	8.5	4641	11.6	11038
2007	4.8	2076	11.5	5858	9.8	9144
2008	3.4	1471	10.4	5210	9.2	8575
2009	4	1892	12	6054	11.2	10657
2010	4.5	1955	9.3	4771	7.9	7060
2011	3.8	1662	8	4271	7.5	6781
2012	3.2	1327	9.1	4946	9.7	8753
2013	4.5	1884	11.2	5967	9.8	8867
2014	3.5	1460	10.6	5605	6.4	5737
2015	3.5	1547	9.1	4678	7.6	6862
2016	5.1	2276	8.7	4480	7.9	7147
2017	2.5	1087	5.9	2965	4.7	4210
2018	2.5	1109	8.8	4289	6.6	5479
2019	2.8	1277	7.1	3406	5.7	4716
2020	2.8	1278	9.4	4216	8.2	6845
2021	2.9	1307	10.1	4465	10	8483
2022	3.5	1600	7.1	3226	6.5	5482

Table 3

Amount of rhenium introduced into the technological circuit with the copper concentrate [mt]

Year	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Rhenium content [kg] in copper concentrate	16 298	24 430	20 744	18 724	17 078	15 256	18 603	13 787	12 713	15 026
Year	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
Rhenium content [kg] in copper concentrate	16 718	12 801	13 087	13 902	8 262	10 877	9 399	12 340	14 255	10 308

question, demonstrating the continuity of geological conditions and the rhenium-bearing capacity of the area. Extending the scope of analyses carried out in the geological departments of the ZG Rudna and ZG Polkowice-Sieroszowice mines to include the content of rhenium in the level of copper-bearing shale will alleviate these doubts as to the potential production capacity of this element.

Since 2017, the KGHM Polska Miedź S.A. copper smelters have also been treating certain quantities of concentrates from other areas. These also contain some rhenium, resulting in some rhenium production from the concentrates purchased. This impact was particularly seen in 2017–2019 when a higher level of rhenium production was reported (Table 1) relative to the rhenium content in the concentrate declared by the enrichment plants (Table 3). Experience over the years has shown the potential KGHM Polska Miedź S.A.'s own treated ore, irrespective of the share of purchased concentrates. In particular, the volume of Kupferschiefer ore provides the basis for maintaining rhenium production at sustainable levels.

CONCLUSIONS

The copper-silver ore deposit of the Fore-Sudetic Monocline is one of the few stratified metal deposits that form the basis for the mining recovery of rhenium. This metal, valuable in many modern areas of the economy, is found in the ore in small quantities and is a classic example of recovery as a by-product from another by-product. Global rhenium reserves in Cu-Mo ore deposits have been estimated at 49 kt (Werner et al., 2023). Currently, 26–35% of the rhenium contained in the ore obtained from this type of deposit is recovered.

The development of technology for the recovery of rhenium from wash acids of smelter gases allowed KGHM Polska Miedź S.A. to set up appropriate facilities at the copper smelters of Głogów I, Głogów II and Legnica and the production of ammonium perrhenate and rhenium metal. Since 2006, Poland's share in global rhenium mine production has been increasing significantly, making Poland a significant and sustainable participant in this market, second to Chile and alongside the USA.

Looking ahead, the exploration of the deposit up until now and the rhenium content in the concentrate indicate a trend towards dilution of this element. Does this imply that, as appears from the map of the distribution of rhenium in the concession areas, the parts of the deposit with the highest rhenium-bearing capacity have been extracted, and new areas do not guarantee the quality of the ore? This perspective can be tested by expanding geological analyses to include rhenium within ongoing deposit exploration. Furthermore, new mining areas demonstrate a favourable ratio of shale-carbonate ore to low-rhenium sandstone ore. Studies of the deep "Nowa Sól" deposit (based on MCC information) also confirm the enrichment of the shale in rhenium, indicating the local distribution of this valuable element. This leads to the conclusion that KGHM Polska Miedź S.A. has the potential for further production of rhenium from its own resources.

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