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A new approach to the problems of recycling spent catalytic converters

Nowe podejście do problematyki recyklingu zużytych katalizatorów

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Keywords: *precious metals, bioleaching, biometallurgy, hydrometallurgy, cordierite substrate, cyanogenic microorganism*

Abstract
In the last decade the main application of precious metals has been the production of auto catalytic converters. The life time of catalytic converters is limited and after that time remains a rich source of platinum group metals. The article presents currently used pyro-and hydrometallurgical precious metals recovery methods. However, particular attention is dedicated to the new trends in biohydrometallurgy, focused on the possibility of using cyanogenic microorganisms potential in biological leaching of precious metals. A review of the achievements and results of laboratory tests for the extraction of precious metals from waste materials by bacteria leaching has been presented. The areas of research that require further explanation and solutions have been indicated. The article also gives suggestions for further laboratory work towards the use of cyanogenic microorganisms for recovery of platinum group metals from solid waste. The work also presents innovative solutions for the management of residues (specifically cordierite carriers) following the processing of used automotive catalytic converters through pyro-, hydro-, or bio-based methods.

Słowa kluczowe: *metale szlachetne, bioługowanie, biometalurgia, hydrometalurgia, nośnik kordierytowy, mikroorganizmy cyjanogenne*

Streszczenie
W ostatniej dekadzie głównym zastosowaniem metali szlachetnych była produkcja katalizatorów samochodowych. Żywotność katalizatorów jest ograniczona i po tym czasie pozostaje bogatym źródłem metali z grupy platynowców. W artykule przedstawiono obecnie stosowane metody odzyskiwania piro- i hydrometalurgicznego metali szlachetnych. Szczególną uwagę poświęcono jednak nowym trendom w biohydrometalurgii, skupiającym się na możliwości wykorzystania potencjału mikroorganizmów cyjanogennych w biologicznym ługowaniu metali szlachetnych. W pracy przedstawiono przegląd osiągnięć i wyników badań laboratoryjnych ekstrakcji metali szlachetnych z materiałów odpadowych metodą wymywania bakteryjnego, wskazano obszary badań wymagające dalszego wyjaśnienia i rozwiązań. W artykule przedstawiono także sugestie dotyczące dalszych prac laboratoryjnych,, w kierunku wykorzystania mikroorganizmów cyjanogennych do odzyskiwania metali z grupy platynowców z odpadów stałych. W pracy przedstawiono także innowacyjne rozwiązania w zakresie zagospodarowania pozostałości (w szczególności nośników kordierytowych) po przetworzeniu zużytych katalizatorów samochodowych metodami pirometalurgicznymi, hydrohydrometalurgicznymi i biohydrometalurgicznymi.

1. INTRODUCTION

Platinum Group Metals – PGMs (platinum, palladium, rhodium and iridium, ruthenium and osmium) are widely applied in many industrial areas such as: electronics sector (hard disks, multilayer ceramic capacitors, integrated circuits), production of liquid crystal displays, jewellery or as catalysts in chemical industry. Catalysts are used in all sectors of chemical industry [21]: in basic chemistry (synthesis of sulfuric and nitric acid, ammonia, methanol and aromatics, in petrochemistry, refining and reactions of fluid catalytic cracking (FCC), resid fluid cracking catalyst (RFCC), hydrodesulfurization (HDS) and hydrotreatment, in auto industry to reduce of pollution by removing NO, CO and hydrocarbons in exhaust emissions, in variety of industrial processes.

The sector of automotive industry where catalytic converters for cars are manufactured is still leading one demand for PGMs (especially Pt, Pd and Rh). The data concerning demand and global use of platinum, rhodium and palladium in various industries in the years 2020-2022 are summarized in Table 1.

Today almost half of the produced platinum, the majority of palladium and rhodium is used for the production of auto catalytic converters. The growing demand for platinum group metals (PGMs) as auto catalysts has been a prominent trend in recent years. This surge can be attributed to the increasing global emphasis on environmental regulations and the transition towards cleaner, more sustainable transportation technologies

Typically composed of a ceramic or metallic substrate, often coated with platinum group metals (PGMs) like platinum, palladium, and rhodium, these catalysts rely on a high surface area to maximize catalytic activity. The substrate provides a structured surface for the PGM coating, allowing for optimal contact with

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Table 1. Demand and use of PGMs in 2020-2022 divided into branches (in '000 oz.) [21]
Tabela 1. Zapotrzebowanie i wykorzystanie PGM w latach 2020-2022 w podziale na branże [21]

Industry branch	Platinum		
	2020	2021	2022
Automotive	2 045	2 353	2 820
Jewellery	1 656	1 478	1 447
Industrial	2 474	2 949	2 627
Investment	1 022	-28	-92
Total demand	7 197	6 752	6 802
Recycling	- 1 702	-1 659	-1 628
Net demand	5 495	5 093	5 174
Movement in Stocks	-559	1 104	-
	Palladium		
	2021	2022	2020
Automotive	8 340	8 411	8 503
Jewellery	91	93	85
Industrial	1 649	1 642	1 556
Investment	17	-	-190
Total demand	10 097	10 146	9 954
Recycling	- 3 363	- 3 211	3 145
Net demand	6 734	6 935	6 809
Movement in Stocks	60	-	-647
	Rhodium		
	2020	2021	2022
Automotive	959	946	962
Jewellery	-	-	-
Industrial	76	86	120
Investment	-	-	-
Total demand	1 034	1 032	1 082
Recycling	-338	-369	-351
Net demand	696	663	731
Movement in Stocks	-85	101	-

exhaust gases. Additionally, the design incorporates a washcoat, typically made of alumina or ceria, to enhance surface area and adhesion of the precious metals.

They facilitate the conversion of harmful pollutants into less harmful substances, significantly reducing emissions from internal combustion engines. Large quantities of spent auto catalysts (SAC Spent Auto Catalysts) offer the potential to recover a significant amount of precious metals (Pt, Pd, Rh). This prospect of PGM recovery holds paramount importance in terms of natural resource preservation and efficient energy management, concurrently reducing the volume of waste deposited in landfills.

Various hydro – and pyrometallurgical methods are employed to extract precious metals from spent catalysts [38]. However, none of these approaches can be universally applied to all types of spent catalysts. Additionally, these recovery methods entail drawbacks: pyrometallurgical techniques necessitate specialized equipment and high temperatures, rendering them not only costly but also energy-intensive. Meanwhile, the utilization of hydrometallurgical methods demands the resolution of the issue of harmful waste solutions generated during the process. Furthermore, the separation of individual precious metals obtained from pyrometallurgical processes or preliminary hydrometallurgical processing requires further complex and costly hydrometallurgical operations, such as ion exchange or solvent extraction.

Presently, extensive efforts are underway to advance the scientific understanding of innovative waste materials recycling strategies, with a primary focus on precious metal recovery while maintaining stringent ecological standards. Emerging methods for metal retrieval from waste materials, particularly biohydrometallurgical technologies, are garnering interest among scientists as potentially economic alternatives that fulfil the aforementioned criteria.

2. Recycling of the used auto catalytic converters

In the global scientific literature and industry, there is a rich source of publications pertaining to potential methods for processing used automotive catalysts, encompassing both pyrometallurgical and hydrometallurgical approaches, as well as mixed technologies dedicated to the separation of individual precious metals. Some of these techniques have been operational in the industry for many years, while others remain confined to a laboratory scale, without transitioning into full-scale implementation (Table 2).

The technology of the recycling process is rather complex and consist of many technological stages such as:

- preparation and homogenisation of carrier,
- upgrading of PGMs content by the pyro – or hydrometallurgical methods,
- PGMs concentrate refining which consists of the following operations: dissolving and removal of non PGMs, separation of PGMs from one another, PGMs purification giving the high grade sponge or powder.

The purification of Platinum Group Metals subsequent to the recovery process yields exceedingly high levels of metal purity; however, this procedure remains prohibitively expensive and intricately complex due to the demanding nature of the purification techniques involved, such as multiple stages of solvent extraction, ion exchange, and advanced refining methodologies.

In pyrometallurgical methods, crushed catalysts are melted with the addition of another metal, in which the PGMs are gathered to form an alloy, while the ceramic portion of the carrier is collected in the slag. The alloy is subsequently separated from the slag and then undergoes a process of purification and separation to extract the individual precious metals.

In hydrometallurgical techniques, Platinum Group Metals (PGMs) present in spent auto catalysts undergo dissolution within an aqueous medium containing chlorate, perchloric acid, Cl2, H2O2, bromate, nitrate, and aqua regia. It is noteworthy, however, that hydrometallurgical processes have the potential to generate significant volumes of liquid waste, which may pose substantial environmental hazards.

3. Precious metal-containing catalytic converter from various processes and their recycling

PGMs from spent catalysts used in other kinds of chemical and petrochemical industries are also recovered (Table 3). Heavily-diluted organic platinum and rhodium solutions come from homogeneous catalytic processes in the chemical industry. Catalysts containing platinum are also used to oxidize ammonia (Fe-containing) and in the gasoline reforming process. Platinum catalysts are also important for silicone production. Rhodium is principally needed for catalytic converters in the automotive industry, but it also finds widespread application in the chemical industry because of its outstanding catalytic properties.

Table 2. Available pyrometallurgical and hydrometallurgical processes applied in PGMs recovery from the used auto catalytic converters [2,25,31,38,40,41]

Tabela 2. Dostępne procesy pirometalurgiczne i hydrometalurgiczne stosowane w procesie odzyskiwania PGM ze zużytych katalizatorów samochodowych

Type of processes
Hydrometallurgical processes
Aqua regia method Catalytic converter is dissolved in aqua regia. PGM chloro-complexes (e.g. PtCl2−6, PdCl2−4, and RhCl3−6) are formed. The PGM-containing salts are then selectively precipitated from the solution. The last stage is platinum, palladium and rhodium refining process.
Cyanide extraction Method applying cyanide under pressure; in standard condition reaction between sodium cyanide and precious metals is not proceeded – kinetics of this process is too weak; however if the temperature is higher (about 120-180°C), then the PGMs can be leached by the sodium cyanide. This technique allows to recover 96% of Pt, 97,8% of Pd and 92% of Rh from used auto catalytic converters
Chlorination method Chlorination is the process of selectively converting PGMs into volatile chloride compounds under high temperature conditions followed by condensation in a cooler zone. The temperature should be higher than 1200°C to evaporate the metallic fraction.
Ion or solvent extraction method Ion extraction employs specific ions to selectively bind with PGM elements, separating them from other materials. Solvent extraction utilizes organic compounds to dissolve and extract PGM, isolating them from the catalyst substrate.
Pyrometallurgical processes
Metal smelting collection The catalytic converters are melted with a metal collector (Cu, Fe, Pb) at the higher temperature (the process temperature is adjusted to the collector metal and fluxes used). The slag, derived from the metallic phase, is separated due to the difference in densities. The resulting alloy undergoes hydrometallurgical processing to remove the collector metal, after which it proceeds through the process of separating individual platinum group metals.
Rose method Grinded (milled) catalytic converter is melted in the electric furnace with copper oxide, coke, calcium, iron oxide and silica. After melting, copper with platinum and slag are obtained. Slag consists of ceramic carrier, calcium, silica and iron oxide. The alloy is proceeded in oxidizing furnace where copper is oxidized and platinum (which does not react with oxygen) is separated. Obtained product contains 75 % of metal and goes to refining section.
Method applying used printed circuits copper, zinc and iron which form printed circuits are treated as a metal collector; used auto catalytic converter carrier and used printed circuits are crushed, incinerated and then melted with the addition of fluxes and carbon.

Table 3. Available methods applied in PGMs recovery from the spent catalytic converters from various processes [1,8,31,41].

Tabela 3. Dostępne metody stosowane w odzyskiwaniu PGM ze zużytych katalizatorów z różnych procesów

Type of catalytic converter	Applied method
Bimetallic reforming catalysts (for eq. $Pt/Re/Al_2O_3$ and $Pt/Ir/Al_2O_3$)	Precious metals on the bimetallic reforming catalysts are recovered by dissolving them with an oxalic acid ($C_2H_2O_4$) solution buffered at pH>3 with ammonium oxalate ($(NH_4)_2C_2O_4$). The spent $Pt/Re/Al_2O_3$ catalyst is calcined and mixed with hot H_2SO_4 to dissolve Re and most of Al_2O_3. Next step is filtration to separate Pt and undissolved Al_2O_3. Then Re is eluted by a mixture of $HClO_4$ and C_2H_5OH. Ethanol is evaporated and the resulting solution containing $HReO_4$ and $HClO_4$ is sulphide with H_2S to harvest Re as Re_2S_7.
The spent catalyst containing Pt, Pd, Rh and Fe alloy	These kinds of spent catalytic converter are recovered by leaching with chloride solution mixed with a small amount of HNO_3. The solution is reducing with powdered Fe after that dissolving the precious metals with HCl and an oxidizing agent selected form Cl_2, H_2O_2, O_2 and air. Pd is extracted with a series of organic extracting agents such as dihexylsulfide for recovery of Pd, and extracting Pt and Rh with tributylophospate for their recovery.
The spent catalyst sieve containing Pt and Rh	The spent catalyst sieve containing Pt and Rh is dissolved in aqua regia, and the concentrated solution is converted to chlorides with HCl. This solution is treated with aqueous saturated by NaCl solution, and contacted with an acidic cation exchanger to separate common elements. Residual solution after the ion exchange is treated with aqueous 25% NH_4OH to pH 9 to obtain NH_4-salts of hexachlorocomplex. The salts are reduced with hydrazine hydrate. After filtration, the resulting Pt-Rh powder is washed with water and dried at 110°C.

Rhodium-based homogeneous catalytic processes hold significant importance in producing specialty chemicals such as plasticizers, acetic acid, acetic anhydride, and pharmaceutical agents. Furthermore, metallic silver and its compounds exhibit strong catalytic properties, particularly in the oxidation of organic substances. Silver finds utility both in its pure state and in various forms—electrolytic coarse powder and as compounds like AgO, $A_{g2}O$, $AgNO_3$, AgSiF, AgClO [19]. Pure silver serves as a catalyst in formaldehyde production from methanol, in the synthesis of ethylene from ethylene oxide (a fundamental material for solvent, detergent, and dye production), and in generating nitriles from aldehydes and ammonia. Powdered silver also serves as an efficient catalyst, often deposited on bauxite or alumina oxide Al_2O_3 for cost-effectiveness. This application extends to petroleum distillate desulfurization [41]. Silver powder, when combined with copper oxide as a carrier, acts as a catalyst in diverse reactions including detonation of air-acetylene mixtures, carbon monoxide oxidation, alcohol oxidation to aldehydes and acids, as well as in the production of ethylene glycol.

4. Microorganisms used for the recovery of precious metals – the current state of the art

Exploration into utilizing biological approaches to extract metals from surplus or discarded raw materials dates back to the mid-1950s. Historically, biohydrometallurgical methods were employed in industrial settings to recover gold from arsenopyritic ores, leach copper from lower-grade materials, process oxidic uranium ores, and reduce sulfur compounds to elemental sulfur. More recently, there's been a surge in research focusing on employing microorganisms in leaching methods for a range of waste materials containing valuable metals. For example, bioleaching has been applied for the removal of metals from fly ash [3,7],

tannery sludge [42], lithium batteries [15], sewage sludge [28], electronic scraps [4, 22], and spent catalysts [14,39]. Microbiological leaching harnesses the natural ability of microorganisms to transform metals present in the waste from solid form (in the solid matrix) to a dissolved form. In addition to *acidophilous microorganisms*, which play a crucial role in biohydrometallurgical techniques and facilitate the biological process of metals leaching in an acidic environment, there is also the possibility of bioleaching metals in an alkaline environment using cyanogenic bacteria. In the presence of cyanide, most metals (except lanthanides and actinides) form well-defined cyanide complexes, which exhibit very good water solubility and high chemical stability. This practical understanding has been effectively utilized for years; cyanide is commercially employed to complex and extract gold (alongside other precious metals) from ores, concentrates, or secondary raw materials.

Among the diverse flora used in biotechnology, there are microorganisms able to form hydrocyanic acid (HCN) e.g. bacteria *Chromobacterium violaceum, Pseudomonas fluorescens, Pseudomonas aeruginosa*, or fungi – *Marasmius oreades, Clitocybe Sp., Polysporus Sp* [32]. Although cyanide formation by microorganisms has been known for many years [11] the knowledge about the possibility of HCN formation by various species of microorganisms and their potential use in biotechnological processes is still incomplete.

Cyanide is formed as a secondary metabolite. It is assumed that its formation by the microorganism allows it to gain advantage in the environment, by inhibiting activity of competing microorganisms. Typically, cyanide is formed during the growth but only during a short period (early stationary phase). Optimal cyanide formation depends on the introduction of a suitable growth media, such as glycine – precursor of cyanide formed by microorganisms [12,23].

In the laboratory *C. violaceum, P. fluorescens* and *P. plecoglossicida bacteria* produced cyanide during the short incubation time (2 days, greater efficiency showed *C. violaceum* and *P. plecoglossicida*). Characteristic decreasing of cyanide concentration with time was observed in the process after its fast generation in the initial stage, which could be caused by the sorption processes, the re-use as carbon and nitrogen source by the organisms or outgassing [10,17]. In contrast to the application of autotrophic sulfur oxidizing microorganisms which form sulfuric acid or heterotrophic microorganisms which form organic acids [23], the use of cyanogenic bacteria allows metals mobilize from solids under alkaline conditions.

For dissolved metals, alkaline conditions may be beneficial – in comparison to the acidic environment, behaviour of a metal may completely change in the alkaline environment, e.g. solubility, mobility, sorption, precipitation, formation of secondary minerals; especially in the presence of cyanide, metal might be recovered more easily, e.g. by sorption onto activated carbon [6]. In addition, formed alkaline leachates are less aggressive (corrosive) to the environment.

Among previous studies on recovery of metals from secondary raw materials by biological methods, only a few works relate to the use of cyanogenic microorganisms in mobilization of precious metals from waste materials. The phenomenon of cyanide formation by bacteria was first noted before the World War First. Since then further work was carried out to detect cyanogenic species. Studies have shown that bacteria *C. violaceum*, many but not all strains of *P. aeruginosa* and *P. fluorescens* and several strains of the genus *Pseudomonas* (*P. chloraphis, P. aureofaciens*) have cyanogenic abilities. Because of insensitive methods of detection and determination of cyanide at that time (using picrate method) probably many microorganisms with ability to create HCN have been missed [17]. Some of the earliest research on the possibility of gold leaching in the presence of *C. violaceum* from gold-containing ore or coupons of pure gold and the subsequent formation of gold cyanide were presented by Smith and Hunt, 1985 [33], Lawson et al., 1999 [24] or later by Campbell et al., 2001 [9] or Farmarzi and Brandl, 2006 [16]. Further research was conducted for the possibility of creating water-soluble metal cyanides and

Table 4. The level of precious metals leached, by means of cyanogenic bacteria in bioleaching process, from waste

Tabela 4. Poziom metali szlachetnych wyługowanych z odpadów za pomocą bakterii cyjanogennych w procesie bioługowania

Genus of microorganisms	Leached material	Level of leached metal	Process conditions	Ref.
C. violaceum	electronic strap	Au 14,9%	time: 7 d, medium supplemented with glycine 0.75 g/l	[17]
C. violaceum, P. fluorescens, P. plecoglossicida	electronic scrap, jewellery waste, automobile catalytic converters	Ag – 5% Au – 65,5% Pt – 0,2%	30˚C, time: 7 d	[6]
C. violaceum	printed circuit boards (mobile phone)	Au- 10,8% Cu – 11,4% with H_2O_2 : Au-11,31% Cu-24,6%	30˚C, pH 8,0-11,0 time: 8 d, supplementing oxygen with 0.004% H_2O_2	[36]
C. violaceum	printed circuit boards (mobile phone)	Au – 11% (pH 11) Cu – 11,4% (pH 10)	30˚C, pH 7,4 –11,0 time: 8 d, various metal ions content	[37]
P. fluorescens and B. megaterium	SAC – spent auto catalysts	Pt – 58%, Pd – 65%, Rh – 97%	a pulp density of 0.5 % w/v pH 10, 1 day, under different conditions	[34]
C. violaceum	SAC – spent auto catalysts	Pt – 76%, Pd – 81%, Rh – 100% With pretreatment of SAC formic before leaching Pt – 91, Pd – 95%, Rh – 100 %	a pulp density of 0.5 % w/v pH 10, 2 days, under different conditions	[35]

their recovery from secondary raw materials. Results and details of these works are summarized below and presented in Table 4.

Studies on extraction of gold from electronic circuit boards were carried out by Faramarzi et al. [16]. In the presence of C. violaceum gold was microbiologically dissolved to form dicyanaoaurate $[Au(CN)_2]^-$. The maximum measured dicyanoaurate $[Au(CN)_2]^-$ referred to 14.9% of the initially dissolved gold.

Brandl et al. [6] used *Chromobacterium violaceum, Pseudomonas fluorescens* and *P. plecoglossicida* bacteria for extraction of gold, silver and platinum from electronic waste, jewellery waste and automotive catalytic converters, respectively. Rate of cyanide complexes (Ag, Au, Pt) formation and their effect on the activity of microorganisms were monitored. Fast mobilization of silver from jewellery waste was observed in the presence of *P. plecoglossicida*. In the initial stage of the process (after 1 day) approximately 5% of silver was mobilized as a dicyanoargentate $[Ag(CN)_2]^-$. After the initial phase of the fast growth, cyanide-complexed silver concentration increased only slightly all through the incubation period. It was found that dicyanoargentate at concentrations >20 mg/L inhibited growth of *P. plecoglossicida*, and as a result mobilization efficiency decreased. In spite of the toxicity of dicyanoargentate, the authors suggest that mobilization of silver by cyanogenic microorganisms proves to be a promising method. However, the process has to be optimized by reducing inhibitory effects, e.g. by trapping formed dicyanoargentate or by applying a sequential two-step process where biological cyanide formation is separated from metal mobilization. Analogically, this has already been proposed to reduce the toxicity of arsenic during the biological treatment of gold containing arsenopyrite by Sulfolobus metallicus. Extraction of platinum from spent automobile catalytic converter was carried out by using *P. plecoglossicida* bacteria. Only a small amount, approximately 0.2%, of the total Pt present in the converter was mobilized. It is assumed that Pt mobilization is prevented by a passivating oxide film. However there is no wider analysis and a complete description of mechanism of this phenomenon. It was stated that pulp density has a major influence on bacterial growth and activity. Oxygen consumption (used as indicator of metabolic activity) was significantly reduced at pulp densities of >50 g/L. Gold was mobilized from shredded electronic scrap by both *C. violeacum* and *P. fluorescens* as dicyanoaurate $[Au(CN)_2]^-$, after a lag-phase of 3 days. *C. violaceum* proved to be more efficient regarding gold mobilization, reaching higher concentrations of dicyanoaurate. When P. fluorescens was applied, dicyanoaurate did not remain stable in a solution with prolonged incubation time. It might be caused by sorption processes on biomass or biodegradation because metal cyanides can serve as carbon or nitrogen source. In addition to dicyanoaurate, cyanide-complexed copper was detected during the treatment of electronic scrap probably due to the high copper content of the scrap and its rapid reaction with cyanide. Pham and Ting [30] applied in the first phase of gold recovery from electronic waste bioleaching by Acidithiobacillus ferrooxidans bacteria. This operation enhanced to remove more than 80% of copper from waste and significantly improved Au recovery, especially with the participation of *C. violaceum*.

C. violaceum was used in bioleaching of gold and copper from the waste mobile phone printed circuit boards containing 34.5% Cu and 0.025% Au [37]. Authors proved that dissolved oxygen (DO) played a significant role during the leaching process. Adding 0.004% H_2O_2 increased DO without seriously affecting bacteria and improved copper leaching from 11.4% to 24.6% at pH 10.0 and gold recovery, only marginally, from 10.8% to 11.31% at pH 11.0. Preferred copper leaching than gold may be the result of high copper present in the sample consuming cyanide produced at higher DO level. The authors suggest that in order to improve gold bioleaching, the content of copper must be decreased by a suitable, prior bioleaching method.

Tran et al. [37] studied the extraction of gold and copper from the mobile phone printed circuit boards using *C. violaceum*. The catalytic roles of Na^+,Mg^{2+}, Fe^{2+} Pb^{2+} and effect of Na_2HPO_4 nutrient addition on cyanide generation efficiency of the bacterium in this medium have been elucidated. Creation of cyanide by cyanogenic bacteria was improved by introducing a small amount of metal ions to the culture medium. An addition of $MgSO_4$ and $FeSO_4$ conduce to the formation of cyanide by the bacteria, and the presence of Na_2HPO_4 and $Pb(NO_3)_2$ enhanced cyanide generation further. The presence of phosphate and $Pb(NO_3)_2$ in the medium improved copper bio-dissolution, but it was not effective for gold leaching.

As literature review indicates, the selected microorganisms are able to mobilize precious metals from a solid to a solution in the form of cyanide complexes. Potential of microbial mobilization of metals as cyanide complex from solid materials (which is a type of microbial metal mobilization) was termed by Brandl and Faramarzi [5,6] as "biocyanidation". Efficiency in formation of metal cyanide in the presence of HCN, diversifies for various species. Bioleaching is a complex process, determined by many factors. Parameters affecting the process kinetics and metabolic activity of microorganisms, inter alia, are: type of culture medium, concentration of dissolved oxygen, pH, temperature, pulp density, qualitative and quantitative composition of waste, degree of material granularity, number of microorganisms and time.

Among HCN-generated bacteria, *C. violaceum* was found to be the most effective for bio-dissolution of gold from different materials because of its cyanide-associated metabolic activities [37]. It is believed that the process of metal cyanides creation using cyanogenic bacteria such as *C. violaceum* follows an indirect mechanism in two stages. In the first, glycine undergoes conversion to HCN (leaching chemical) by the associated enzymes under the metabolic activity of HCN synthase. The second stage involves reaction of cyanide ions from the gold/copper substrate, leading to dissolution of metal (Fig. 1) [5].

With regard to cyanogenic bacteria the ability of microorganisms to conduct biodegradation processes should also be considered (produced metal cyanides can be used by microorganisms as a source of carbon or nitrogen [6,13]). Extensive information on the biodegradation of cyanide compounds by microorganisms can be found in [20,29].

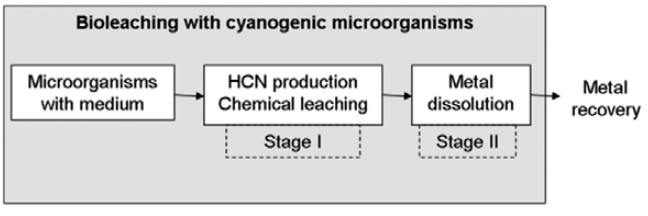

Fig. 1. Flow diagram of precious metals bioleaching in the presence of cyanogenic bacteria [5]

Rys. 1. Schemat bioługowania metali szlachetnych w obecności bakterii cyjanogennych [5]

5. Potential of cyanogenic microorganisms – proposed directions for further research

Previous studies on application of cyanogenic microorganisms to extract precious metals from waste materials focus primarily on bioleaching of gold. Limited research was carried out on the bioleaching of PGMs from waste. An example of waste material as a carrier of PGMs are spent catalysts. Simplicity of pre-treatment of the material (milling) and simple material composition

(as compared to the other waste, such as electronic waste) indicate the possibility of testing this material to be applied in bioleaching method to extract PGMs directly from the waste.

Knowledge about the extraction of platinum metals from polymetallic materials, using cyanogenic bacteria, is incomplete. It requires solving some research problems, which would give explanation and recognition of the bacterial leaching operation of metals in biological HCN. In order to increase the efficiency of bacterial culture, the analysis of the external factors influence (pH, temperature, breeding of bacteria culture) and several types of standard media, to select an option that allows to obtain a large amount of biomass which produces the desired metabolite should be carried out. The number of parameters influencing dynamics of PGMs extraction from a solid phase to form cyanide soluble complexes (with the presence of bacteria) require verification, e.g.: number of microorganisms, concentration of dissolved oxygen, pH, pulp density, presence of additional metals and substances. Also phenomena accompanying bioleaching process (e.g. passivation) and influencing decisively the kinetics of metals dissolution, are not fully recognized.

Further studies on the use of cyanogenic microorganisms require a follow-up, inter alia in the range of:

- optimization of biological HCN forming and the presence and stability of cyanide complexes of PGM and associated metals;
- analysis of physicochemical factors influencing the dissolution kinetics of precious metals and phenomena accompanying bioleaching process – determining the existence of the passivation process;
- comparison of effectiveness of selected bacteria strains in biological techniques to recover precious metals.

Acquired knowledge will allow to evaluate the effectiveness of the PGM bioleaching process from recycled materials with the participation of cyanogenic bacteria and to identify possibility of further application of this process.

6. The possibilities of reusing the ceramic carriers from spent auto catalysts

The management of ceramic cordierite substrate SAC after leaching/bioleaching processes or after pyrometallurgical processing is currently a significant challenge due to environmental and economic issues related to the volume of accumulated secondary waste in the form of solid residues remaining after the recovery of PGM. Previous concepts of utilization [38] have included conversion of the cordierite substrate in the slag phase after smelting to the amorphous glass, which is further crystallized as glass ceramics like $CaAl_2 – SiO_8$ and $CaMgSi_2O_6$ at high temperature for reuse [43,44]. For the case of cordierite residue after hydrometallurgical or biohydrometallurgical PGM recovery, the proposed solution is to transform aluminium or magnesium from cordierite material into useful products (e.g., catalyst supports, coatings, polymer additives, or water treatment substances) [18,26]. However, so far, these methods have not found practical application.

On the other hand, an innovative approach to managing the residual SAC cordierite material after leaching/bioleaching is the concept of using it as a sorption material. Preliminary studies assessing the sorption potential of waste SAC cordierite for the regeneration of industrial oils unequivocally confirmed its effectiveness as a sorption bed for removing contaminants from industrial oils [27]. Currently, this concept is in the advanced research phase, employing an electromagnetic mill for surface activation and physicochemical modification of cordierite from waste catalyst to transform it into a material with enhanced sorption properties. With this approach, scientists aim to develop an efficient solution characterized by high environmental values and minimal environmental footprint in the processing and management of waste SAC cordierite.

7. Conclusions

In this review pyro – and hydrometallurgical methods applied to waste processing, containing in its composition PGMs were characterized. Particular attention was given to the new trends in the field of biohydrometallurgy, focused on the possibility of using potential of cyanogenic microorganisms in biological leaching of PGMs from waste. Directions for future research were proposed by the authors. The results will determine the efficiency of PGMs extraction in the bioleaching and will enable to determine the prospects for further application of this method.

For the last few years much attention has been given to the research on microbiological recovery of precious and basic metals from waste. Although previous works were not processed beyond the stage of laboratory tests, these methods are considered to be promising, hoping they can lead to the development of more efficient and less costly processes.

The possibility of the producing of hydrocyanic acid by cyanogenic bacteria has been known for years. Prospects for the practical use of this phenomenon and potential of microorganisms in leaching precious metals from waste require further and more advanced research done by specialists of microbiology and experts in the field of biohydrometallurgy. Continuation of research is required in the range of stimulation of microorganisms for the production of HCN at a satisfactory level or work on the kinetics and the influence of external factors on the degree of precious metals leaching.

Current activities are mainly focused on the bioleaching of Au and Cu from solid waste and little attention is paid to PGMs. A rich source of PGMs are spent catalysts, which are currently processed by pyro – and hydrometallurgical methods. Initiation of studies on the possibility of leaching these metals in the presence of biological HCN and the solution of problems analysed in this article can clarify whether is it possible to recover PGMs using biohydrometallurgical methods.

Data Availability

The specific sources of the data shown in Table 1-3 have been web archived from the footnoted websites and the archival links will be made available upon request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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