

PRODUCTION OF PLATINUM FROM PRIMARY AND SECONDARY MATERIALS – A REVIEWSATERNUS Mariola¹, FORNALCZYK Agnieszka¹, WILLNER Joanna¹¹*Silesian University of Technology, Faculty of Materials Engineering and Metallurgy, Katowice, Poland, EU***Abstract**

Platinum have become a metal, which is today necessary for every new car production due to its catalytic role, mainly reduction of toxic gases. Prices and demand for platinum are shown as well as the possibilities of recovery this metal from secondary materials, especially spent auto catalyst. Paper presents the short review of platinum production from primary materials – the kind of ores, places where platinum is mined. However, resources of primary platinum are limited and quickly depleted. Platinum is also received from by-product obtained from the treatment process of other metals such as copper or nickel and these methods are also shortly shown. Finally, to meet the future demand and protect the platinum resources the hydrometallurgical, pyrometallurgical and even biometallurgical processes of platinum recovery from different waste e.g. electronic scrap, spent catalyst are counted and briefly characterized. The main focus was given on the spent auto catalyst – the general way of platinum recovery was given in more detail.

Keywords: platinum, production, recovery, spent catalyst**1. INTRODUCTION**

Platinum was brought from America to Europe in 1750. In those times people regarded this metal as a poor variety of silver. What is more interesting also the price of platinum was very low comparing to present days – see **Table 1**).

Table 1 Prices of platinum [1,2]

Year	1880	1900	1930	1960	1990	2000	2010	2011	2012	2013	2014
Price, US\$/kg	129	193	1,415	2,675	15,013	17,491	51,730	55,359	49,881	47,805	44,551

It is not possible to imagine the today's world without the platinum. The main application of this metal is in car industry. All newly produced cars should be equipped with the catalyst in which the catalytic role plays, among other metals such as palladium and rhodium, platinum. There are many platinum–base catalyst e.g. Pt-Rh or Pt-Pd-Rh alloys for catalytic oxidation of ammonia to nitrogen oxide by air, Pt gauze catalyst for oxidation of ammonia to produce nitric acid, Pt/Rh bimetallic catalyst for catalytic reforming to upgrade the low octane naphtha to higher octane aromatic hydrocarbons, bimetallic Pt-Cu catalyst for nitrate reduction, Pt-Co catalyst for Fischer-Tropsch process to produce hydrocarbons from synthesis gas [3]. Apart from catalytic application platinum is also used in electric and chemical industry, jewellery, glass and also as investments – see **Table 2**.

Table 2 Demand for platinum in Mg taking into account the application [4]

Year	Catalyst	Chemical industry	Electric industry	Glass	Investments	Jewellery	Others	Total sum
2010	95.6	13.7	7.2	12.0	20.4	75.3	21.8	246.0
2011	99.1	14.6	7.2	16.0	14.3	77.0	23.7	251.9
2012	99.2	14.0	5.1	5.0	14.2	86.5	25.8	249.8
2013	97.2	16.8	6.4	7.3	23.8	85.2	25.2	261.9

Platinum is mainly produced in South Africa in the amount of 130,000 Mg, which provides 70% of this metal production, the second place belongs to Russia (20,000 Mg), whereas the third and other places to Zimbabwe, USA and Canada (several thousand of Mg). **Table 3** shows the classification of PGM (platinum group metals) ores. Different platinum deposits or ores should be treated using different methods of receiving taking into account their mineralogical features and many other factors. Generally, platinum ores are divided into those which are prone to gravity separation, flotation and those where platinum is by-products of base metal sulphides (Cu or Ni). Small amount of platinum (some grams in 1 Mg of ore) and the big depth, from which this ore should be mined cause that the average cost of mining is really high [6].

Table 3 Classification of PGM (platinum group metals) ores types and their characteristics [5]

Ore	Types/class	Characteristics
PGM dominant	Type: Merensky, placer, chromite, dunite pipes	Exploited mainly for their PGMs content due to economic importance; associated metals such as Cu, Ni and Co are produced as by-products.
Ni-Cu dominant	Class: I to IV and other	Mined mainly for the value of Ni and Cu; PGMs are recovered as by-products; the economic importance of PGMs in these ores is minor.
Miscellaneous ore	Porphyry Cu ore, Cu-Mo ore carbonatite ore, Ni laterites, black shales	Contain low level of PGMs compared to the previous two types of ores; the value of PGMs is little or no economic advantage compared to the primary product.

Platinum can be also obtained as a by-product from copper, nickel and sometimes lead production. In the electrorefining process of copper the platinum and other precious metals go to the slime. After many technological stages it is possible to obtain silver from this slime, then gold and at the end also Pt-Pd slime (**Table 4**); which in this form is sold (in Poland in KGHM) or purified to separate palladium and platinum.

Table 4 The chemical composition of Pt-Pd slime coming from copper electrorefining process [7]

Element	Pt	Pd	Au	Bi	Se	Te	Sb	H ₂ O
Content in %	25-40	15-30	2-12	2-20	2-15	3-7	0.2-0.4	1-5

The prices of platinum and its limited resources cause that very often, if it is possible, platinum in cars is replaced by cheaper palladium (this can be observed in the case of cars with petrol engine). However, platinum in the nearest some years and even some decades will be still playing catalytic function in cars. Thus, the more and more important have become platinum recovery from waste. Although, analyzing the data from **Table 5** it can be stated that the amount of recovered platinum is still too low comparing to market demand. Therefore, in the nearest years the new methods for platinum recovery should be appeared and many companies will be encouraged to this recovery. In the article the most important methods, which are known and applied, are shortly presented and characterized.

Table 5 Comparison of platinum recovery from spent auto catalyst and the demand for this metal needed for catalyst production in year 2009-2013 [4]

Year	2009	2010	2011	2012	2013
Demand for the production of the auto catalyst in Mg	68.0	95.6	99.1	99.2	97.2
Recovery from spent auto catalyst in Mg	25.8	33.7	38.6	35.1	39.7

2. RECOVERY OF PLATINUM FROM SPENT CATALYST

Table 6 presents the methods of treating spent catalyst to recovery platinum. Firstly, the material should be homogenized to estimate the level of platinum. When the level of platinum is lower than 30%, the material should be concentrated. The choice of method depends on the chemical composition of treated material. After concentration, platinum is dissolved and then isolated and separated from other precious metals.

Table 6 Processes of spent catalysts treatment to recover platinum [3,8,9]

Catalyst	Characteristics
Catalyst from fuels reforming: Pt/Re/Al ₂ O ₃ Pt/Ir/Al ₂ O ₃ Fe/Pt/Re/Al ₂ O ₃ Fe/Pt/Ir/Al ₂ O ₃ Pt/Al ₂ O ₃	Catalyst carriers are dissolved in oxalic acid with ammonium oxalate as a buffered solution (pH=3).
	Catalyst carriers are dissolved in aqua regia and NH ₄ Cl, then (NH ₄) ₂ PtCl ₆ is precipitated, which is further decomposed in the temperature 1073 – 1173 K into platinum black.
	Catalyst carriers are dissolved in aqua regia, concentrated solution is treated with NaCl saturated solution to obtain pH=1-1.4 and to conduct ion exchange; obtained solution is treated with 25% NH ₄ OH solution (pH=9) to get ammonia salts, which are reduced by hydrated hydrazine; after filtration powder Pt-Rh is washed by water and dried in the temperature 383 K.
	Pt/Re/Al ₂ O ₃ catalyst carriers are roasted, then dissolved in hot H ₂ SO ₄ to separate Re and the majority of Al ₂ O ₃ ; obtained solution with Pt is purified.
	Catalyst carriers containing Fe are leached by chlorides solution with addition of HNO ₃ , then reduced with powdered iron; obtained precious metals are dissolved in HCl and chosen oxidative compound (Cl ₂ , H ₂ O ₂ , O ₂); Pt is extracted from the solution using tributylphosphate.
Pt gauze dust	Catalyst carriers with 13.7% Pt are refluxed with aqua regia for 1.5 hour to solubilize Pt; Pt is separated using trioctylamine and recovered by precipitation, 95.5% of Pt is achieved.
Pt/Rh bimetallic reforming catalyst	Catalyst carriers are refluxed with aqua regia at liquid to solid ratio 5; process is conducted during 2.5 hours; more than 95% of Pt and Rh is recovered.
Fischer-Tropsch catalyst	Catalyst carriers are dissolved in acidic and alkaline solutions and aqua regia; calcinations is conducted in 1073 K to remove wax; then different leaching agents are used to recover Co, Al and Pt; 89% Al is dissolved in NaOH; Co and Pt is then leached by acid-aqua regia or alkali pressure leaching-aqua regia; the solution could be used for production of Pt sponge or Pt salt.
Catalyst from production of hydroxylamine sulfate Pt-C	Catalyst carrier are incinerated by the current of 2500 W power; the ash is dissolved in aqua regia during 1 hour in the temperature 353 K; the obtained platinum is again used for the production of Pt-C catalysts, the recovery level is higher than 95% of platinum.
Catalysts from naphtha reforming	Platinum is extracted by blowing the catalyst carriers with vapours of carbon chloride using air or nitrogen as a protection, the recovery level is 95% of platinum.

3. RECOVERY OF PLATINUM FROM ELECTRONIC WASTE

Electronic waste (like cell phones, calculators, printed circuit board scraps, e.g.) has become more and more interesting material due to the fact of containing many precious metals such as gold, silver, platinum and palladium. Today there are many methods available worldwide to recover all these metals – see **Table 7**. Pyrometallurgical processes are based on: incineration, smelting in blast furnace, drossing, sintering, melting at high temperatures. Generally, the crushed scrap is melted in furnace to separate alloys containing all precious metals from slag with all impurities. Ceramic parts of the scrap increase the amount of creating slag and as a consequence the loss of precious metals from the scrap. It is possible to use the organic substitutes such as plastic to reduce the energy cost, but only at the beginning. The pyrometallurgy is applied only for separating precious metals and metal collector from ceramic parts; then electrochemical or hydrometallurgical processes are needed. Hydrometallurgical processes are based on a series of acid or caustic leaching of solid material. The obtained solutions are then separated and purified in order to get the platinum and other precious metals by means of precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the metals of interest. Applying biotechnologies to recover metals from waste has become at present the most promising technologies. Two main methods are applied: bioleaching and biosorption. Bioleaching is used to recover metals from metallic sulfides. However, this method is today used only for recovery copper and gold for the industrial scale. Biosorption is based on interaction between the groups of microorganisms such as algae, bacteria, yeasts, fungi and ions in solution. Living as well as dead organisms can be used. The main advantages of the process are low operating costs and minimization of the chemical and/or biological sludge volume.

Table 7 Processes of electronic waste treatment to recover platinum [10-11]

Method/process	Characteristics
Pyrometallurgical methods	
Noranda process (Quebec, Canada)	Process used for simultaneous treatment of copper concentrates and electronic waste (about 100,000 Mg per year – 14% of total throughput); materials, which enter the furnace, are immersed in molten metal (1523 K) and blown by air (enriched with oxygen - 39%); combustion of plastics and other flammable materials helps to reduce energy cost; impurities such as Fe, Pb, Zn are converted into oxides creating slag; Cu matte contains precious metals including Pt, then it is transported to the converters; obtained blister copper (99.1% Cu and 0.9% Pt, Pd, Au, Ag, Se, Te, Ni) is electrolytically refined; Pt goes to the slime, from which is separated.
Boliden technology (Rönnskär, Sweden)	Possibilities of processing 100,000 Mg of scrap (including electronic) every year; scrap containing high level of copper is introduced directly into converting process; whereas low grade e-waste goes into Kaldo furnace; charge with electronic waste and lead concentrates is introduced into the Kaldo furnace, everything is blown by oxygen, as a consequence the alloy of copper (which is then converted to recover metals like Cu, Ag, Au, Pd, Pt, Ni, Se, Zn) and the dusts (which is then processing to recover Pb, Sb, In and Cd) are obtained.
Umicore technology (Hoboken, Belgium)	In this technology it is possible to process waste such as: by-products from nonferrous industries (e.g. drosses, mattes, speiss, anode slimes), precious metals bullions, spent industrial and auto catalysts, printed circuit boards; the plant treats 250,000 Mg of different waste every year (including 10% of electronic waste); the first stage is smelting in IsaSmelt furnace; plastics or other organic substances from the charge allow to reduce the energy costs; precious metals including Pt go to the copper alloy, which then is leached and electrolytically refined; other metals go to the lead slag, which further is treated in the lead refinery (Harris process).
F.G. Day's patent	Patent for treating refractory ceramic precious metals scraps; scrap is melted in the plasma arc furnace at the temperature higher than 1673 K; as a result the alloy containing metal collector (mainly Cu or Ag) and precious metals is obtained as well as slag containing ceramic residues.
S. Aleksandrovich, E. Nicolaevich, E. Ivanovich's patent	Patent for recovery of precious group metals and gold from electronic scraps – scrap is fused together with carbon as a reducing agent; the melted materials is then settled and cooled, solidified and finally precious metals and gold separated.
Hydrometallurgical methods	
Cyanide leaching	Maximum dissolution of gold, silver, palladium and platinum in cyanide solution can be obtained when pH equals 10–10.5; the order of activity for noble metals is the following: $Au > Ag > Pd > Pt$; because of the negative effect on environment some substitute are used instead of cyanide, the most effective are thiourea and thiosulfate.
Halide leaching	From halide only chlorine/chloride is used industrially on a big scale; the process is optimal at: low pH, high chloride and chlorine levels, increased temperatures, high surface areas; the main medium for dissolving Au and Pt is aqua regia; chloride leaching is more difficult to apply than cyanide extraction, because chlorine is poisonous and must be controlled to avoid health risk.
Thiourea leaching	Thiourea $(NH_2)_2CS$ dissolves metals in the form of cationic complex; reaction in acidic conditions is rather rapid; results are promising, however it is more expensive than cyanide and additionally thiourea consumption is high.
Thiosulfate leaching	Thiosulfate $S_2O_3^{2-}$ dissolves metals in the presence of cupric ions as a catalyst; pH of 9–10 is generally preferred; the main disadvantages of the process are: high consumption of reagent during extraction, slow process, problem with separation precious metals.
Recovery of metals from solutions obtained as a results of leaching	<ul style="list-style-type: none"> • By cementation – mainly Zn is used at pH = 8-11. • By solvent extraction – organophosphorus derivatives, guanidine derivations and mixture of aminesorganophosphorous derivatives (TBP, DBBP, Cyanex 921, LX 79) are used as an extractants; Cyanex 921 is the most common used to recover gold, silver or platinum. • By activated carbon – 2 methods are used: CIP (carbon-in-pulp) and CIL (carbon-in-leach). • By ion exchange – using ion exchange resins such as: IEX, Dowex G51, Dowex 21K and amberlite IRA-410, these resins contain small amount of ammonium, two methods are applied: RIP (resin-in-pulp) or RIL (resin-in-leach).
Biometallurgical methods	
Biosorption	Biosorbents are prepared from the naturally abundant and/or waste biomass of algae, fungi or bacteria; biosorption by chitosan derivatives provides an alternative for recovery of precious metals from solution - relatively higher adsorption capacities was obtained for Au^{3+} , Pt^{4+} , Pd^{2+} ; different adsorbents are used for platinum recovery: bacteria <i>Desulfovibrio desulfuricans</i> (pH=2.0), <i>Desulfovibrio fructosivorans</i> (pH=2.0), <i>Desulfovibrio vulgaris</i> (pH=2.0); proteins Lysozyme, Bovine serum albumin (BSA), Ovalbumin; others Bayberry tannin immobilized collagen fiber (BTICF) membrane (pH=3.0), Thiourea derivative of chitosan (TGC) (pH=2), Glutaraldehyde crosslinked chitosan (GC) (pH=2), Chitosan derivatives (pH=2.0).

4. RECOVERY OF PLATINUM FROM SPENT AUTO CATALYST

Because the lifetime of catalyst is limited; so it should be periodically regenerated and after some working time, changed. As a consequence all spent auto catalysts are treated using pyro- or hydrometallurgical methods to recover precious metals, especially platinum. The first step is to collect and dismantle catalyst, and then it is necessary to know the chemical composition in order to determine the level of platinum. Some catalyst carriers contain high level of platinum; they can be used as a complete unit in some methods. Catalyst carriers with medium or small platinum level can be milled and homogenized. If platinum level is lower than 30%, the thickening operation is applied. There are many pyrometallurgical, hydrometallurgical and mixed methods – see **Table 8**. In hydrometallurgical method catalyst carrier is dissolved in water solution of chlorides, chlorates, chlorine, hydrogen peroxide, bromates, nitrates and aqua regia – as a result platinum and other precious metals go into chloride complexes (MCl_6^{2-}). The concentration of platinum and other PGM metals in such solutions is small. Thus, the process of concentration of the solution is needed and then PGM metals extraction and separation. The main disadvantage of these methods is creating many liquid wastes which become the potential threat to the natural environment. In pyrometallurgical methods catalyst carrier is grinded and melted with the addition of other metal in solid or vapour state which is treated as a metal collector – see Fig. 1. As a consequence platinum and other PGM metals go to the alloy, whereas a ceramic part of the carrier creates slag, which is separated and becomes a waste.

Table 8 Processes of spent auto catalysts treatment to recover platinum [8,12,13]

Method	Characteristics
Rose method	Grinded catalyst is melted with CuO, FeO, coke, lime and silica in electric furnace; PGM metals including Pt are extracted from molten Cu, ceramic carrier goes to the slag; obtained product contains 75% of metals and goes to refining process.
Melting method	Catalysts are melted with iron in temperature higher than 227 K, slag from metallic phase is separated due to the difference between its density; obtained metallic phase is leached in H_2SO_4 ; consequently iron is removed from the platinum solution; in lower temperature other metals can be used to collect Pt; then the obtained slag is less aggressive.
Methods based on blowing metal vapours	Grinded or whole catalyst is blown by gaseous vapours of Cu, Mg, Ca; as a result alloy of metal collector with PGM metals and slag are obtained and separated; obtained alloy should be purified to obtain pure Pt.
Metal collector method	Grinded or whole catalyst is melted with metal collector such as copper, magnesium, calcium; as a result alloy of metal collector (Cu, Mg, Ca) with PGM metals and slag are obtained and easily separated; the obtained alloy can be refined electrolytically, Pt goes to the slime, whereas copper splits on cathode.
Aqua regia method	Catalyst is dissolved in aqua regia; H_2PtCl_6 is obtained and precipitated by Al/Zn powder; additionally a lot of liquid waste is produced; platinum should be separated from the solution by purification process.
Chlorination	Catalyst is chlorinated in high temperature (higher than 1473 K) to evaporate the metallic fraction; a lot of waste is created - chlorine is dangerous to environment.
Cyanide extraction	Expensive method, which is based on leaching catalyst using sodium cyanide under pressure at temperature 393-453 K; cyanides are dangerous to environment.
Segregation method	Grinding process used the small addition of KCl and NaCl, then heating is applied to concentrate the solution; as a consequence a part of solution is evaporated; during the Pt extraction oxygen blow is used; a lot of liquid waste is produced, solution has relatively low level of Pt concentration, so it must be concentrated.

5. CONCLUSION

Today almost half of produced platinum is used for the production of catalyst, especially auto catalyst. Natural resources of platinum are rather limited and not sufficient taking into account increasing demand. Additionally, the process of obtaining platinum from ores is very complicated, costly and during it a lot of solid and liquid waste is created. Platinum can be also obtained as a by-product from copper, nickel and lead production. However, the most promising have become recovery of platinum from spent materials such as industrial and auto catalyst and electronic waste. The process is very beneficial because it limits the amount

of disposed wastes, saves the natural resources and limits the energy consumption. Additionally, pollution emitted during recycling is lower than during production from primary raw material. High purity of recovered metal allows to use it again and does not cause any financial problems. There are many technology of platinum recovery from spent materials, however, all of them are rather complex and consists of many stages (see **Fig. 1**) such as: preparation and homogenisation of spent material, upgrading platinum content by pyro- or hydrometallurgical methods, refining PGM metals concentrate to separate platinum and obtain in the form of sponge or powder. All of the applied methods have some advantages and disadvantages. Really interesting seems to be pyrometallurgical methods, because there is no liquid waste and obtained alloy contains high concentration of platinum and other precious metals. However, to obtain pure platinum still hydrometallurgical method is needed (**Fig. 1 b and c**). More and more popular become also biometallurgy.

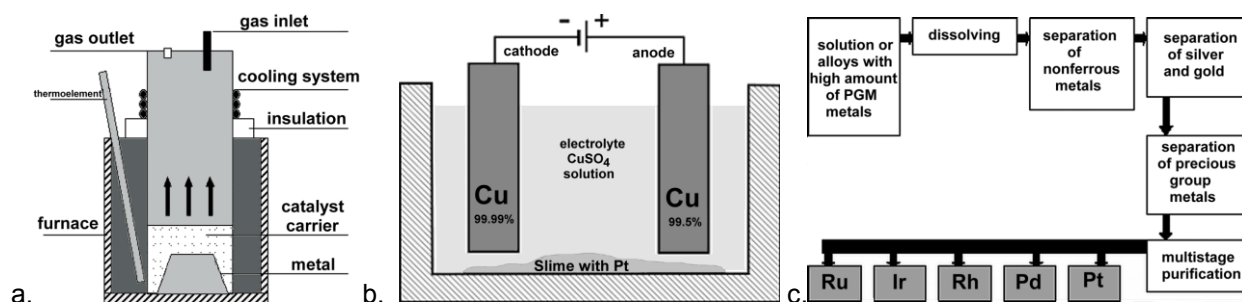


Fig. 1 Recovery of platinum from spent auto catalyst: a) metal collector method, b) electrorefining process of copper alloy with platinum, c) scheme of purification/separation of particular PGM metals [12,14-16]

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