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POSSIBLE WAYS OF REFINING PRECIOUS GROUP METALS (PGM) OBTAINED FROM RECYCLING OF THE USED AUTO CATALYTIC CONVERTERS

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Used auto catalytic converters contain PGM metals. There are many methods of recovering these metals from used auto catalytic converters, e.g. Rose method, cyanide extraction, chlorination, segregation, melting methods, blowing with metal vapours and metal collector method. They are based on pyro- and hydrometallurgical processes. As a result of such treatment the solution or metal collector with PGM metals is obtained. Then the important task is to separate the particular precious metals. In the paper review of such methods and short characteristics are presented. To those methods belong: classical pr ecipitation method, solv ent ex traction method, solid–phase ex traction method, chromatographic separation.

Keywords: PGM recovery, used auto catalytic converters, PGM purification

INTRODUCTION

PGM belong to the most valuable metals. Their obtaining is rather expensive and complicated. For instance, the current prices (March 2012) for 1 kg of:

- platinum = 54 013 US$,
- palladium = 22 634 US$,
- rhodium = 49 030 US$,
- iridium = 34 884 US$,
- ruthenium = 4 180 US$ [1].

At present Pt, Pd and Rh are mostly used in the production of auto catalytic converters. Every new car should have such equipment. A catalytic converter may contain up to 2 g $\cdot$ kg^{-1} of PGM metals in the ceramic carrier. This is significantly higher than the contents of gold and PGM metals in primary ores (on average < 0,01 g $\cdot$ kg^{-1}) [2]. Therefore, recycling of used auto catalytic converters have become the more and more popular. From economic point of view recycling is very profitable due to high intrinsic metal values and additionally helps to protect environment against many wastes produced during mining of ores and their processing.

METHODS OF PGM METALS RECOVERY FROM USED AUTO CATALYTIC CONVERTERS

First, the used catalytic converters are dismantled, then the stainless steel shell is removed and the pure catalytic carrier without fibrous material is obtained. Now, it can be treated as a whole carrier or can be grinded and homogenized.

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Two types of processing methods have been commercially used: hydro- and pyrometallurgical. The short characteristics of these methods is presented below:

- in hydrometallurgical methods catalytic carrier is dissolved in water solution of chlorides, chlorates, chlorine, hydrogen peroxide, bromates, nitrates and aqua regia, then PGM metals change into the form of chloride complexes (MCl_6^{2-}). Obtained solution is concentrated and PGM metals are extracted; drawbacks: many liquid wastes dangerous to the natural environment are created; Figure 1 presents available hydrometallurgical methods and their short characteristics,
- in pyrometallurgial methods grinded or whole catalytic converter carrier is melted with the addition of metal collector such as copper, magnesium, calcium or blown by its gaseous vapours; as a result alloy of metal collector (Cu, Mg, Ca) with PGM metals and also slag are obtained; then slag is separated, whereas the alloy of metal collector and PGM metals is purified to obtain pure platinum and other metals or used then in this form for some other application; Figure 2 presents available hydrometallurgical methods and their short characteristics.

AVAILABLE WAYS OF PGM METALS PURIFICATION

In recent years considerable changes can be observed in the process of precious metals refining. Improved separation and refining processes have been developed based on solvent extraction and ion exchange. These processes used the differences in the chemistry of their anionic chloro-complexes. Figure 3 presents the

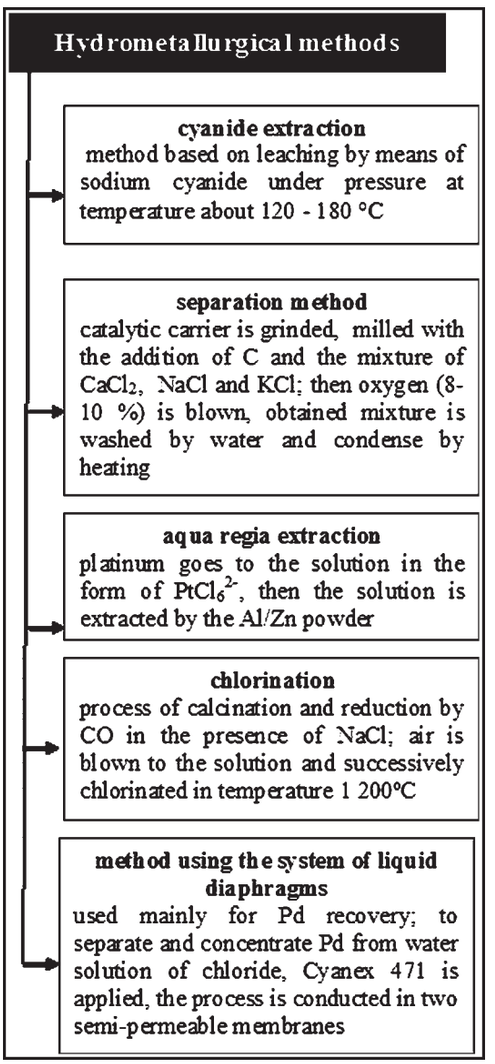

Figure 1 Short characteristics of available hydrometallurgical methods applied in recycling PGM metals from used auto catalytic converters [3-6]

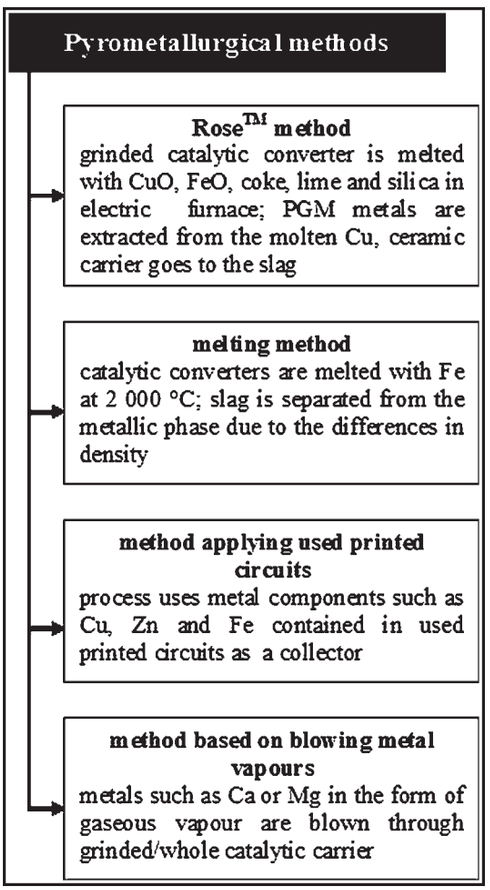

Figure 2 Short characteristics of available pyrometallurgical methods applied in recycling PGM metals from used auto catalytic converters [3-10]

general scheme of classical refining method for separation of the PGM metals, whereas Table 1 shows short characteristics of particular stages of the method. This method was modernized by introducing a number of solvent extractants.

Three different types of extractants are used today [13]:

- for complex formation: dialkyl sulfides, hydroxyoximes,
- for anion exchange (strong base): tri-n-octylamine,
- for anion exchange (strong base): dibutyl carbitol, isodecanol, methyl-iso-butyl ketone, tri-n-butyl phosphate.

Figure 4 presents the modern refining method which uses solvent extraction. At present there are many other available methods of PGM metals refining:

- solid-phase extraction – methods used for complimenting or replacing solvent extraction methods, extractants include commercial anion-exchange resins like Amberlite IRA 400 or Superlig® series of media,
- chromatographic separation of the PGM – such separation is based on the rate of anion exchange: $[MCl_6]^{2-}$> $[MCl_4]^{2-}$> $[MCl_6]^{3-}$>aquo-species,
- separation of a reduced PGM feed – Ir(IV) and Ru(IV) are reduced to Ir(III) and Ru(III) by means of Sephadex® and in this form the chromatographic separation is conducted and four different PGM streams are obtained:
  - stream containing Ir (III), Ru(III) and Rh(III),
  - stream containing Pd(II),
  - stream containing Pt(IV),
  - stream containing Os(IV),
- three–liquid-phase extraction TLPS [15,16] – used for separation of Pt(IV), Pd(II) and Rh(III) from multi-metal complex aqueous solutions, the main driving force is salting-out induced phase-splitting behaviour in the system: S201-CH_3CN-NaCl-H_2O or sugaring-out in the system: S201-acetonitrile-glucose-water; the main limitations of these methods seem to be high cost of phase-forming polymers used for extraction and the difficulties in polymer recovery.

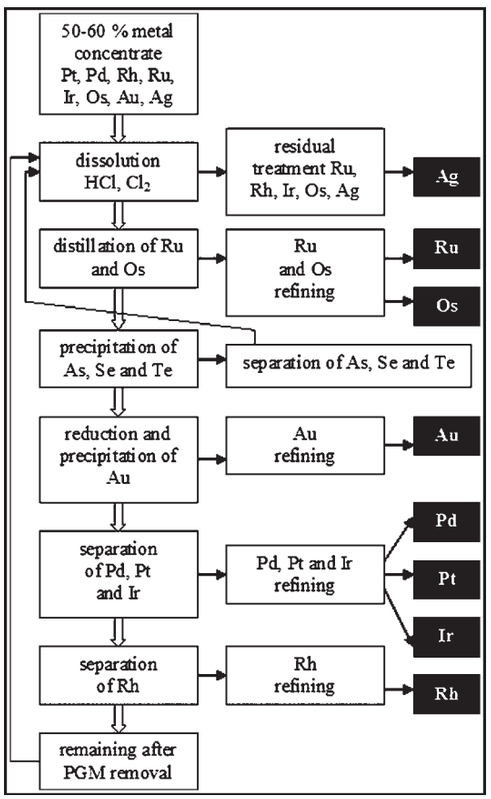

Figure 3 General scheme of classical refining method of PGM metals separation [11,12]

Table 1 **Short characteristics of stages of classical refining method used in separation of the PGM metals [11,12]**

Stage	Characteristics
Dissolution HCl	PGM sample (ore concentrate) is dissolved in HCl, more than 98 % of Pt, Pd and Au, more 90 % of Rh, ir and Ru should be dissolved during dissolution, Ag remains undissolved in the form of AgCl
Distillation of Os and Ru	Ru should be separated as early as possible below 50 ppm because it negatively influences the quality of Pd, Pt and Ir solvent extraction and Rh precipitation
Precipitation of As, Se, Te	Pregnant solution obtained after Ru and Os separation is treated by precipitation in order to remove As, Se, Te and Fe (this process is necessary only if the amount of this element is high)
Reduction of Au	Au is separated by reductive precipitation of solution obtained after removing As, Se and Te; it is possible to remove gold by solvent extraction too
Separation of Pd	Pd is separated by solvent extraction applying DnHS or DnOS as the extractant; there are 3 stages: extraction (Pd changes into organic form), scrubbing (removal of coextracted impurities), stripping (transfer of Pd back into pure aqueous phase)
Separation of Pt and Ir	Pt and Ir are separated from the solution obtained after Pd extraction; if Ir concentration is low it is recommended to concentrate the solution before Ir extraction or separate Ir from Pt during Pt extraction cycle
Separation of Rh	Rh is separated from the residue obtained from Pt and Ir extraction by precipitation applying highly selective organic compounds under appropriate conditions

All these methods could be used in separating PGM metals obtained from used auto catalytic converters. However, in catalytic carrier only three PGM metals are present: Pt, Pd and Rh. Therefore, the above processes should be modernized or some stages of the processes omitted.

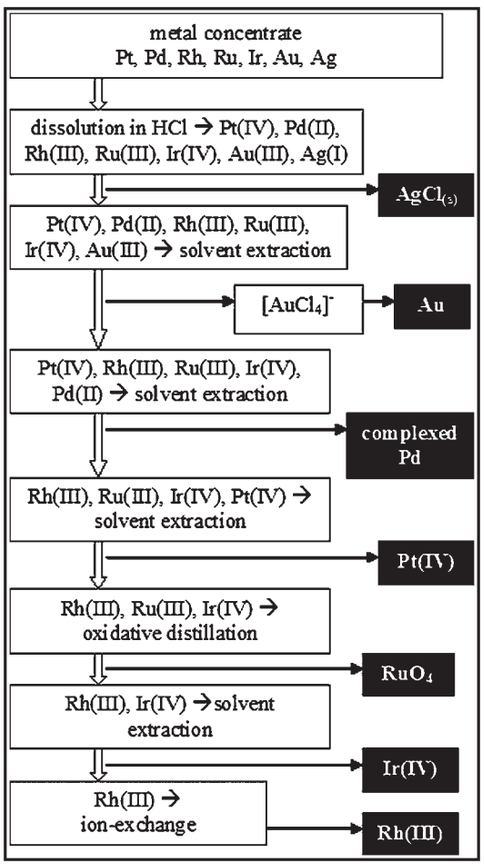

Figure 4 Modern refining method using solvent extraction (ion-exchange) [13,14]

The available purification or separation methods that can be applied for PGM metals obtained from used auto catalytic converters are the following [17-21]:

- application of TBP (tributyl phosphate) and Aliquat 336 in selective extraction of Pt(IV) from the solution after leaching used auto catalytic converters containing Pd(II), Fe(III), Ni(II), Mn(II) and Cr(VI) by solvent extraction,
- separation of Pt(IV) and Pd(II) from associated metals like Fe(III), Cu(II), Ni(II), Zn(II), Al(III) by the extraction of the solvent with 0,5 % LIX 841 and Alamine 336,
- separation of Pt(IV) and Pd(II) from chloride solution using Alamine 300,
- liquid-liquid extraction of Pt, Pd and Rh with Cyanex 921 from aqueous hydrochloric acid media.

CONCLUSIONS

Recycling of used auto catalytic converters is necessary if we take into account the economy and environmental protection. The ways in which catalytic carrier can be treated are different, from hydrometallurgical to

pyrometallurgical or even mixed. After blowing gaseous vapours through the catalytic converters metal powder with platinum (Ca-Pt or Mg-Pt) is obtained. This product could be used in such a form for removing NO_x in power boiler or coming from combustion gases produced from firing process of coke oven or especially Pt-Mg powder in magnesium machining. If metal collector is used for gathering platinum it is harder to obtain it, but then the solvent extraction is used as in case of hydrometallurgical treatment of the catalytic converters. Figure 5 presents the scheme of possible treatment of alloy of metal collector (in this case – iron) with platinum obtained in pyrometalurgicall way. Presented and characterized solvent extraction processes of platinum (IV) ions is quite simple, rapid and a suitable method for separating metals ions from the solution after leaching (hydrometallurgical treatments).

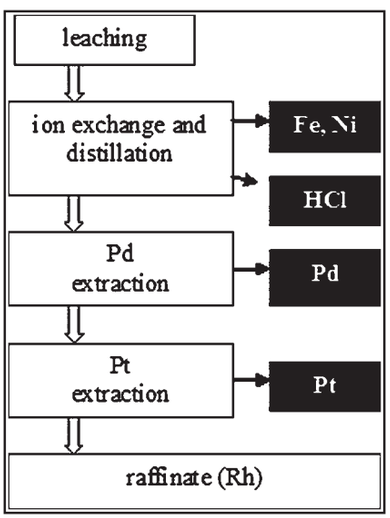

Figure 5 Scheme of possible treatment of alloy (metal collector with Pt) obtained after melting [22]

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Note: The responsible person for English language is: M. Kingsford-Golinowska, Poland.