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THERMAL BALANCE OF THE MAGNETO-HYDRO-DYNAMIC PUMP FOR RECOVERY OF PLATINUM GROUP METALS FROM SPENT AUTO CATALYSTS

Every new car should be equipped with the catalyst, which limits the amount of harmful chemical compounds such as NO_x, CH and CO emitted to the air. Auto catalyst consists of the ceramic or metallic carrier, on which is the layer with Platinum Group Metals playing catalytic role. There are many methods using for recovery those valuable metals from spent auto catalyst, however evry of those methods have some limitations. Proces described in the article is the modified method of metal collector, which used magnetohydrodynamic pump. Rotary electromagnetic field generates in the liquid metal rotary current, which as a consequence washing out the PGM metals from the ceramic carriers. Considering the possibilities of commercialization of the described method, the energy balance was made. From that balance the energetic efficiency of the unit was determined and the analysis of the temperature distribution was shown thermographycally.

1. Introduction

Millions of cars driving every day on the roads have become the potential source of air pollution. To minimize emission of harmful compounds to the atmosphere every car is equipped with the catalyst, which as a consequence protect the atmosphere before noxious compounds such as nitrogen oxides (NO_x), hydrocarbons (CH) and carbon monoxide (CO).

Auto catalyst is built from metallic or ceramic carrier, which is covered by the layer of Platinum Group Metals (PGM), mainly platinum, rhodium and palladium – they play the catalytic function. The carrier is then wrapped with the fibrous material and closed in the stainless steel shell. 96 % of all applied catalysts have ceramic carrier made from alumina (Al_2O_3 with addition of cerium oxide CeO_2). Catalyst structure is very similar to honey comb - dense net of square holes. Such structure increases the active surface, therefore the contact zone of the catalytic substances (Pt, Pd, Rd) with the exhaust gases, which are flown through channels [1]. To main advantages of ceramic carriers belong low thermal expansion and big area, which enables good distribution of catalytic active phase. Whereas, the disadvantages of such carriers are: lower heat and mechanic resistance of the elements, necessity of applying the ceramic fibrous materials, which protect against the cracking during shocks and reduce the differences in the thermal expansion taking into account the metallic shell [2].

The increase of PGM metals consumption in the motorization is connected with the growing amount of produced cars; in 2013 the production of catalyst applied 37 % of produced platinum, 77 % of palladium and 80 % of rhodium [3]. New and modern catalysts, which are serial assembled in cars, should work at least for 80,000-90,000 km – however, in practice they are used considerably longer, although their efficiency is rapidly falling down. The life time of catalysts is limited, and at their end they should be appropriately disposed. The law regulations, saying that every catalyst should be dismounted from the car and then destined to the further segregation and processing, have improved the situation of PGM recovery in the European Union. Additionally, there are more arguments for such solution (PGM recovery): the limited sources of PGM metals, scarceness of their occurrence, expensive and energy-intensive process of PGM metals production, and the substantial amount of created waste during the production process. Spent catalysts management is appreciated good point in the limitation of waste disposal, and mainly lower emission of harmful compounds to the atmosphere during recovery process comparing with the production from raw materials [4]. There are many factors influencing the profitability of the PGM metals recovery process such as: the market of secondary materials, law regulations, working costs, charge for waste deposit, applicable technologies of treatment, level of quality and the professionalism of the collecting and dismantling [5].

To recover PGM metals from spent catalysts many methods are used basing on hydrometallurgical, pyrometallurgical or both processes. When hydrometallurgical processes are used the PGM metals are obtained as the solution in the form of chloric complexes (MCl_6^{2-}). As solving agents aqua solutions of chlorides, chlorates, chlorine, hydrogen peroxide, bromates, nitrates and aqua regia can be used. In the obtained solution the concentration of PGM metals is rather small, so the next step of the process is to concentrate it and to extract the PGM metals. The main disadvantage of those technologies is waste solutions, mainly acidic ones, which became a big danger to the natural environment [6-11]. Those methods demand to be particularly careful due to using cyanides, concentrated acids and chlorine.

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When the pyrometallurgical processes are used the grinded carriers covered by PGM metals are melted with the addition of other metal, which plays the binding role – it is metal collector. PGM metals went to the alloy, whereas the ceramic carriers to the slag – temperature of the process is lower than the melting temperature of the carrier. As a result the alloy with appropriate high concentration of PGM metals is obtained, which should be then refined. In the case of pyrometallurgical methods there is necessary to apply suitable aggregates, which can reach the required temperature, so they are expensive, and also energy-consuming [4]. Even if the pyrometallurgical methods are applied at the beginning stages, then also hydrometallurgical processes (e.g. precipitation) should be used to separate the PGM metals from the metal collector; the alternative is to find to this alloy the appropriate application in the form in which it was obtained.

To sum up, there is no universal method to recover PGM metals from spent auto catalyst; there is necessary to do suitable segregation of catalysts and decide which method should be applied. In Poland there is no recovery of PGM metals from spent auto catalyst – the collected carriers are transported to Germany or other countries, in which they recovered mainly platinum. However, many plants are interested in finding adequate method and recovery of platinum on the spot.

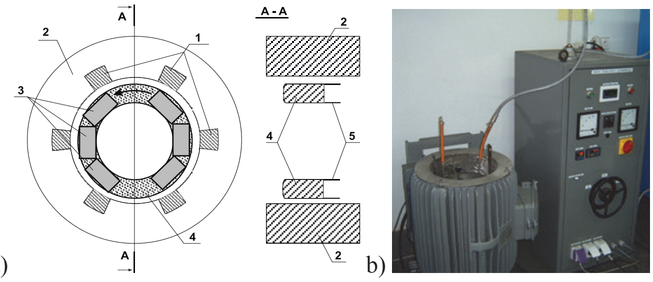
2. PGM recovery using magneto-hydro-dynamic pump

One of interesting method of platinum recovery from spent auto catalysts seems to be metal collector method. This method is basing on dissolving the PGM metals in liquid metal. However, the biggest problem is the efficiency of PGM metals elution from catalysts.

The modification of this method uses the Lorenz force created in the liquid metal as a result of action of rotary electromagnetic field. Applying magneto-hydro-dynamic pump to recover PGM metals from spent auto catalysts is based on the fact that the liquid metal (Fig. 1) is placed in the ring-shaped channel, around which is located inductor winding on the core, generating vortex field with the axis compatible with the ring axis. Rotary electromagnetic field creates in the liquid metal the rotary currents, which interact with electromagnetic field of inductor generating Lorenz force causing the rotary motion of the metal. Placing catalysts carriers in such created flux of liquid metal enables to wash out platinum, palladium and rhodium from the channels of carriers. The constant motion of the metal in essential way intensifies the process of elution. Applying the same metal for washing out the great amount of catalyst causes that the concentration of PGM metals in the solution is increasing, which as a consequence guarantees the profitability of their extraction from the liquid metal. Using the closed cycle of the liquid metal limits the unfavourable influence on the environment.

This method is universal – it can be used for metallic and ceramic carriers. As a metal collector lead was used. The working temperature of the aggregate is much lower than in the case of conventional methods. The described method is an original project, protected by patent, it is probably the one using the magneto-hydro-dynamic phenomena for the recovery of PGM metals from the spent auto catalysts. In this method there is no necessity to grind and crush the catalyst carriers before the process. Thus, the cost of these operations is saved. Additionally, there is no dust, in which valuable metals can be lost, and which can be of course captured in the special units.

Considering the possibilities of commercialization of the described method, the energy balance was made – it gives possibility to estimate the energetic efficiency of the unit and as a consequence to decide if the process is profitable [12].



a) b)

Fig.1. A) Scheme and b) laboratory version of the aggregate for PGM metals recovery from spent auto catalyst carriers using magneto-hydro-dynamic pump: 1 – winding; 2 – magnetic core; 3 – catalyst carriers; 4 – liquid metal; 5 – channel

3. Energy balance of the unit

The described process of precious metal recovery in the laboratory version is powered by electricity. After set working the experimental stand, during the warming up in order to shorten the time of reaching the given temperature, the system works with the higher power. In that time the flux of supplied energy is used mainly to heat up the lead charge from the ambient temperature T_1 (about 20°C) to the temperature T_2 (about 400°C, in which the experiments are conducted). The summary power delivered to the system is maximally 2900 W. After reaching the working temperature the power of heating system is limited to the 1100 W, whereas the supplied flux of electricity is used for heating the new portion of treated charge and to keep the given temperature of the process. The mass of melted lead in the reactor is used not only to solve platinum from the carriers, but also as a heat accumulator.

New portion of the charge with the ambient temperature is replaced every 300 seconds and is made up of three selected mechanically fragments of spent catalysts with the mass 80 grams every. Basing on own research and literature data [1,4,7,8] it was assumed that the average platinum content in the processing samples is 0.43 %.

In the reactor the new portion is heating up again from T_1 to the temperature of the molten lead. In the thermal calculations it was assumed that the catalysts carrier consists of Al_2O_3 and it is an inert. Basing on data of thermal values from JANAF 98 tables [13], change of specific thermal capacity for Al_2O_3 ($c_{p\ Al_2O_3}(T)$) in the range of temperature 0°C ÷ 400°C and for platinum ($c_{p\ Pt}(T)$) in the range of temperature 25°C ÷ 400°C was determined in the form of the following equations:

$$c_{p\ Al_2O_3} = -2\cdot 10^{-9} T^4 + 2\cdot 10^{-6} T^3 - 0.0028\cdot T^2 + 2.049\cdot T + 707.94 \quad \text{J/(kg·K)} \tag{1}$$

$$c_{p\ Pt} = -4\cdot 10^{-11}T^4 + 5\cdot 10^{-8}T^3 - 3\cdot 10^{-5}T^2 + 0.0327\cdot T + 131.78 \quad \text{J/(kg·K)} \tag{2}$$

In equation (1) and (2) temperature T is given in °C.

Heat absorbed by the charge during heating up (ΔQ_w) from the initial temperature T_1 to the temperature of the molten lead T_2 was calculated from the equation:

$$\Delta Q_w = m_{Al_2O_3}\int_{T_1}^{T_2} c_{p\,Al_2O_3}(T)dT + m_{Pt}\int_{T_1}^{T_2} c_{pPt}(T)dt\,, \tag{3}$$

where: $m_{Al_2O_3}$ – mass of Al_2O_3, kg; m_{Pt} – mass of the platinum, kg.

In the energy balance the time of periods between exchanging the new portion of the charge, and also the flux of energy needed for heating the crucible (Q_d) together with the melt in order to keep the required temperature were considered. After the made up the energy balance:

$$Q_d = \Delta Q_w + Q_{ot} \tag{4}$$

the efficiency of the process was determine. Such efficiency is about 28 %. The residual part of the delivered energy flux is lost to the surroundings (Q_{ot}).

The losses of heat to the surroundings go mainly on the surface of liquid metal by convection and radiation during the loading the new portion of catalyst carriers. During the course of technological process the surface of liquid metal is covered by the shield limiting the heat losses ($\dot{q}_{r,e}$), which can be determined from the equation [14]:

$$\dot{q}_{r,e} = \frac{1}{1+n}\cdot \dot{q}_{r,1-2} \tag{5}$$

In calculations according to (5) n=1 due to applying the single shield, which the area is 660 cm^2. Reciprocal emissivity (ε_{1-2}) was assumed to be for the molten lead 0.28 and for the shield 0.35 [14]. Application of the shield also prevents the melt oxidation, because of limiting the atmospheric oxygen and possibilities of forcing the argon in the area of molten lead and shield. Part of the heat is also transferred by the shield not only by radiation, but also by convection ($\dot{q}_{r,e}$) described by the Newton`s equation:

$$\dot{q}_{k,e} = \alpha_k \cdot (T_e - T_1) \tag{6}$$

where Te is the shield temperature in °C.

To determine the heat penetration coefficient (α_k) during the experiment course is analytically difficult due to natural convection occurring at the shield area (it is disturbed by switching on the fan to cool the winding of the hydro-magneto-electric stirrer). The average values of heat penetration coefficient for the crucible walls is 7-13 W/(m^{2}K) considering the area.

When determining the heat losses to the surrounding from the working aggregate, the analysis of temperature distribution obtained thermographycally were used. Fig. 2 and 3 present the exemplary views.

To prevent the surface of molten lead before oxidation, in the area between the surface of molten lead and the shield, argon was introduced. Argon flux was 20 dm$_n^3$/h. It ensure the small overpressure of inert gas above the metal surface. The flowing argon heats from the ambient temperature to the temperature close to the molten lead temperature. From calculations result that the flux of enthalpy (which value is about 2 W) leaving the aggregate area with heating up argon (in the energy balance) can be omitted considering the fact that the argon flux is very scarce (9.91.10^{-6} kg/s).

Analytically determination of heat losses to the surroundings from the side walls of the inductor is difficult taking into account the construction and action of hydro-magneto-electric stirrer. The construction of inductor was based on the classical three-phase asynchronous motor, which winding is cooled by natural convection of the finned rolled part. In some work states of test stand in order to intensify the cooling the fan is switched on to direct the air flux in the fin of the stator enclosure changing the natural convection into forced convection. To ensure the better stability of the temperature and limit the heat losses to the surroundings the crucible is covered by the thermal insulation. In the conducted analysis heat that is emitted in the charge because of vortex current working was not considered due to fact that the amount of such heat is scarce. The whole system was reheated resistancially, such solution enable to keep the system in the thermal equilibrium.

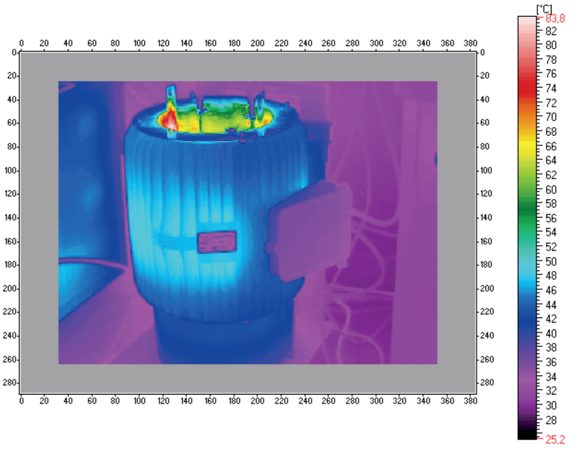


Fig. 2. Temperature distribution in the charge door of the crucible without the shields

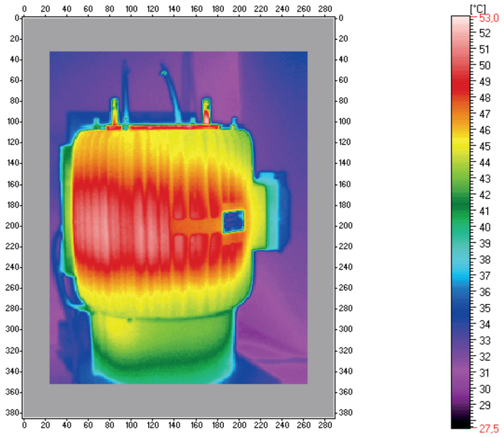


Fig. 3. Temperature distribution at the side walls of the stirring aggregate

4. Summary and conclusions

Environment protection as well as using the valuable secondary materials, which as a result limits the waste production, is undoubtedly the requirement of our times. Thus, it is really important to recover such valuable metals like platinum, palladium and rhodium. For this recovery many methods basing on pyrometallurgical and hydrometallurgical processes can be applied. One of the new methods is modified metal collector technology using magneto-hydro-dynamic pump. This method seems to have some advantages, so the necessary is also to check the energy balance for this aggregate. Due to complicated character of the aggregate working it is convenient to treat the heat losses to the surroundings as a complement to the heat accumulated during the heating up the charge in comparison to the flux of delivered energy. Calculations of balance energy are in agreements with measurements, whereas the unidentified losses of flux energy to the surroundings are 2.3%. The calculated heat efficiency of the aggregate was 28% and was comparable with real heating processes, which take place in the typical industrial technologies.

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