International Journal of Mineral Processing 145 (2015) 108–113

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro

Recovery of platinum group metals from spent catalysts: A review

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ARTICLE INFO

Article history:
Received 20 January 2014
Received in revised form 22 April 2015
Accepted 5 June 2015
Available online 7 June 2015

Keywords:
Platinum group metals
Spent catalyst
Recovery
Pyro/hydrometallurgy

ABSTRACT

This paper provides an overview of the various processes used in the recovery of platinum group metals (PGMs) from spent catalysts. PGM recovery is interesting due to their vast industrial applications and high market prices. From the use of renewable resources and environmental protection viewpoints, recycling of PGMs receives wide concerns as the amounts of spent catalyst increases dramatically. PGM recovery from spent catalysts is a challenge due to the fact that spent catalysts are diverse and complex in terms of material and component makeup as well as the original catalyst's manufacturing processes. The state of the art recovery of PGMs from spent catalysts by pyrometallurgy and hydrometallurgy techniques is highlighted and existing advantages and disadvantages of these techniques are analyzed in this paper. This review also pointed out that the promising processes of PGM recovery are economical, environmentally friendly and large-scale means.

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1. Introduction

Platinum group metals (PGMs), including platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os), are widely used in the field of many industries due to their distinct properties, such as catalytic activity, chemical inertness, corrosion resistance, thermoelectric stability and magnificent color. In the industrial application, PGMs are employed as the active species for the catalyst. A number of PGMs-based catalysts are available and applicable for various purposes (Hagelüken, 2006). Commercial application field and composition of some catalysts are given in Table 1. Therefore, PGMs are also called '*Vitamin of modern industry*' and '*First and foremost high-technology metal*'.

PGM natural resource deposits are very limited, only 66,000 tons all over the world. The most extensive deposits have been found in the norite belt of the Bushveld Igneous Complex covering the Transvaal Basin in South Africa, the Stillwater Complex in Montana, United States, the Thunder Bay District of Ontario, Canada, and the Norilsk Complex in Russia. Generally, PGMs associate with base metal sulfide

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http://dx.doi.org/10.1016/j.minpro.2015.06.009
0301-7516/

Table 1
The application field, composition of some spent catalysts.

Application fields		Catalyst type support	PGMs	PGMs loading/%	Life (year)
Oil-refining	Reforming	Al_2O_3	Pt; Pt/Re, Pt/Ir	0.02–1	1–12
	Isomerisation	Al_2O_3, zeolites	Pt; Pt/Pd		
	Hydrocracking	SiO_2, zeolites	Pd; Pt		
	Gas to liquid	Al_2O_3, SiO_2, TiO_2	Co + (Pt; Pd; Ru; Re)		
Bulk & specialities	Nitric acid	Gauzes	Pd	100	0.5
	H_2O_2	Powder (black)	Pd	100	1
	HCN	Al_2O_3 or gauzes	Pt; Pt/Rh	0.1; 100	0.2–1
	PTA	Carbon granules	Pd	0.5	0.5–1
	VAM	Al_2O_3, SiO_2	Pd/Au	1–2	4
	KAAP	Activated carbon	Ru		
Homogeneous	Oxo Alcohols	Homogeneous	Rh	100–500 ppm in process solution	1–5
	Acetic acid		Rh; Ir/Ru		
Fine Chemicals	Hydrogenation	Activated carbon	Pd; Pd/Pt Ru; Rh; Ir	0.5–10	0.1–0.5
	Oxidation				
	Debenzylation				
Automotive	Catalysts	Cordierite monolith ceramic pellets	Pt/Rh Pt–Pd–Rh Pt	0.1–0.5	>10
		Metallic monolith			
	Diesel particulate filter	SiC or cordierite	Pt/Pd		

minerals, and their content in the ore are within the range of 2–10 g/ton. PGMs are recovered as byproducts or co-products depending on their concentration in the ore (Liu, 2013; Jha et al., 2013).

PGM demands are increasing worldwide because of numerous applications in various industries. The global supply and demand for PGMs in 2012 are presented in Table 2. Gross demands for Pt, Pd and Rh are over 590 tons, while total recycling for Pt, Pd and Rh from secondary resources is almost 150 tons. Recovering PGMs from secondary resource will become more and more significant because of the limited natural resource.

In China, PGM natural resource deposits are extremely poor; the reserve is only approximately 350 tons. Nowadays, 90% of PGMs from natural resource are produced by Jinchuan Group Company, only 2.5–3 tons per year. Meanwhile, gross demands for Pt and Pd were 137 tons in China in 2012. PGMs produced from natural resource cannot meet the increasing demand of the Chinese PGM industry development. Therefore, it is necessary to process secondary resources, such as spent catalysts, electronic scraps, used equipment, fabricated ware and membrane electrode assemblies to recycle PGMs. On the other hand, recycling PGM secondary resources also avoids environmental contamination. Except that, it will decrease electricity consumption and diminish pollutant emission (Barakat et al, 2009).

It was reported by Johnson Matthey that, in 2012, gross demands for Pt, Pd and Rh in the field of auto-exhaust catalyst were 97.2 tons (over 44% of gross Pt demand), 216.8 tons (72% of gross Pd demand), and 24.9 tons (78% of gross Rh demand), respectively. And the recycled Pt, Pd and Rh from auto-exhaust catalyst were 39.7 tons, 57.9 tons and 8.7 tons, respectively. Although many researchers are studying new catalysts to replace or decrease the dosage of PGMs in the auto-exhaust catalyst, the net PGM demands are still very high in the future due to increasing automobile number and environmental pressure. In 2011, automobile yield was 18 million in China. It is estimated that after the auto-exhaust catalysts reach their service life, the generated spent catalysts will be 20,000–30,000 tons per year, which contains 25–40 tons of PGMs. The spent auto-exhaust catalyst will become the biggest target market of PGM secondary resources. In 2012, the demands for Pt and Pd in the chemical industry are 4.0 tons and 5.9 tons, respectively, and PGM amount in the servicing and accumulated catalysts in the chemical industry has run up to hundreds of tons in China.

Table 2
The total supply and demand of PGMs in 2012.

Item	Pt	Pd	Rh	Ru	Ir
Total supply/t	178.5	200.0	22.4	Not available	Not available
Gross demand/t	261.9	299.5	31.6	25.8	6.2
Total recycling/t	64.5	76.5	8.7	Not available	Not available
Total net demand/t	197.4	223.0	22.9	Not available	Not available
Movements in stocks	18.9	23.0	0. 5	Not available	Not available

Spent PGM catalysts contain the following traits: (1) High PGM content, about several kilograms per ton. (2) Simple composition, main impurities are Al_2O_3, cordierite, activated carbon and so on. In conclusion, recovering PGMs from spent catalyst has these superiorities with simple process, small scale, low investment and cost, short production cycle, less environmental pollution and good economic benefits. Recovering and refining PGMs from spent materials have already been successfully practiced in many industries (e.g., Umicore, Belgium; Heraeus, Germany; BASF/Engelhard, USA; Johnson Matthey, UK; Nippon/Mitsubishi, Japan). In China, PGM recovery from secondary resources started late and faced with these problems of backward technology and equipment, small scale, low metal recovery, incomplete recovery management system, serious pollution and so on. In recent years, by developing and introducing advanced technologies and equipments, Sino-Platinum Metals Resources (Yimen) Co. Ltd., China, has set up a recovery production line of PGM secondary resources. The line will come into operation in 2015, and the processing capacity of PGM secondary resources will be 3000 tons/a, with PGM production capacity of 5 tons/a.

The efficient recovery and purification of PGMs from spent catalyst are economically desirable. There are three basic factors that influence the recyclability of spent PGMs catalysts: (1) the intrinsic metal value; (2) the compositions; and (3) the application segment and the associated lifecycle structure, including the recycling chain, business model and turnaround speed (catalyst life). The exact determination of the PGM content in the spent catalyst received is absolutely crucial.

2. Recovery techniques of PGMs from spent catalysts

The accurate sampling and assaying of spent catalysts are the decisive factors for the monetary results which a supplier achieves when supplying material for recycling (Hagelüken, 2006). Therefore, the spent catalyst needs to be well prepared and homogenized through screening, blending and separation in order to obtain a representative sample for composition analysis. The selection of efficient and economical recycling techniques, not only depends on the catalyst's supporter, but also involves PGM loading content and other base metals. PGM recovery from spent catalyst can be broken into five basic steps: homogenization/sampling, pre-concentration, dissolution and metal-isolation, and finally purification.