UDC 669.054.8:669.28

G.A. Kolobov [(1)], professor, c.t.s.
A.S. Medvedev [(2)], professor, d.t.s.
L.P. Kolmakova [(3)], associate professor, c.t.s.
A.V. Karpenko [(1)], assistant

NEW TECHNOLOGIES OF EXTRACTION OF MOLYBDENUM FROM EXHAUST CATALYSTS

[(1)] Zaporozhe state engineering academy, Ukraine,
[(2)] National research technological university «MISandA», Moscow, Russian Federation,
[(3)] Institute of the coloured metals and материаловедения Siberian federal university, Krasnoyarsk, Russian Federation

It is executed the review of new technologies for extraction of molybdenum, and also nickel, cobalt, vanadium, bismuth and cesium from exhaust catalysts. There are indicated the optimal parameters of operations, used at processing of exhaust catalysts: oxidizing burning, sublimation of molybdenum trioxide, lixiviating, chemical deposition, persorption, ionic exchange and extraction. There are brought quantitative indexes over of extraction of molybdenum and other important components at the use of different technologies of processing for exhaust catalysts.

Keywords: exhaust catalysts, molybdenum, nickel, cobalt, vanadium, bismuth, cesium, pyro- and hydrometallurgical technologies of processing, extraction

One of important sources of secondary raw material for rare metals are exhaust catalysts. Basic molybdenum containing catalysts are catalysts of mark ACM (≈ 4 % *CoO* and 12 % MoO_3), ANM (3-4 % *NiO*, 12-14 % MoO_3), ГКД-202 (*Ni-Mo*), ГК-35 (*Ni-Mo*). Exhaust catalysts, except for connections of rare and coloured metals, contain different admixtures: coke deposits, tarry residuum, sulphuric-, azoth- and phosphorus containing connections and other, are toxic wastes, unauthorized to the burial place.

Most pyro- and hydrometallurgical methods for processing of exhaust catalysts it is considered in works [1,2]. There are presented new technologies of extraction molybdenum from exhaust catalysts, beginning from simple on composition (with primary content MoO_3), after catalysts of the systems of *Mo-Co*, *Mo-Ni* and *Mo-Ni-Co* and further more difficult on chemical composition catalysts, containing, except for a molybdenum, such metals, as vanadium, cesium and bismuth.

For extraction of molybdenum from the tarry organic residuum of exhaust catalysts two methods are offered: deposition as fallouts with higher amines or as *MoS*. Extraction of molybdenum from muriatic solutions was 83-90 % and 96-99 % accordingly. For sulfate environments the method of deposition of MoS_3 is suitable only with the degree of extraction 97-99 %.

At the hydrometallurgical variants of processing of exhaust catalysts a molybdenum can be extracted by extraction with the use of mixture of organic solvent with water at a temperature 50 °C during 30 min. At the use of solution *HCl* together with molybdenum the considerable quantity of vanadium and nickel passes to solution. The real extraction of molybdenum in solution on this technology does not exceed 85 %. The soda and ammoniac lixiviating of exhaust catalysts of form ACM-1,

ACM-2, ACM-3 is investigated in work [3]. At the hydrometallurgical processing of exhaust catalysts of mark ACM-1 extraction of molybdenum in solution with the use of soda was 92.7 % while at an ammoniac method - less than 63.7 %.

Processing of molybdenum-cobalt exhaust catalysts of mark HDS (analogical on composition to the catalysts of type ACM) was carried out in two stages: muriatic lixiviating and subsequent liquid extraction [4]. A degree of extraction for molybdenum and cobalt is 99 %.

$CoMo/Al_2O_3$ exhaust catalysts after burning at a temperature 700 °C during 20 minutes lixiviated solution $NaOH$ in a quantity double in relation to stoichiometrical for education Na_2MoO_4. At a temperature 60 °C after 4 hour a more than 90 % mo-lybdenum passed to solution.

In works of Krasnoyarsk academy of the coloured metals and gold [5] the technological scheme of molybdenum extraction and nickel from exhaust catalysts is offered. The worked out technology is wasteless, effective, economic advantageous, foresees the regeneration of reagents and can be fixed in basis of techniques-economical validation of building of experienced-industrial workshop on processing 1000 t/year of exhaust catalysts.

In work [6] the technological scheme of the industrial processing of exhaust catalysts of hydrorefining (composition, %: 6-12 *Mo*; 35-40 *Al*; 2.5-3.0 *Ni*) is offered with a receipt as eventual foods of PMA, coagulants on the basis of aluminium, slimes, which can be added to the charge for the production of lime-sand brick.

In work [7] it is investigated the process of lixiviating of exhausts catalysts $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$-SiO_2. Extraction of molybdenum, nickel and cobalt about 90 % arrived at treatment of material by acids (HCl, H_2SO_4), by mixtures $HCl+H_2SO_4$ and $HCl+HNO_3$ for the short interval of time.

The selective lixiviating of molybdenum from the exhaust catalysts of desulphurizing was studied on the standards of nickel-molybdenum and cobalt-molybdenum catalysts, burnt at a temperature 500 °C, at a microwave radiation. Extraction of molybdenum for a nickel-molybdenum catalyst was 89 %, for a cobalt-molybdenum catalyst – 91 %.

For processing of exhaust molybdenum containing catalysts in the institute «Hipronickel» the process of the oxidizing burning was investigated [8]. Depending on a temperature and duration of burning low-carbon and low-sulphur candle-ends can be got at the minimum losses of molybdenum with sublimates. These candle-ends can be used for the receipt of metallic alloys on the basis of the system *Co*(*Ni*)-*Mo*.

Technology of separate extraction of bismuth and molybdenum from exhaust catalysts and data about possibility of the effective use of such catalyst in composition a complex modifier for iron-carbon alloys are presented in work [9].

For extraction of nickel, vanadium and molybdenum from the exhaust catalysts of cleaning of oil the two-phase process of lixiviating is worked out [10]. At the optimal regime of bioleaching extraction made, %: 97 *Ni*, 92 *V*, 53 *Mo*. Common extraction for two stages of lixiviating made: for a nickel and vanadium 97 %, molybdenum – 99 %.

Conclusion. Exhaust catalysts can be examined as a secondary source of raw materials of molybdenum. Investigational pyro- and hydrometallurgical operations

(oxidizing burning, sublimation, lixiviating, chemical deposition, sorption, including. burdening, extraction) were foundation for suggestion of technological scheme of processing of exhaust catalysts, allowing to extract from them, except for a molybdenum, connection of such metals, as a nickel, cobalt, vanadium, bismuth, cesium, and in passing to get coagulants and burdening materials on the basis of aluminium.

LIST LITERATURE

1. Никитина, Л. С. Переработка отходов тугоплавких металлов (вольфрама, молибдена, рения) [Текст] / Л. С. Никитина. – М. : Цветметинформация, 1977. – 53 с. – Библиогр. : с. 49-52.
2. Колобов, Г. А. Извлечение редких металлов из отработанных катализаторов [Текст] / Г. А. Колобов, В. И. Иващенко // Технологии и оборудование для утилизации трудно-перерабатываемых отходов : научн. труды ДонИЦМ. – Донецк : ДонИЦМ, 1995. – С. 116-128.
3. Хомутова, А. С. Анализ способов переработки отработанных катализаторов, содержащих редкие металлы [Текст] / А. С. Хомутова, Н. М. Вострикова // Инновационные процессы в современном образовании России как важнейшая предпосылка социально-экономического развития общества и охраны окружающей среды : науч.-практ. конф., Ачинск, 26-27 апр. 2012. : сб. статей. – Красноярск, 2012. – С. 282-289.
4. Recovery of valuable metals and regeneration of acid from the leaching solution of spent HDS catalysts by solvent extraction [Text] / *R. Banda*, T.H. Nguyen, S.H. Sohn, M. Lee // Hydro metallurgy. – 2013. – Vol. 133. – P. 161-167.
5. Переработка дезактивированных молибденсодержащих катализаторов [Текст] / *А. Д. Михнев*, Л. П. Колмакова, Н. С. Перфильева, Т. Е. Грачева // Редкие металлы и порошковая металлургия : Всерос. науч.-практ. конф., 3-5 дек. 2001 : тезисы докладов. – М. : МИСиС, 2001. – С. 25-26.
6. Перехода, С. П. Исследование научных основ и разработка технологии комплексной переработки отработанных катализаторов гидроочистки [Текст] / С. П. Перехода, Ю. А. Лайнер // Известия вузов. Цветная металлургия. – 2010. – № 4. – С. 27-33.
7. De Lima, T. S. Metals recovery from spent hydrotreatment catalysts in a fluoridebearing medium [Text] / T. S. De Lima, P. C. Campos, J. C. Afonso // Hydrometallurgy. – 2005. – Vol. 80, No 3. – P. 211-219.
8. Исследование процесса окислительного обжига отработанных молибден- и вольфрамсодержащих катализаторов [Текст] / А. К. Евграфова, Л. А. Павлинова, Л. Ш. Цемехман и др. // Цветные металлы. – 1995. – № 5. – С. 41-44.
9. Технология переработки молибденсодержащих отработанных катализаторов [Текст] / О. С. Комаров, В. И. Волосатиков, Д. О. Комаров и др. // Литье и метал. – 2013. – № 2. – С. 37-40.
10. A novel sequential process of bioleaching and chemical leaching for dissolving *Ni, V* and *Mo* from spent petroleum refinery catalyst [Text] / D. Pradhan, A. K. Patra, D-J. Kim etc. // Hydrometallurgy. – 2013. – Vol. 131-132. – P. 114-119.