

Processing of Spent Molybdenum-Bearing Catalysts from Petrochemical Synthesis

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Abstract—Technologies for processing spent molybdenum-bearing catalysts from petrochemical production are reviewed. The degree of molybdenum-trioxide extraction from the spent catalysts is presented for different technologies. Pyrometallurgical and hydrometallurgical methods, when used individually, do not ensure the required molybdenum-trioxide extraction. The pros and cons of direct alloying of steel with spent catalysts through the slag phase are outlined. The processing of hydrometallurgically treated catalysts to obtain slag mixtures for steel refining is described. An optimal multistage processing method for the catalysts is considered. By that means, waste-free processing of the spent catalysts is possible. On that basis, calcium molybdate may be used instead of ferroalloys for steel treatment in the ladle–furnace unit.

Keywords: spent catalysts, molybdenum, pyrometallurgy, hydrometallurgy, direct alloying, extraction, catalyst processing

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Today, catalysts are used in about 75% of all reactions in the petrochemical industry. The industrial catalysts used in oil processing are one-, two-, three-, and four-component mixtures based on the oxides of non-ferrous metals [1].

Catalysts based on oxide systems may be produced by various methods that include the mixing of components, shaping, and subsequent sintering [2]. In catalyst preparation, the active component is most often applied by steeping a porous substrate with a solution of the active component; steeping is followed by drying, roasting, and sometimes reduction or sulfiding [3].

In the course of operation, the activity of the catalyst declines as a result of structural changes, mechanical screening, poisoning, coking, or other factors [4].

The catalyst life depends on many factors; it fluctuates from a year and a half to three years [5]. Spent catalysts are regarded as potentially hazardous waste, and their underground storage is forbidden, for environmental reasons [6].

Spent catalysts may be used in metallurgy and elsewhere after preliminary treatment—in particular, the removal of impurities such as sulfur, coke, and petroleum residues. After primary treatment in roasting furnaces to ensure the removal of harmful impurities, the catalysts may be used for the direct alloying of steel or processed further to obtain alloying blends.

AKM aluminum–cobalt–molybdenum catalysts (with 8–18% Mo and up to 4% Co in oxide form) and

ANM, GK-35, and GO-117 aluminum–nickel–molybdenum catalysts are of considerable interest. These catalysts are used at oil-processing plants.

Catalysts for the hydraulic purification of various petroleum materials are based on the universal composition Co(Ni)Mo(W)S, with a γ Al₂O₃ substrate [8].

Spent molybdenum-bearing catalysts contain 5–20% Mo, 1–5% Co/Ni in oxide form, and 1–10% S. Such catalysts may be used in the alloying of steel through the slag phase [9].

Numerous pyrometallurgical and hydrometallurgical technologies permit the extraction of molybdenum, cobalt, and nickel from spent catalysts. However, one- and two-stage processing methods do not always yield sufficient extraction of the useful elements. Accordingly, we need to develop a processing technology permitting maximum and economical extraction of the useful elements.

DIRECT ALLOYING OF STEEL BY MEANS OF SPENT CATALYSTS

Molybdenum-bearing mixtures based on spent catalysts have been successfully used as an analog of ferromolybdenum at steel plants. They reduce the need for ferromolybdenum in steel production. In laboratory conditions, the assimilation of molybdenum from the catalysts in direct alloying may be as much as 98% [10]; in production conditions, the assimilation of molybdenum is 80–95%.

The alloying element is introduced directly in the arc furnace. If the molybdenum added from the spent catalyst is insufficient, then ferromolybdenum is introduced.

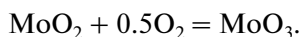
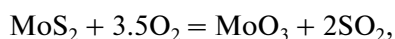
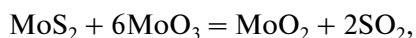
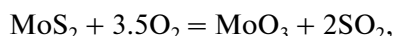
Direct alloying is only possible because the oxygen affinity of molybdenum, and likewise of W and Cu, is greater than that of iron. That permits unobstructed reduction of the oxides of those metals in the furnace. Mostly, the reduction process is exothermal and requires no other energy [11].

The main problems in direct alloying by molybdenum-bearing mixtures based on spent catalysts are the high sulfur content in the unroasted catalysts and the relatively low molybdenum content. That calls for the use of ferromolybdenum. However, the use of catalysts in direct alloying reduces alloying costs and eliminates the need for the storage of spent catalysts.

REGENERATION OF SPENT CATALYSTS

The catalysts of hydraulic purification are often sent to the regeneration columns used in petroleum cracking so as to restore their catalytic activity and permit their reuse in the petrochemical industry. However, such regeneration alone only restores 30% of the catalysts; the remaining 70% are unusable and require safe disposal [12].

In the regeneration of catalysts outside hydrocracking columns, sulfur is removed, molybdenum is converted from MoS_2 to MoO_3 , and petroleum residues are removed. The catalysts are roasted in rotary pipe furnaces at 500–700°C. The following reactions occur on roasting in a pipe furnace [13]



PYROMETALLURGICAL PROCESSING OF CATALYSTS

The boiling point of molybdenum trioxide is 1155°C [14]. That permits the production of industrial-grade molybdenum trioxide by sublimation.

The vaporization rate of molybdenum trioxide depends on the quantity of impurities in the catalysts. Their presence reduces the vapor pressure of the molybdenum-trioxide vapor and hence reduces the vaporization [15]. In catalysts with a high cobalt content, the molybdenum-trioxide extraction is significantly reduced. In that case, nonvolatile molybdates—in particular, CoMoO_4 —are formed at the sublimation temperatures [16]. However, molybdenum-trioxide extraction from cobalt molybdate is possible by hydrometallurgical methods.

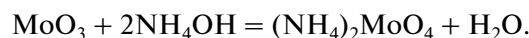
The molybdenum trioxide obtained by the pyrometallurgical method has a low packing density. It may be increased to 0.8–1.2 g/cm³ if the product is dissolved in ammoniacal water and deposited from a solution of ammonium paramolybdate. The benefit of pyrometallurgical processing of spent catalysts is the relatively low cost of MoO_3 production [17].

HYDROMETALLURGICAL PROCESSING OF CATALYSTS

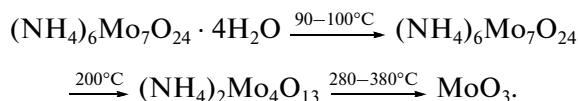
In hydrometallurgical processing, molybdenum trioxide is obtained from the catalysts by leaching with ammoniacal water, soda solution, and other solvents, and then the catalysts are processed. The final product of hydrometallurgical processing may be ammonium paramolybdate, molybdenum trioxide, or calcium molybdate.

For most hydrometallurgical methods, the catalysts must first be roasted for increased extraction of the useful elements. If the molybdenum is present as sulfides, dioxide, or salts with nickel, cobalt, and aluminum, leaching is hindered [18].

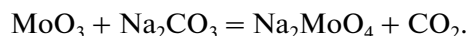
The molybdenum extraction in ammoniacal leaching is low if the catalysts contain molybdates insoluble in ammonia from the previous stages of processing. In catalyst processing by ammonia solution, the molybdenum trioxide is converted to ammonium paramolybdate [19]



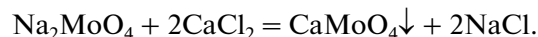
Further roasting of the ammonium paramolybdate at 400°C yields molybdenum trioxide [20]



The molybdenum extraction in soda leaching is greater, on account of the decomposition of some molybdates [21]. However, for catalysts containing many insoluble molybdates, soda and ammonia leaching methods prove ineffective [22]. However, processing is possible by sintering of the molybdenum with soda, followed by aqueous leaching [23]



The molybdenum may then be deposited as calcium molybdate by means of calcium chloride



The calcium molybdate may be used for alloying in ferrous metallurgy.

The steel is alloyed with calcium molybdate in the ladle–furnace unit. The calcium oxide present will promote the production of synthetic slag and hence desulfurization.

To increase the molybdenum extraction, a soda solution with added oxidant may be used, according to

[24]. Thus, for a solution with 160 g/L Na_2CO_3 and 6% H_2O_2 , the extraction after 60 min is as follows: 97.9% Mo, 85.0% V, 0.6% Ni, 4.9% Co, and 1.9% Al.

Processing of spent catalysts containing 4–10% molybdenum and nickel by leaching with ammonia–carbonate solutions for 1 h at 60–80°C was proposed in [25, 26] (with a solid/liquid ratio of 3.5). The solutions from leaching and washing of the solid residue are combined and sent for distillation and concentration in the presence of a sorbent for the extraction of nickel. After concentration and distillation of ammonia, the resulting pulp is filtered and the solution is cooled, to obtain ammonium-paramolybdate crystals.

CATALYST PROCESSING IN SOLID SLAG MIXTURES AFTER MOLYBDENUM EXTRACTION

Today, the Al_2O_3 present in the catalyst in large quantities (up to 85% in fresh catalyst) is lost together with the furnace slag when the catalyst is charged in the arc furnace. In pyrometallurgical or hydrometallurgical processing, there is waste in the form of practically pure Al_2O_3 with some nickel or cobalt (depending on the particular catalyst). It is expedient to use the residue from previous catalyst processing in solid-slag mixtures for the production of refining slag in the ladle–furnace unit or as modifiers. In that case, the spent catalysts will be completely utilized, with considerable economic benefit.

HYBRID PROCESSING

We recommend a very effective hybrid processing method, with extraction of the useful elements in several stages.

The first stage is oxidative annealing at 600°C. The second stage is pyrometallurgical processing of the catalyst with the extraction of most of the molybdenum trioxide at 1250°C. By the proposed method, the same equipment is used for roasting and sublimation of the catalysts: a continuous electrical furnace with a rotating hearth. The heaters are silicon-carbide rods around the furnace perimeter. The catalyst is placed on the furnace hearth. First, it is heated to 600°C for oxidative roasting. After the sulfur concentration in the catalysts is less than 0.5%, the temperature is boosted to 1250°C and direct sublimation of molybdenum trioxide begins. The air supplied to the furnace carries the molybdenum-trioxide vapor through a series of holes at the hearth level to a common collector and then through a system of conduits to bag filters [27].

The losses in roasting are estimated as 1%, in terms of molybdenum oxide. In pyrometallurgical processing at industrial enterprises, the degree of extraction is 80%.

With decrease in the molybdenum content in AKM catalysts, the degree of extraction in soda extraction

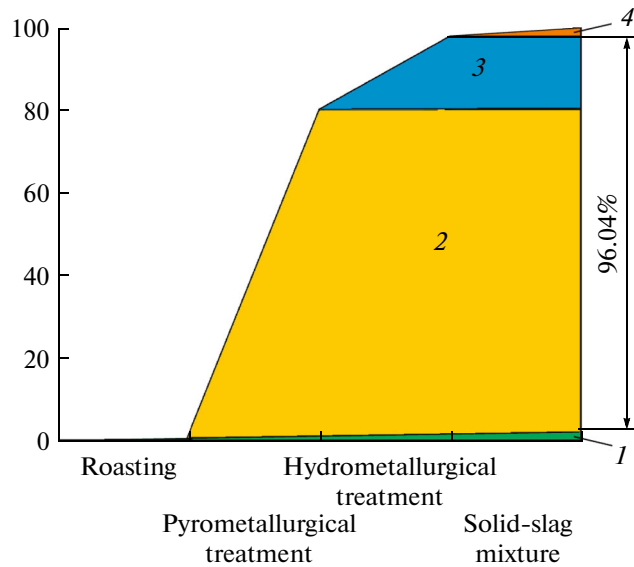


Fig. 1. Extraction and losses of molybdenum at different stages of catalyst processing: (1) losses of molybdenum (2.00%); (2) extraction by sublimation (78.4%); (3) extraction by leaching (17.64%); (4) molybdenum in solid-slag mixture (1.96%).

increases, as shown in [28]. That is associated with local stoichiometric equilibria. Accordingly, soda leaching of molybdenum is expedient after pyrometallurgical processing.

The next stage is hydrometallurgical processing, with extraction of the remaining molybdenum in the form of ammonium paramolybdate or calcium molybdate. The degree of molybdenum-trioxide extraction in hydrometallurgical processing for catalysts with a small content of molybdenum oxide is around 90%.

The residues from hydrometallurgical processing are then used as components of a solid-slag mixture. We propose a mixture consisting of 30% catalysts (after leaching), 30% CaO, 25% $(\text{CaMg})(\text{CO}_3)_2$, and 15% aluminum shavings. Briquets of the mixture are used as synthetic refining slag in the ladle–furnace unit. This mixture composition ensures protection of the slag belt (increases the wear resistance of the lining), permits reduction of the steel by aluminum, and ensures desulfurization and the required viscosity of the slag.

We now calculate the molybdenum-trioxide extraction when the losses in each stage are taken into account but the residual molybdenum trioxide in the solid-slag mixture is disregarded. In Figs. 1 and 2, we show the molybdenum extraction at different stages of processing and its loss, as well as consolidated data for the molybdenum extraction at different stages of pro-

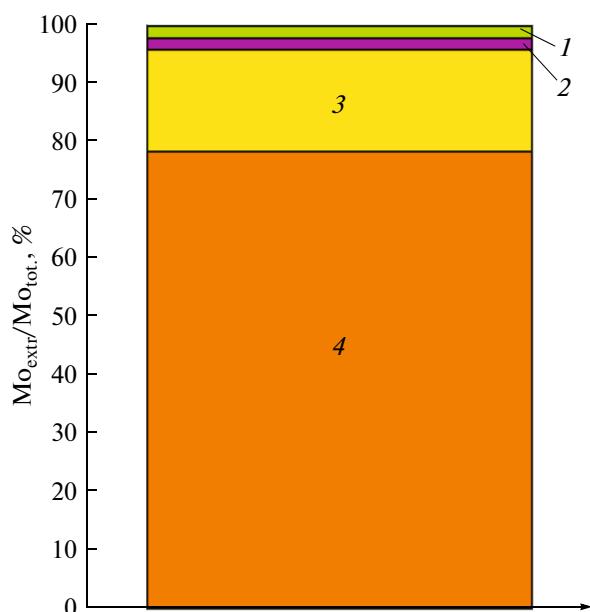


Fig. 2. Consolidated data on molybdenum extraction and losses at different stages of catalyst processing: (1) losses of molybdenum (2.00%); (2) molybdenum in solid-slag mixture (1.98%); (3) extraction by hydrometallurgical processing (17.64%); (4) extraction by pyrometallurgical processing (78.41%).

cessing. The molybdenum-trioxide extraction may be calculated in the form

$$E_{\text{tot}} = \frac{(C_0 - \sum \Pi_i - C_{\text{ssm}})}{C_0} = 96\%,$$

where Π_i denotes the losses in stage i ; C_0 is the initial molybdenum content in the catalyst; C_{ssm} is the molybdenum concentration in the solid-slag mixture.

The table presents the extraction and losses of molybdenum trioxide in the multistage process. Thus, the total extraction of molybdenum in the proposed technology is 96%. The residual molybdenum content in the catalysts may be reduced to 0.3%.

Extraction and losses of molybdenum trioxide in the multistage process % (initial molybdenum-trioxide content 16%)

	Roasting	Sublimation	Leaching
Molybdenum content after processing	15.82	3.14	0.31
Mo extraction	0	80	90
Losses in processing	1.0	0.7	0.3
Molybdenum extraction relative to its initial content	0	78.4	17.64

CONCLUSIONS

The introduction of spent molybdenum-bearing catalysts at charging does not offer the required economic benefit, on account of the constantly increasing requirements on steel quality and the inefficient use of the Al_2O_3 . Used alone, pyrometallurgical and hydrometallurgical methods do not adequately extract molybdenum from the spent catalysts. The proposed multistage process permits 96% molybdenum extraction, while the catalyst residues, consisting almost entirely of Al_2O_3 , may be used in the synthetic solid-slag mixtures for the production of refining slag in the ladle–furnace unit.

Alloying of steel with calcium molybdate is of interest on account of the low concentration of harmful impurities.

The introduction of multistage catalyst processing will reduce the costs in alloying the steel and reduce the environmental impact of the petrochemical industry.

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