



Recovery of molybdates from an alkaline leachate of spent hydrodesulphurisation catalyst – proposal of a nearly-closed process



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ABSTRACT

In this work, we developed a simple, effective, low-cost and more environmentally friendly process (with low energy requirements and minimized effluent emissions) to recover molybdenum from an alkaline leaching solution of a spent hydrodesulphurisation catalyst, as a final product with high purity and in high yield. Alkaline leaching of spent Ni–Mo hydrodesulphurisation catalysts results in a solution that mainly contains molybdenum and aluminum. Before recovering molybdenum, previous separation of aluminum from the solution, as a precipitate of aluminum hydroxide, was performed by lowering the pH to 8, at room temperature, with a yield of 99.2%. Recovery of molybdenum was studied by precipitation in the form of a salt of strontium or lead molybdate. The first process allowed a recovery of 96% of Mo at 25 °C, as tetragonal SrMoO₄, with high purity (99%). Precipitation with lead at 25 °C resulted in a maximum recovery of 99.8% of the molybdenum, as tetragonal PbMoO₄, with a purity of 99.5%. Finally, the destination of the final solution is discussed and a flow sheet considering the production of strontium/lead molybdate is proposed.

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1. Introduction

Petroleum refining industries extensively use alumina-based catalysts in hydrodesulphurisation (HDS) units. Due to continuous activity, the deposition of contaminants and gradual deactivation of the catalysts occurs, and regeneration steps are required (Lai et al., 2008; Marafi and Stanislaus, 2008). When the catalysts can no longer be regenerated, they become hazardous wastes and cannot be disposed of (Rapaport, 2000). The quantity of spent non-reusable HDS catalysts produced per year is around 120,000 tons (dry basis) (Dufresne, 2007). The presence of valuable metals, such as molybdenum (Mo) (4–12%), nickel (Ni) (1–5%) or cobalt (Co) (0–4%) (Park et al., 2006), makes the recycling of catalysts the most environmentally friendly and economically attractive solution since both the exploitation of primary mineral resources and the deposition of hazardous wastes are reduced.

In order to recover valuable metals, these residues can be treated using pyrometallurgical and/or hydrometallurgical processes. Hydrometallurgical processes allow better control of the recovery of by-products, are theoretically more environmentally friendly and use lower temperatures; however, some reagents are

expensive, the reaction rates are much slower and large quantities of concentrated solutions are required (Ghosh and Ray, 1991; Kim et al., 2009). Acid or alkaline leaching, bioleaching and salt leaching are among the most studied techniques to extract metals from spent catalysts (Zeng and Cheng, 2009a). The interest of recovering Mo from spent catalyst leaching solutions is to produce metal compounds, which can be incorporated into other industries. Alkaline leaching allows for selectively dissolving Mo over Ni and/or Co (Pinto and Soares, 2012); this leaching strategy may reduce subsequent separation steps to obtain pure metal products.

Among the possible applications of Mo compounds, we can mention oxidation catalysis, lubrication, advanced structural and heating materials, anticorrosion agents, coatings, paints and pigments, flame and smoke retardants and pyrotechnics (Braithwaite and Haber, 1994).

Strontium molybdate is a slightly soluble Mo salt that can be used in paints and coatings to act as corrosion inhibiting pigments. The use of lead molybdate in paints is known and major chemical industries sell pigments that consist of mixed crystals of lead chromate, sulfate and molybdate (Sebenik et al., 2000; Stiefel, 2000). Molybdate based pigments are usually prepared by precipitating the compound on a less expensive core material; they can replace chromium based pigments with the advantage of having low toxicity, unlike chromium. Due to its luminescence properties, strontium molybdate may also be applied in optical devices and lasers (Mao et al., 2010; Sebenik et al., 2000). Recent investigations,

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focused on the morphological and luminescence characteristics of strontium molybdate, have shown a great interest in finding low cost and convenient methods of synthesis (Sczancoski et al., 2008). The use of lead molybdate in paints is limited because of its toxicity, however, new applications for this compound, namely in acoustic and optical devices (Anandakumar and Khadar, 2008) and photocatalysis (Hernandez-Uresti et al., 2012), have been studied in recent years.

Methods for producing strontium or lead molybdate from aqueous solution usually start from a synthetic solution of sodium molybdate or molybdic acid followed by the addition of a solution of the respective salt. In the present work, a new process for recycling Mo from an alkaline leaching solution of a spent hydrodesulphurisation catalyst was developed. For this purpose, a simple, nearly closed and more environmentally friendly process (characterized by low energy requirements and minimized effluent emissions) was implemented for the production of strontium molybdate or lead molybdate, with high yield and purity, from the leaching solution. Taking into account the large quantities of spent Ni–Mo catalyst produced every year, the accomplishment of all these objectives will contribute to a more sustainable and cost-effective management of this residue.

2. Background of the present research

Our previous work (Pinto and Soares, 2012) focused on the selective leaching of Mo from spent catalysts (Ni–Mo and Co–Mo). The use of a diluted NaOH aqueous solution under microwave-assisted conditions allowed for faster and more efficient removal of Mo; however, some Al was also dissolved. After the leaching step, the resulting solution contained Mo and Al and its pH was around 10.5. This solution must be treated to separate Mo from Al and to fulfill our goal of recovering Mo from spent HDS catalysts through an efficient and more environmentally friendly process.

Common methods to separate and recover Mo consist of precipitation, solvent extraction, ion exchange, adsorption with activated carbon and biotechnological adsorption or a combination of more than one method (Zeng and Cheng, 2009b). Solvent extraction has been widely studied to separate Mo from other metals and to concentrate the solution. A considerable number of recent studies have investigated this problem. Chen et al. (2006a) separated Mo from V present in an ammonia leaching liquor using trialkylamine N-235 acidified with HCl; this extractant was also used by Zhao et al. (2011) to extract Mo from an alkaline leaching solution of Ni–Mo ore, at pH 3. Mishra et al. (2010) chose solvent extraction with LIX-841 to separate Mo and V from Ni, Fe and Al in a sulfuric acid leaching solution. Alamine 304 and Alamine 336 were tested by Valverde et al. (2008) to separate Mo from an acid leachate of a spent catalyst at room temperature containing Mo, Ni/Co and Al. Zeng and Cheng (2010) separated Mo and V from Ni, Co, Al and Fe present in an acid leaching liquor by solvent extraction, at pH 1.5 and 40 °C using LIX-63. Park et al. (2010) studied LIX-84, in different diluents, to isolate Mo from Ni and Al, at pH 0.5. Solvent extraction implies the stripping of metals from the organic phase, usually using ammonia solution. Then, Mo can be recovered by precipitation as ammonium molybdate, ammonium polymolybdate or molybdic acid, at low pH and temperatures up to 90 °C; finally, these compounds are transformed into molybdenum oxide (MoO_3) during calcination. Using a combination of solvent extraction, ammonia stripping, precipitation and calcination, almost total extraction of Mo (generally higher than 98%) from the mother liquor, as a final product of high purity, can be achieved.

Other types of Mo products may be obtained by precipitation from solution in the presence of other compounds. Molybdenum sulfide can be obtained by the addition of H_2S gas to an acidic

solution, at 80 °C, with Mo recovery of 99.8% (Zeng and Cheng, 2009b). Barium molybdate was produced by adding a barium salt to an alkaline solution: about 93% of Mo precipitated at 80 °C, although Al was also partially precipitated (Chen et al., 2006b). Calcium molybdate precipitation led to a recovery of 95%, at pH 6–9 and a temperature above 80 °C, from a solution containing 1100 ppm of Mo (Evans et al., 1998). Swinkels et al. (2004) also recovered Mo, as calcium molybdate, at 55–60 °C, with previous separation of Al by precipitation as aluminum hydroxide at pH > 5.

The application of adsorption with activated carbon to separate Mo from Ni and Al solution is also possible, under very acidic conditions, and the metal can be desorbed using ammonia, precipitated as ammonium molybdate and calcined to form MoO_3 (Pagnanelli et al., 2011; Park et al., 2007, 2006). Lai et al. (2008) combined acid leaching and electrolysis for recovering metals from spent catalysts achieving Mo recovery of 15% by electrolysis.

Although solvent extraction seems to be an effective process to recover Mo and produce MoO_3 , several steps are involved. In all the studies mentioned above, very acidic conditions were needed for the solvent extraction stage, and an alkaline solution of ammonia hydroxide and/or carbonate for stripping Mo and the new addition of acid are required to obtain solid molybdate; so, large quantities of acid are necessary to lower the pH, especially if Mo extraction from the catalyst is achieved by alkaline leaching, as it was our case. Precipitation of other solid molybdates also appears to be efficient and is a simpler and less expensive technique because it does not require the use of organic reagents (Zeng and Cheng, 2009b); thus, the motivation of the present work was to determine if different compounds, such as strontium or lead molybdate, can be produced from the leaching solution, i.e., from a secondary resource of Mo.

3. Experimental

3.1. Computer chemical simulations

Species distributions diagrams were constructed based on chemical speciation calculations that were executed using MINEQL+ Version 4.5 (Schecher and McAvoy, 2003). Chemical equilibrium concentrations of all species considered in the model by the program reactions were generated based on component stability constants (Martell and Smith, 2004) and molar concentrations.

3.2. Catalyst leaching

The aqueous solution, used in this work, was obtained by alkaline leaching of a spent Ni–Mo hydrodesulphurisation catalyst (Pinto and Soares, 2012). Briefly, a roasted (500 °C for 90 min, in air) catalyst (30% Al, 12.1% Mo and 2.6% Ni) was leached with 10 g L^{-1} sodium hydroxide (NaOH) solution from an analytical grade solid, $S/L = 50 \text{ g L}^{-1}$, using PTFE bombs (23 mL) and a domestic microwave oven (800 W, 2.45 GHz). The system was heated for 30 s, removed from the microwave and allowed to cool at room temperature. This procedure was repeated four times. After four cycles, the solid and liquid phases were separated by filtration and the leachate was used to perform the precipitation studies.

3.3. Aluminum precipitation

To separate Al from the leaching solution, the pH was lowered using concentrated HNO_3 p.a.; the solid was separated by centrifugation (2500 g, 10 min) and dried at 105 °C until a constant weight was achieved. Rigorous amounts (~150 mg) of the solid were dissolved in 10% HNO_3 and the volume was made up to 50 mL. Concentrations of Al and Mo present in the supernatant and in the dissolved solid were determined by atomic absorption spectroscopy

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