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RECOVERY OF MOLYBDENUM (MO) METAL FROM SPENT CATALYSTS BY BIOLEACHING

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ABSTRACT

Spent catalysts are generated in large quantities as solid waste on a yearly basis from different industries (fertilizer, petroleum and others chemical industries). Due to their hazardous nature, environmental regulations for discarded spent catalysts are very strict. Consequently, from ecological and economical view point, metals recovery from spent catalysts is very important. Molybdenum (Mo) is one of the elements present in spent catalysts at high concentrations. The rapidly growing demands for Mo and its products create a need to develop novel recovery processes from secondary resources, i.e. spent catalysts, as there is a projected shortage of the primary resources for this element. This paper mainly focused on Molybdenum (Mo) recovery from spent catalysts using bioleaching .The rapid industrialization generates a variety of spent catalysts from different industries. These spent catalyst wastes mostly contain Ni, Cu, Zn, Cr, Mo, Co and Fe like metals in it. Hence these waste (spent catalyst) materials which are causing serious environmental problems, can act as potential source for metals. In this sense these spent catalyst wastes can act as a artificial ores. The use of a bioleaching process to recover metals from such spent catalyst materials before disposal is a logical but challenging application. Bioleaching is a relatively new concept in which various microorganism (bacteria and fungi) are employed to recover metal values from spent catalyst wastes. Bioleaching is a process based on the ability of microorganism to transform solid compound into soluble and extractable elements, which can be recovered. It represents a "clean technology" given its associated lower cost and energy requirements when compared with non-biological processes.

KEYWORDS: Bioleaching, spent catalyst, recovery, microorganism, eco-friendly extraction.

INTRODUCTION

The challenge of sustainable development at the beginning of the 21st century has become a systemic one, with environmental, social and economic dimensions on an equal footing .Our contributions need to be systematic, for example through the promotion of resource efficiency, improved materials recycling and life-cycle thinking (Kar, 2004). It may not be easy to identify a metal leaching/recovery method of choice. Material requirements on the design and construction of equipment used for the leaching and recovery are rather different. Fluctuations in the market prices for the metals and their concentration in the secondary resources are important factors which influence the economic viability of metal recovery (Marafi and Stanislaus, 2008b). Therefore, future studies should be more focused on the assessment of the metals speciation in secondary resources (catalysts, mineral sludge, sediment etc.), which can indicate the ease of their leachability and recovery and help better decision making in term of a technique of choice.

Recycling has become increasingly difficult today and much value is lost due to the growing complexity of products and complex interactions within recycling systems (Marafi and Stanislaus, 2008b). Recycling of metals can be optimized on an economic and technological basis along product life cycles in the move towards sustainable metals management. Sustainable metals management requires more than improving recycling rates of selected materials. The whole mind-set on recycling of metals need to be changed, moving away from a material-centric approach to a product-centric approach.

Molybdenum (Mo) is valuable element to all living organisms because of its functional role in cofactors in various bacterial, plant, and animal enzymes and its specific geochemical behavior. Mo also has widespread industrial importance. On account of its high melting point, high strength at higher temperatures, high thermal conductivity and good corrosion resistance Mo is extensively used in a variety of industrial processes .Among all other industrial uses, Mo catalysts are vastly

utilized in fertilizer plant and petroleum desulfurization to minimize sulfur dioxide emissions from combustion of fuel .Mo also has its use in alloys, corrosion inhibitors, flame retardants and lubricants.

Numerous industries (e.g. metal-finishing, fertilizer, electroplating, electronic, steel and nonferrous processes, petrochemical and the used electronic/household goods), discharge a variety of toxic heavy metals such as Mo, Ni, Co, Cu, Cd, Cr, Zn etc. Metal containing wastes/byproducts of various industries are potential pollutants of human habitation including air, surface and water, if not treated properly. Some metals can be toxic to living organisms. Man, who is on top of the food pyramid, will receive the pre-concentrated metals from plants and animals. Therefore, not only the environment, but also the human beings will suffer of the negative consequences of heavy metal pollution. As environmental regulations become ever more stringent, particularly regarding the disposal of toxic wastes, the costs for ensuring environmental protection continue to rise. In addition, high price, high demand and future shortage of metals such as Mo, Ni and Co create a need to develop novel recovery processes from secondary resources (i.e. spent catalysts, mineral sledges, etc.), as there is a projected shortage of the primary resources for these metals. Therefore, there is a need to utilize more efficient technologies to recover metals from wastes/secondary resources in order to minimize capital outlay, environmental impact and to respond to the metal increased demand.

The advancement in science and technology there is rapid industrialization, over the world leading to mechanized farming and urbanization. It has caused blatant destruction of the natural environment. So many industries(fertilizer, petroleum and others chemical industries) generates lot of spent catalyst as solid waste byproduct which contain valuable metal such as Ni, Co, Cu, Mo, Zn, Mn and Fe. Therefore, concerted efforts are put to develop eco-friendly processes especially in the field of mineral processing and extraction of metal from spent catalyst solid waste, which have been the mainstay of world economy. Usually, metal values are recovered from the respective ores through pyrometallurgical and hydrometallurgical processes or a combination of both. But due to gradual depletion of high-grade ores, efforts are now being directed to recover metal values from spent catalyst wastes of industrial byproduct. The reuse of such materials not only conserves the non-renewable resources but also solve the problem of environmental degradation. The important technique that has been developed so far to treat the spent catalyst solid waste materials for recovery of metals comes under the domain of hydrometallurgical processing. It involves aqueous media processing with the help of various acids alkalis, organic solvent etc. in addition to employing conventional industrial process steps. Biohydrometallurgy is a relative new concept in which various microorganisms are employed to recover metal values. It is also relatively free from environmental concerns unlike conventional hydrometallurgy steps. This technique exploits microbiological processes for recovery of metal from spent catalyst. In last few decades the concepts of microbiological leaching have played a great role to recover valuable metals from various sulphide minerals or low grade ores. Now the microbiological leaching process has been shifted for its application to recover valuable metals from the different spent catalyst wastes. There are many microorganisms which play important role in recovery of heavy metals from spent catalyst industrial wastes. Among the bacteria Acidithiobacillus Ferrooxidans, Acidithiobacillus thioxidans, Leptospirillum Ferrooxidans and sulfolobus sp., are well known for the bioleaching activity while penicillium, and Aspergillus niger are some fungi those help in metal leaching process. The process of recovery makes some only if the cost of recovery is much less than the the value of the metal. The main advantage in the bio-hydro technique is the ease of operation as well as limited use of process controls thus making the operation more users friendly. The technique can also be applied to different types of materials, especially lean and so for unusable resources, by which metal values can be recovered. Therefore in biohydrometallurgy, the process is carried out in close loop generating minimum effluents and thus is preferred as green technology.

Bioleaching is also widely used for valuable metals recovery in comparison with chemical leaching. Bioleaching can offer attractive features, especially considering environmental issues; processes are more cost efficient (they can be performed at mild conditions), simpler (there is no need for a complex machinery) and more environmentally friendly than their chemical counterparts (Zeng and Cheng, 2009b). Some of the disadvantages are that bioleaching has relatively long leaching cycles (usually around 20 days) and extraction efficiencies of Mo, Ni and Co are rather low (< 70%). The bioleaching process requires only 1/5th of the cost of the chemicals required for leaching and recovery of metals compared to the traditional chemical methods (Asghari et al., 2013b). Bioleaching processes are less costly in terms of chemical cost, but could prove costly in terms of capital cost, energy cost and maintenance cost associated with them. In addition to the costs of chemicals, the costs of mixing, aeration, construction of holding tank and operational maintenance will have to be added to the total cost for carrying out a satisfactory cost analysis (Asghari et al., 2013a).

Disposal of spent catalyst represent an increasing environmental problem due to the metallic content, being considered as hazardous waste (Zeng and Cheng, 2009b). The cost for safe disposal of this hazardous material is quite high in terms of the amount of waste produced and the limited storage capacity of landfills and/or dumpsites. Therefore, concepts of reutilization and recycling of materials are appearing in order to minimize the wastes. Furthermore, substitution of raw materials by the

recycled products provides both reduction in production costs and the preservation of raw materials, thus environmental protection. In order to achieve recycling of large amounts of incoming used catalysts, the recycling plant designed a process allowing the recovery of precious metals from used spent catalysts.

The high demand, high price and projected future shortage of the Mo primary mineral resources creates a need to develop secondary resources and to find more beneficial ways of Mo recovery from industrial waste materials, especially spent catalysts (Marafi et al., 20078b). Spent catalysts discarded by industries are undoubtedly very important, because of the inherent metals (Mo, Ni, Co, Zn, Cr, Fe, Al, W etc.). Worldwide generated amount of spent catalysts is in the range of 150,000 - 170,000 tons year-1 (Amiri et al., 2011). In fertilizer plant during ammonia synthesis, different, types of catalysts are used(Prajapati, R. P., Sharma Anand and Tiwari, D. R. ,2010) . At least eight kinds of catalysts are used in the whole process, where natural gas or naphtha is used as feedstock and steam reforming is used to produce synthesis gas. These catalysts are Co-Mo hydrocarbon catalyst, zinc oxide desulfurizer, primary and secondary steam reforming catalysts, high and low temperature shift catalysts, methanation catalyst and ammonia synthesis catalyst etc. Details of the various catalysts used in the ammonia synthesis plant are given in table-1.

Table 1: Catalysts used in the ammonia synthesis plant (fertilizer industry).

S. N.	Process	Catalyst	Catalytic Reaction	Life (years)	Nature of spent catalyst
1	Hydrosulfurisation	$Co/Mo/Al_2O_3$	$R_2S + 2H_2 \rightarrow 2RH + H_2S$	5-7	Pyrophoric
2	Desulphurisation	ZnO	$H_2S + ZnO \rightarrow ZnS + H_2O$	depends on the S-content in Natural gas	Non-Pyrophoric
3	Primary reforming	NiO	$CH_4 + H_2O \rightarrow CO + 3H_2$	5-7	Pyrophoric
4	Secondary reforming	NiO	$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$	5-7	Pyrophoric
5	High temperature shift converter	$Fe_2O_3 \& Cr_2O_3$	$CO + H_2O \rightarrow CO_2 + H_2$	5-7	Pyrophoric
6	Low temperature shift converter	$CuO, ZnO \& Al_2O_3$	$CO + H_2O \rightarrow CO_2 + H_2$	5-7	Pyrophoric
7	Methanation converter	Ni	$CO/CO_2 + 6H_2 \rightarrow CH_4 + H_2O$	5-7	Pyrophoric
8	Ammonia Converter	Fe_3O_4	$N_2 + 3H_2 \rightarrow 2NH_3$	5-7	Pyrophoric

Metals like Ni, Mo, Co, Cu, Zn and Fe are coldly used as a catalyst in ammonia synthesis plant. They are generally supported on porous materials like alumina and silica. After periodical use of the catalysts (5-7), due to poisoning effect of foreign material and impurities, which deposit on the surface of the catalyst, they will become inactive. In such cases, fresh catalysts have to be substituted and the spent catalyst will be discarded as waste materials. Disposal of spent catalyst is a problem as it falls under the category of hazardous industrial waste. Therefore the spent catalyst is attracting the attention of environmental authorities in many countries and the refiners are experiencing pressures from environmental authorities for safe handling, management and utilization of spent catalysts (Prajapati, R. P., Sharma Anand and Tiwari, D. R., 2011).

The volume of spent catalysts discarded as solid waste has increased significantly in recent years due to the following reasons: (i) A rapid growth in the distillates hydrotreating capacity to meet the increasing demand for ultra-low sulfur transportation fuels. (ii) Reduced cycle times due to higher severity operations in diesel hydrotreating units. (iii) A steady increase in the processing of heavier feedstock's containing higher sulfur and metal contents to distillates by hydrogen addition technology. (iv) Rapid deactivation and unavailability of reactivation process for residue spent catalysts.

Spent catalyst characterization is an important part of the evaluation process when determining the ultimate fate of the catalyst and which leaching and/or recovery technique is the most suitable for metal recovery. Recovery of metals from spent catalysts depends on several factors: chemical composition, the price of metals, the environmental directories and the operational costs. Since the cost of transportation and disposal in industrial dumps, the severity of environmental directories, and the price of some metals have been rising, spent catalysts have been recognized as a secondary source of valuable metals.

Bioleaching of molybdenum from spent catalysts

Bioleaching of waste has become increasingly important in recent years, due to its vast potential, simplicity and

eco-friendly operation (Chen et al., 2011). Bioleaching utilizes the potential of different microorganisms to mobilize and leach out metals from solid materials. Soluble and extractable elements can be recovered due to the ability of microorganisms (bacteria and fungi) to modify solid compounds, via the production of organic or inorganic acids Two bacterial metal leaching mechanisms have been suggested in the literature (Bayat and Sari, 2010). Firstly (Eq. 1), bacteria interact directly with the minerals and increase the speed of mineral dissolution (biological mechanism):

$MoS_2 + H_2O + 3.5\ O_2 \rightarrow$ bacteria $MoSO_4 + H_2SO_4$ (1)

The second mechanism involves bacterial oxidation of Fe^{2}+ to Fe^{3}+ (Eq. 2) and subsequent chemical leaching of metal-bearing minerals by Fe^{3}+ (Eq. 2). During this indirect (chemical) mechanism, Fe^{3}+ produced by the bacteria plays a crucial role in metal solubilisation.

$14Fe^{2+}+3.5O_2+14H^{+} \rightarrow$ bacteria $14Fe^{3+}+7H_2O$ (2)

$MoS_2 + 8\ H_2O + 14\ Fe^{3+} \rightarrow Mo^{4+} + 14\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^{+}$ (3)

The reaction presented in Eq. (2) needs the involvement of bacteria, while Eq. (3) is a entirely chemical process (Bayat and Sari, 2010). Since Fe^{2+} created in the chemical reaction (Eq. 3) is reused to the iron oxidizing conversion (Eq. 2), large quantity of heavy metals can be continuously leached out from solid substrates.

Table 2 Mo bioleaching from spent catalysts along with its extraction efficiency shows that a lot of investigations have been performed on Mo extracting from spent catalysts with mesophilic bacteria, but ended up with low Mo leaching yields (less than 70%) and relatively long leaching cycles (more than 1 day, usually 20 days). In spent catalysts Mo is strongly bound on the alumina support in the form of a MoO_3/MoS_2 (Asghari et al., 2013b). Additionally, Mo is a toxic element to some bacteria (Acidithiobacillus ferrooxidans), and concentrations as low as 1.5 - 2 mg L-1 of Mo are enough to inhibit the microorganism. Therefore, the Mo speciation in the spent catalysts and its potential toxicity towards the microorganisms are the possible reasons why the bioleaching of Mo from spent catalysts is less effective than the bioleaching of other metals.

Table 2: Molybdenum bioleaching processes from spent catalysts using different microorganisms and recovery (%).

Type of treatment	Microorganism used	Temp. (°C)	Time (days)	Other conditions	Mo bioleaching yield (%)
Bioleaching with bacteria	A. ferrooxidans	30	30	pH 1.8 - 2.0	84
-	A. thiooxidans	30	30	pH 3.9 - 4.4	95
-	Acidianus brierleyi	30	6	Pulp density 1% (w/v)	67
Bioleaching with fungi	Penicillium simplicissimum	30	5	Pulp density 4% (w/v)), sucrose (90 g L-1), $NaNO_3$ (2 g L-1), yeast extract (0.36 g L-1)	98
	Aspergillus niger	30	5	Particle size 150 - 212 µm, sucrose 93.8 g L-1, pulp density 3% (w/v) and pH 7	99

Bioleaching with bacteria

Iron/sulfur oxidizing bacteria (Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans) are commonly used microorganisms for metal bioleaching. A. ferrooxidans and A. thiooxidans were used for Mo, mobilization from the spent catalysts in batch cultures. After indirect bioleaching using A. ferrooxidans, maximum extractions efficiencies of 84% Mo were achieved after 30 days at pH 1.8 - 2.0 (Gholami et al., 2012). The highest Mo extraction efficiencies using A. thiooxidans were 95% after 30 days at pH 3.9 - 4.4. The same two bacteria were used in another study for bioleaching of the exhaust catalyst that was rich in Mo (Beolchini et al., 2010).

Metals bioleaching from spent catalysts was attempted in two stage process (Mishra et al., 2008). First stage included change of elemental sulfur particles into sulfuric acid via oxidation process by A. ferrooxidans .In the second stage, acidic medium (sulfuric acid) was used for the Mo. At pulp density 5% (w/v) of spent catalyst and 20 g L-1 elemental sulfur, 46.3% Mo was recovered after 7 days .Bioleaching for instance, spent catalyst by the thermophillic archae Acidianus brierleyi was studied. The spent catalyst was characterized, and the effect of pretreatment on two-step leaching was investigated at 1% w/v pulp density .Pretreatment (decoking) affected the solubility of metals via oxidization of the metal sulfides (Bharadwaj and Ting, 2013). Close to 100% metal extraction efficiency was reached for Mo. Chemical (i.e. abiotic) leaching with bacterially produced H_2SO_4 resulted in lower leaching efficiencies (only up to 30%).

Bioleaching with fungi

Bioleaching with fungi is ground on their capacity to transform solid compounds, via an indirect mechanism by the production of organic or inorganic acids, into

soluble elements that can be recovered (Amiri et al., 2011). The most active leaching fungi, which have been isolated and used, are from the genera Penicillium or Aspergillus applied and optimize the bioleaching of spent catalyst by Penicillium simplicissimum. The combined effect of different variables (pulp density, sucrose, $NaNO_3$ and yeast extract concentrations) on metal bioleaching was investigated. The optimal values of the variables for maximum metal bioleaching were pulp density (4.0% (w/v)), sucrose (90 g L-1), $NaNO_3$ (2 g L-1) and yeast extract (0.36 g L-1). The maximal predicted Mo extraction efficiency was 97.6%.

The kinetics of bioleaching of Mo from spent catalyst using Aspergillus niger was also studied The four most effective bioleaching variables were selected as follows: particle size 150 - 212 µm, sucrose 93.8 g L-1, pulp density 3% (w/v) and pH 7. The maximum metal leaching efficiencies were 99.5% Mo.

Bioleaching experiments in batch cultures using Aspergillus niger in a one-step process to mobilize Mo, from hazardous spent catalysts were also carried out by Gholami et al. (2012). Maximal Mo extraction efficiencies of 69% were achieved at a pH of 5.0, a temperature of 30°C, a pulp density of 2 g L-1, a rotation speed of 115 rpm, and using 12% inoculums.

Evaluation of bioleaching of molybdenum from spent catalysts

Bioleaching can offer attractive features, especially considering environmental issues (Beolchini et al., 2010); processes are more cost efficient (they can be performed at mild conditions), simpler (there is no need for a complex machinery) and more environmentally friendly than their chemical counterparts (Asghari et al., 2013b, Zeng and Cheng, 2009b). Some of the disadvantages are that bioleaching has relatively long leaching cycles (usually around 20 days) and extraction efficiencies of Mo are rather low (less than 70%). The bioleaching process requires only 1/5th of the cost of the chemicals needed for leaching and recovery of metals compared to the traditional chemical methods. Bioleaching processes are less costly in terms of chemical cost, but could prove costly in terms of capital cost, energy cost and maintenance cost associated with them. In addition to the costs of chemicals, the costs of mixing, aeration, construction of holding tank and operational maintenance will have to be added to the total cost for carrying out a satisfactory cost analysis.

Molybdenum recovery from spent catalysts

Following the solubilisation of Mo via bioleaching Mo recovery technologies have been summarized (Table -3). Precipitations are used for Mo recovery from leach liquors. Mo purification and recovery from leach liquors that simultaneously contain other extractable metals is difficult due to co-precipitation. In this case selective recovery of metals under the controlled manipulation of operational parameters (especially pH) needs to be applied.

Table-3 M**olybdenum recovery technologies from spent catalysts and recovery (%).**

Type of treatment	Recovery agent	Temperature (°C)	Time (h)	pH	Mo recovery (%) yield
Precipitation	Biogenic H_2S	25	5	2	36-72
	Ammonia	90	5	2	97
	Barium hydroxide and barium aluminate	25	24	5	92
Adsorption	Activated carbon	25	3	2	99
Ion exchange	Acrylic anion exchanger's	25	24	2	99
Solvent extraction	Alamine® 304-1	25	4	2	99

Precipitation

(a) Sulfide precipitation

Precipitation is designed to precipitate metals by surpassing their solubility limits. Additional recovery can be achieved by co-precipitation or adsorption on the precipitate during the precipitation reaction. Sulfidogenic bioreactors have been utilized to recover metals from different metal-containing waters (Cibati et al., 2013; Zeng and Cheng, 2009b), assessed the feasibility of using biogenic H_2S to selectively precipitate Mo, from synthetic spent refinery catalyst leach liquor containing 15.3 g L-1 Mo. Biogenic H_2S eased the selective precipitation of MoS_2 (oxidation state IV) at pH - 2 with recoveries of 36 - 72%.

(b) Ammonium salt precipitation

Precipitation of Mo from a leach solution containing 22.0 g L-1 Mo, 0.015 g L-1 was investigated .An ammonium molybdate product of 97.3% purity was obtained .To convert Mo to ammonium molybdate $(NH_4)_2MoO_4$ the solution was neutralized with ammonia at pH 11 (Zeng and Cheng, 2009bt5). Subsequently, the solution was acidified by HCl to pH 2 and heated up to 90°C to enable the formation of ammonium molybdate precipitates.

(c) Barium hydroxide and barium aluminate precipitation

Selective precipitation of Mo from spent catalysts alkaline leachate was investigated by adding barium hydroxide and barium aluminate (Zeng and Cheng, 2009b). Mo precipitated with 92.6% efficiency at 80°C

for 40 min. The precipitation of Mo is more favorable when its concentration in solution is high.

Evaluation of recovery of molybdenum from spent catalysts

Precipitation, adsorption, ion exchange and solvent extraction are the commonly applied technologies for Mo recovery and purification from spent catalyst leach solutions (Banda et al., 2013b). The use of traditional recovery approaches, such as precipitation and adsorption, offers simple operations and good Mo recovery (more than 90%), but high purities of Mo are very hard to achieve by these technologies. Ion exchange and solvent extraction, offer a useful means for almost complete recovery of high purity Mo. However, these methods are very expensive and their scale of application in industry is limited. Among all these techniques, solvent extraction is one that is mostly used in hydrometallurgy for commercial production of high purity metals.

CONCLUSIONS

This paper gives better understanding of the alternatives for leaching and recovery of Mo from spent catalysts and the gained knowledge will allow more informed decision making when it comes to handling of spent catalysts. The summarized results display that the Mo leaching and recovery efficiency utilizing various methods is similar. Thus, it may not be straightforward to determine a method of choice. Also, material requirements on the design and construction of equipment used for the leaching and recovery are rather different. Fluctuations in the market prices for the Mo and its concentration in the spent catalysts are important factors which influence the economic viability of metal recovery from spent catalysts. Therefore, future studies should be more focused on the assessment of the Mo speciation in spent catalysts which can indicate the ease of its leachability and recovery from the spent catalysts and help better decision making in term of a technique of choice. Biohydrometallurgy encompass different disciplines on the basis of interaction between metals and microbes in industrial spent catalyst waste like bioremediation, biosorption, bioaccumulation and bioleaching. All these processes are usually slow but more environments friendly require less energy consumption then physiochemical processes which require more energy and release harmful gases and produce environmental hazards. In future, to improve the yield of metal through bioleaching of low grade ore and spent catalyst solid waste, new strains have to be identified that should be capable of sustaining higher metal concentration. For this purpose strains of genetically modified or selected by mutation can be considered. This can reduce the residence time and simultaneously enhance the economy of the process. It is time that corporations, universities, and governments work together to transform the state of today's metal recycling by demonstrating the need for continuing research on improved technologies, the potential benefits of deployment of the improved technologies now available, and the promise suggested by regulatory and financial initiatives that speak to these challenges. If as a global society, we can collect and reuse almost everything, design products with optimized recycling in mind, and use transformative technology to make the whole process exemplary, we will be helping to ensure that the materials scientists of the future have for their use the full palette of the wonders of the periodic table, and thereby provide society with increasingly innovative and remarkable products.

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