

POTENTIAL OF SPENT CATALYSTS AS A SOURCE OF CRITICAL METALS*

R. E. SIEMENS, B. W. JONG and J. H. RUSSELL

Albany Research Center, Bureau of Mines, U.S. Department of the Interior, Albany, OR 97321, U.S.A.

Abstract — Characterization and hydrometallurgical research was conducted by the Bureau of Mines to devise procedures for recovery of metals such as Co, Ni, V, W, Mo, Cr, Fe, Cu, or Zn from waste catalysts. The research effort was concentrated on recovery of metals from spent hydroprocessing, hydrogenation, and high-temperature shift catalysts. Results showed that 73-99% of the contained critical metals were extracted by a variety of processing approaches, including anhydrous chlorination, ammoniacal, acid, or caustic leaching, and Na_2CO_3 roasting followed by water leaching.

INTRODUCTION

To assure an adequate supply of critical metals for the United States, the Bureau of Mines evaluates the potential recovery of these metals from secondary sources as well as from natural resources. Waste hydroprocessing, high temperature shift, and hydrogenation catalysts were identified in a Bureau contract study as a potential source of Ni, Co, Mo, W, V, Cr, Cu, and Zn [1]. Generally, less than half of the metals discarded in waste catalysts has been recovered or recycled. The effort to recover the metals has fluctuated somewhat with the market price and demand for the contained metals.

A greater effort has been directed toward recycle and regeneration of the waste catalyst materials than has been directed toward recovery of the critical metals from the waste [1]. Only a few domestic firms have processed waste catalysts to recover the metals, and most firms have emphasized recovery of one metal, such as molybdenum or tungsten. One firm has, however, announced plans to construct a plant to recover essentially all of the metals contained in spent hydroprocessing catalysts [2]. For most domestic firms, as with the above mentioned firm, the technology used is proprietary. For a short time Cotter Corporation operated a plant that utilized either ammonium carbonate or sodium hydroxide at elevated temperatures and pressures to leach Ni, Mo, W, and V from spent catalysts [3]. INMETCO has treated hydrogenation catalysts containing greater than 6 wt% Ni with a direct reduction, submerged arc melting procedure to produce remelt charges for stainless steel production [1].

A variety of processing approaches for recovering metals from spent catalysts has been proposed in the patent literature. A representative list of these approaches is referenced in a Bureau contract report [1]. The procedures discussed are predominantly for treating spent hydroprocessing catalysts and generally involve leaching with alkaline or acidic solutions or roasting with Na_2CO_3 , NaCl, or Cl_2 gas. Most procedures emphasize Mo, V, and W recovery and suggest 'known technology' for nickel and cobalt recovery or utilize combinations of extraction approaches to recover all of the metals. In many cases extraction of some metals is poor and metal separation is incomplete. Only limited attempts have been made to recover all of the metals from spent catalysts with a single extractant. One researcher used an anhydrous

Received 12 April 1985; in revised form 16 May 1985.

*This paper was presented at the 114th Annual AIME Meeting, New York, NY, 24-28 February 1985.

Table 1. Critical metals in spent catalysts,
U.S. 1981

Metal	Amount in spent catalyst, kg/yr
Co	560,000
Ni	4,626,000
Cr	480,000
Mo	920,000
W	86,000
V	205,000
Cu	1,135,400
Zn	931,000

chlorination approach, but the method described to selectively adsorb the volatile chloride species was found to be very difficult to quantitatively reproduce [4].

The Bureau is conducting research to identify suitable total processing schemes for recovering all of the critical metals present in spent hydroprocessing, high-temperature shift, and hydrogenation catalysts. Following characterization studies, the Bureau evaluated a variety of extraction approaches that included anhydrous chlorination, ammoniacal, caustic, or acid leaching, and sodium carbonate roasting followed by water leaching. Metal and impurity separation and recovery schemes are also under evaluation. Processing schemes that are technically feasible will be evaluated for economic feasibility by the Bureau's Process Evaluation Group. This paper presents the results to date of the Bureau's research to recover critical metals from spent catalysts.

RESOURCE POTENTIAL

A Bureau-sponsored study revealed that about 12 million kg/yr of non-noble critical metals were discharged in spent catalysts and that less than half of this amount was being recycled [1]. Table 1 shows the amount of Co, Ni, Cr, Mo, W, V, Cu, and Zn disposed of annually in these materials. The study also revealed that the listed amounts were conservative because many firms using catalysts were reluctant to provide data on catalyst consumption and constituents. This viewpoint was also emphasized by industrial people visiting the Bureau to discuss the technology for recovering metals from the spent catalysts.

MATERIALS DESCRIPTION

Representative samples of various types of spent catalysts were received from INCO Research and Development Center as part of a Bureau contract. These materials were analyzed and examined with an electron microprobe or scanning electron microscope. Characterization studies showed that, generally, for those spent catalysts in which alumina was the substrate (hydroprocessing), the critical metals were uniformly distributed and associated with the alumina. On the other hand, for those materials in which silica was the substrate (hydrogenation), the critical metals did not tend to be in the substrate matrix. In the spent hydrogenation catalysts studied, nickel was generally present as an oxide or was associated with aluminum and silicon. In some cases, shells of nearly pure nickel surrounded oxide particles. One spent hydroprocessing sample (Co-Mo) and a spent high-temperature shift catalyst contained critical metals in both oxide and metallic particles.

The critical metals content, bulk density, and particle size range of the spent catalyst types studied are shown in Table 2. Although vanadium is not in the original catalyst material, it is commonly removed from some oils into spent hydroprocessing catalysts. The vanadium concentration in the samples studied by the Bureau was insignificant. The Co–Mo spent catalyst also contained 1.9% As, which caused some concern for proper disposal.

Table 2. Selected physical properties of spent catalysts

Catalyst type	Metal (wt%)		Bulk density (g/cm ³)	Particle size (Tyler mesh)
Hydroprocessing	2Ni	9Mo	0.91	– 10 + 100
	3Ni	13W	0.66	– 10 + 100
	2Co	6Mo	0.74	– 8 + 20
Hydrogenation	7–14Ni			
	13Ni	5Cu	1.20	– 10 + 100
High-temperature shift	5Cr	61Fe	1.02	– 10 + 100

EXTRACTION PROCEDURES

Conventional bench-scale equipment was used to evaluate extraction and recovery procedures utilizing anhydrous chlorination, sodium carbonate roast–water leaching, or ammoniacal, caustic, or acid leaching schemes. Generally, 50-g samples were used for all procedures, and in the leaching approaches, 1.0 l. of solution was used. Initially, the leaching was conducted under oxygen pressure; later it was found that pressure was not required except for the Co–Mo spent catalyst. Each parameter was varied over a wide range in each system, but the following conditions resulted in optimum extraction:

For ammoniacal ammonium sulfate leaching, the samples were leached with 100 g/l NH₄OH and 300 g/l (NH₄)₂SO₄ for 2 h at 80°C. The sulfuric acid leaching was done with 100 g/l H₂SO₄ for 1 h at 100°C. The caustic leaching was done with 20 g/l NaOH for 2h at 100°C. The maximum extraction was achieved at 5% solids for all leaching except the ammoniacal leaching. For the latter, the maximum was achieved at 10% solids.

In recovering chromium from a high-temperature shift catalyst, one part sodium carbonate was roasted with four parts spent catalyst for 2 h at 600°C. The roasted charge was then leached in water for 1 h at 100°C.

Chlorination studies were conducted with a fluidized bed system. The samples were roasted in nitrogen for 30 min at 400°C to remove essentially all of the contained sulfur and moisture. The samples contained from 0.3 to 5.7% sulfur and 4 to 5% moisture. The Ni–Mo samples were then chlorinated for 30 min at 450°C with a gas flow of 100 ml/min each of chlorine and air and 800 ml/min N₂. The Ni–W and Co–Mo samples were chlorinated for 30 min at 450°C with a gas flow of 50 ml/min each of chlorine and carbon monoxide and 900 ml/min N₂. Because of the ‘fluffy’ nature of the Ni–W material, only 25 g were used for chlorination studies. Dechlorination studies were also conducted with a fluidized bed system.

Except for the dechlorination approach, all metal recovery was done in aqueous systems. Metals in solution were separated and recovered by precipitation, crystallization, or solvent extraction and electrowinning.

Table 3. Metal extraction from spent hydroprocessing catalysts

Spent catalyst	Extraction method	Extraction (wt. %)			
		Ni	Mo	Al	
Ni - Mo	Anhydrous chlorination	94	90	6.0	
	NH ₄ OH - (NH ₄) ₂ SO ₄ leach (100 g/l catalyst)	90	89	0.1	
	H ₂ SO ₄ leach	98	93	96	
	NaOH leach	0.08	96	34	
		Ni	W	Al	
Ni - W	Anhydrous chlorination	73	82	4.7	
	NH ₄ OH - (NH ₄) ₂ SO ₄ leach	44	64	0.04	
	H ₂ SO ₄ leach	94	28	76	
	NaOH leach	0.03	91	25	
		Co	Mo	Al	As
Co - Mo	Anhydrous chlorination	78	96	43	97
	NH ₄ OH - (NH ₄) ₂ SO ₄ leach	29	28	0.06	34
	H ₂ SO ₄ leach	59	5	45	60
	NaOH leach	0.03	31	3	54
	H ₂ SO ₄ leach (2068 kPa O ₂)	99	77	—	97
	NaOH leach (2068 kPa O ₂)	<1	99	—	97

PROCESSING RESULTS

The emphasis to date in this research has been on metal extraction; therefore, total process flowsheets will not be illustrated. Metal separation and recovery procedures are being evaluated, however, and where results have been obtained, the recovery approach will be described.

Hydroprocessing catalysts

Metal recovery from three types of spent hydroprocessing catalysts (Ni - Mo, Ni - W, and Co - Mo) was evaluated. Maximum metal extractions obtained from these materials with various approaches are shown in Table 3.

Generally, as shown in Table 3, anhydrous chlorination was the most effective extraction approach for recovering both critical metals from all three hydroprocessing materials. Aluminum was also coextracted in chlorination tests. The amount of aluminum extraction was minimized but often at the expense of decreased Ni, Co, Mo, or W extraction. Chlorination with chlorine alone resulted in extraction of about 97% each of Ni and Mo, and in excess of 30% Al from the spent Ni - Mo catalyst. The aluminum extraction was reduced to about 6% by controlling the carbon dioxide : carbon monoxide ratio. This was accomplished by chlorinating with equal flows of chlorine and air at relatively low (450°C) temperature. Under these conditions, the Ni and Mo extraction with still 90% or greater (Table 3). This material had sufficient carbon content (5%) to effect good chlorination. Most of the testing in varying conditions was done with Ni - Mo catalysts because more of this material was provided for the initial research. For the Ni - W and Co - Mo material, carbon monoxide was used with chlorine

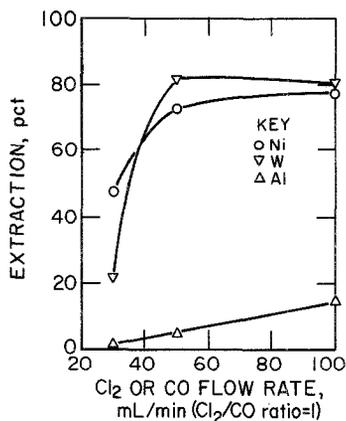


Fig. 1. Extraction of Ni, W and Al by fluidized bed chlorination.

because only about 1% C was present in the spent catalysts. By limiting the temperature and time of chlorination, and, as shown in Fig. 1 for Ni–W materials, by controlling the chlorine and carbon monoxide flow, aluminum extraction was minimized with reasonable Ni and W extractions. Similar results were obtained for Co–Mo materials (Table 3). Future tests with Ni–W and Co–Mo samples will utilize carbon additions and air mixed with chlorine as was used with the Ni–Mo material. Because the Co–Mo material also contains arsenic, most of the research with this spent catalyst has been directed toward selective removal of the arsenic into an inert or marketable form.

About 25% of the aluminum extracted by chlorination was volatilized along with molybdenum or tungsten. Hydrolysis of the volatile product resulted in a 98.4% pure WO_3 or H_2MoO_4 product. These final products contained about 1.5% Al (~10% of the Al volatilized) and 0.09% Ni or Co. Tungsten oxide precipitated without heating when the chloride was dissolved in water, but the molybdic acid precipitated only after boiling. Fluidized bed dechlorination was also evaluated to determine the potential for recycling chlorine in addition to transforming the critical metal chloride into a marketable oxide. Dechlorination of molybdenum oxychloride with equal flows of air and nitrogen at 150–200°C for 60 min resulted in conversion of about 50% of the oxychloride to MoO_3 .

In chlorination approaches applied to spent catalysts by other researchers, excessive amounts of aluminum were volatilized which required an aluminum separation step in the proposed processing scheme [4,5]. In one approach the aluminum reportedly was removed by passing the chlorinated products through a salt column [4]. For those conditions in the Bureau research in which a large quantity of aluminum chloride was transferred with the critical metal chloride this approach was tried, but was not found to be selective for aluminum.

The nonvolatile chlorides containing nickel or cobalt and some aluminum were dissolved in water. The preferred approach for recovering these metals at this stage of the research is to remove nickel or cobalt by solvent extraction and precipitate the aluminum as a hydroxide.

Ammoniacal ammonium sulfate leaching was effective for extracting nickel and molybdenum from spent Ni–Mo catalyst but was not effective for Ni–W and Co–Mo material (Table 3). The nickel selectively was extracted from the leachate with LIX 64N, stripped with sulfuric acid, and electrowon. The molybdenum in the raffinate was recovered through crystallization as molybdic acid.

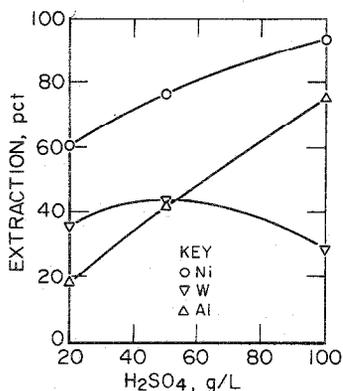
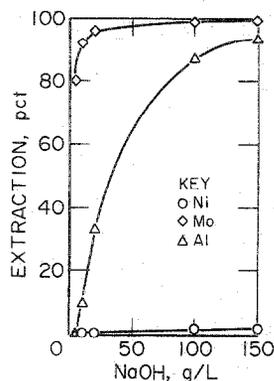
Fig. 2. Extraction of Ni, W and Al with H₂SO₄.

Fig. 3. Extraction of Ni, Mo and Al with NaOH.

As shown in Table 3, sulfuric acid leaching was effective in extracting nickel from spent Ni-Mo and Ni-W catalysts and molybdenum from the Ni-Mo material. The approach was ineffective for extracting tungsten from Ni-W samples and either critical metal from Co-Mo spent catalyst except under pressure. With the maximum critical metal extraction, the amount of aluminum coextracted was also high. For Ni-Mo catalysts, the aluminum extraction was decreased from 96 to 68% by decreasing the acid concentration from 100 to 50 g/l. Under these conditions 94% Ni and 88% Mo were extracted. An increase in the percentage of solids to 10% with the acid concentration at 50 g/l decreased the aluminum extraction to 33%, the nickel extraction to 86%, and the molybdenum extraction to 81%. Although the extraction of Ni, Mo and Al all generally increased with acid concentration, the extraction behavior was different in the Ni-W system. As shown in Fig. 2, the extraction of nickel and aluminum increased with increasing acid concentration, but the tungsten extraction reached a maximum at 50 g/l H₂SO₄.

The molybdenum in the sulfuric acid filtrate was selectively removed with 5% Alamine 304 in 2% isodecanol and 93% kerosene, stripped with NH₄OH, and precipitated as ammonium molybdate. Nickel was recovered from the molybdenum raffinate with a mixture of 15% dinonylnaphthalene sulfonic acid (DNNS), 20% LIX 63, 5% isodecanol, and 60% Naphtha 140. The nickel was stripped from this solvent with either sulfuric or hydrochloric acid. The acid level required for stripping was too high for practical electrowinning; therefore, other Ni recovery schemes are under evaluation. Ammonium hydroxide was added to the nickel raffinate to precipitate Al(OH)₃, which was then calcined to form Al₂O₃. Similar metal recovery schemes are under evaluation for sulfuric acid leaching of Ni-W and Co-Mo materials.

As shown in Table 3, molybdenum or tungsten was selectively extracted from spent hydroprocessing catalysts by caustic leaching, although pressure was required for the Co-Mo material. Figure 3 illustrates the extraction behavior of Ni-Mo material with NaOH concentration. A similar extraction profile was observed with the other hydroprocessing catalysts, although the aluminum extraction varied somewhat over the range of extractant concentration. Table 3 also illustrates that a combination of sulfuric acid and caustic leaching may be effective in extracting the critical metals from spent hydroprocessing catalysts.

Molybdenum was recovered from the caustic filtrate as molybdic acid by crystallization of the caustic leach solution for either Ni-Mo or Co-Mo catalysts. Tungsten was recovered

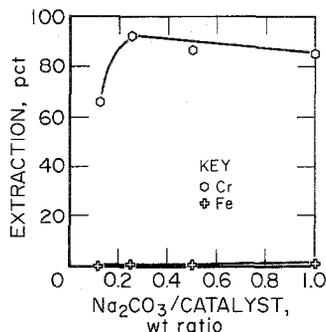


Fig. 4. Extraction of Cr and Fe from a spent high-temperature shift catalyst.

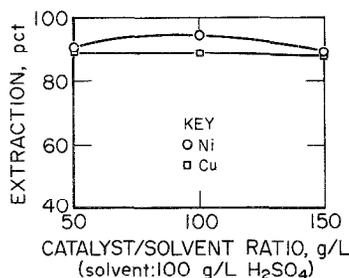


Fig. 5. Extraction of Ni and Cu from a spent hydrogenation catalyst with sulfuric acid.

from the caustic filtrate as CaWO_4 after addition of CaCl_2 to the pregnant solution. Extraction of nickel or cobalt from the caustic leached residue is being evaluated using sulfuric acid leaching or low-temperature anhydrous chlorination.

High-temperature shift catalysts

Up to 92% of the contained chromium was selectively extracted from a high-temperature shift catalyst with Na_2CO_3 roast followed by water leaching. The chromium in solution was concentrated by solvent extraction with Aliquat 336 and stripping with NaOH . The resulting Na_2CrO_4 was recovered by evaporation and crystallization. Figure 4 illustrates the chromium and iron extraction with the Na_2CO_3 roast – water leach procedure.

Hydrogenation catalysts

A lesser effort was placed on recovering metals from hydrogenation catalysts, because they generally contain only nickel, which is relatively easy to extract, and because nickel is being recovered from these materials commercially if the nickel content exceeds 6 wt%. A more complex hydrogenation catalyst containing copper and nickel is being evaluated. Although 93% Ni and 95% Cu were extracted from this material with anhydrous chlorination, research is being concentrated on a sulfuric acid leach because of the potential of direct recycle of the leach solution. As shown in Figure 5, over 89% of the contained copper or nickel was extracted over a range of catalyst to solvent ratios with a fixed volume of solvent containing 100 g/l H_2SO_4 . Copper was selectively removed from the leach solution with LIX 64N, stripped with sulfuric acid, and electrowon. Nickel recovery with a mixture of DNNS and LIX 63 is under evaluation.

CONCLUSIONS

A Bureau contract study showed that a significant quantity of critical metals such as Ni, Co, Cu, Mo, W and Cr is being discharged annually in spent catalysts. Bureau research showed that 73–99% of the metals contained in spent catalysts can be extracted by a variety of processing approaches including anhydrous chlorination, ammoniacal, acid, or caustic leaching, and sodium carbonate roasting followed by water leaching. Anhydrous chlorination overall was the most effective extraction approach. Relatively high metal extraction was achieved with this approach from all materials processed except the spent high-temperature shift catalyst. Additional research is required to optimize recovery and impurity control schemes so that the most economical processing scheme can be identified for each spent catalyst type.

REFERENCES

1. Inco Research & Development Center, Inc., Assessment of critical metals in waste catalysts (contract JO215042). BuMines OFR 197–82, 1982, 169 pp; NTIS PB 83-144832.
2. U.S. Bureau of Mines, *Minerals & Materials — a Monthly Survey*, p.3. April (1982).
3. W. A. Millsap and N. Reisler, Cotter's new plant diets on spent catalysts—and recovers Mo, Ni, W, and V Products. *Eng. and Min. J.* 179, 105–107 (1978).
4. G. Gravey, J. Le Goff and C. Gonin, Preparation of anhydrous metallic chlorides from waste catalysts. U.S. Pat. 4,182,747, 8 January (1980).
5. J. Y. Welsh, P. C. Piquet and P. D. Schyns, Process for recovering metals from catalysts for the hydrodesulfurization of hydrocarbons. U.S. Pat. 4,292,282, 29 September (1981).