Separation of cobalt from spent catalyst CoMo by precipitation and Ion exchange techniques

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Abstract

Two methods were established to separate cobalt from the spent catalyst CoMo which also contain Co, Al and Fe. The first method was the precipitation technique by controlling the pH. At pH 5, 76% of the cobalt which was collected with 1.4% Al and 0.5% Fe as contaminants. The second method was the anion exchange by using Amberlite 400 resin, 100% of the cobalt and was collected with 99.46% purity.The only contaminant was Fe with 0.54% with no Al.

For a large scale production of cobalt from this spent catalyst, a batch process was designed with a production of 80 grams per batch by using the anion exchange technique. Kilograms quantities of Co were collected.

Introduction

The catalyst CoMo is used extensively in the oil refinary plants to get the oil derivatives. The catalyst is in a form of rice-grain size pellets which contains as the name indicates the valuable metals cobalt and molybdenum. This catalyst is poisoned after several months of use and is replaced by a fresh catalyst. The spent catalyst is removed and collected in large quantities and considered as a waste since no method of regeneration of this spent catalyst is known. Cobalt and molybdenum are valuable metals which have many uses especially in the chemical industry such as glass, petrochemicals and ink. The separation of molybdenum was carried out by another research group in the same research center(1). The residue after the separation of Mo was received by our research group for the separation of Co.

Two separation methods were established to separate cobalt from the spent catalyst constituents by using:
 a) Precipitation technique by controlling the pH.
 b) Anion exchange technique using Amberlite 400 resin(2-5).

   The amino exchange technique which was then applied on a large scale for the production of cobalt.

Experimental

The spent catalyst CoMo was firstly dissolved in ammonium hydroxide to separate the valuable metal Mo. This work was carried out by another research group as mentioned

earlier(1). The residu, after washing with water, was dissolved in ahot concentrated hydrochloric acid.

Dissolution of cobalt in catalyst the spent CoMo

The spent CoMo catalyst was dissolved in 31% HCl according to the following reactions(6,7).

$$Co_3O_4 + 8HCl \rightarrow 3CoCl_2 + Cl_2\uparrow + 4H_2O$$
$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$
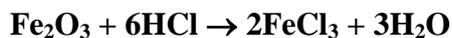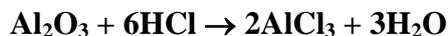
The dissolution of the CoMo pellets was not complete, thus filtration was done and the filterate was analyzed by an atomic absorption for Co, Al and Fe, while the residue was found to contain silicate.

A set of experiments were carried out to optimize the dissolution of CoMo in 31% HCl at different temperatures and dissolution time.

In another experiment the CoMo pellets were fused in a platinum crucible and analyzed for percentage of Co.

Separation of Cobalt

Two methods were separately applied:

a. By controlling the pH of solution between 3-5 by gradually adding ammonia solution, then Co and the coprecipitated components Fe and Al were analyzed by AAS.

b. Anion exchange: The separation of Co was carried out by using anion exchange resin (Amberlite 400), 40 grams of the wet resin was washed with 1M HCl and packed in 1.5cm x 35cm column and finally was adjusted the column molarity to 9M. The solution containing Co and impurities was adjusted to 9M and passed on the column with a flow rate of 0.5 ml/min. The effluent solution was analyzed by AAS.

To the column 350ml of 4M HCl was passed with a flow rate of 1ml/min and an effluent solution was analyzed by AAS.

To the column 250ml of 0.1M HCl was passed with a flow rate of 1ml/min. The effluent solution was analyzed by AAS.

Large scale production of cobalt

For a large scale production of cobalt, a large column was designed, 150cm height and 4cm diameter packed with 4kg of Amberlite resin. The flow rate was 40ml/min. The batch production of cobalt from this column was 80g.

Results and Discussion

Table (1) showes the composition of dissolution solution of CoMo spent catalyst, which consists of 1.80% Al, 1.83% Co, 0.07% Fe and the remaining percentage is undissolved silicate. Table (2) showes the % of Co in a set of four fusion experiments, where an average Co percentage of 2.16 was obtained. The dissolution time was varied between one and two hours and a temperature range between 25-100°C Table (3). One can conclude that the maximum Co dissolved is at 100°C after 2 hours of heating.

Table (4), showes the results of the separation using the precipitation technique. At pH=3, 90.4% of Al and 40.9% of Fe are coprecipitated with Co. At pH=4 a lesser extend of Al and Fe are coprecipitated being 13% and 9.9% respectively. Yet a   better   result   is obtained at pH=5 only 0.46% Al and 1.4% Fe are coprecipitated with Co. This can be attributed to the aqueous chemistry of the elements under investigation, due to the formation

of hydrox ides to a certain extend at low acidic solutions such as $[Fe(H_2O)_5OH]^{+2}$, $[Fe(H_2O)_4(OH)_2]^+$ and $[Al(H_2O)_5OH]^{+2}$(7). Also from table (4), it is clear that more than 20% of Co is lost with these hydroxides at the pH range investigated. Thus separation of Co is possible from both Fe and Al by controlling the pH to 5, but more than 20% of the cobalt is lost with the hydroxides of Fe and Al.

Another method was chosen for the separation of cobalt from Al and Fe, namely anion exchange method. Table (5) showes the results of the effluent solution analyzed by the atomic absorption spectroscopy, where all the cobalt and some of the Fe are held by the column and a negligible amount of Al. Since at 9M HCl, Co forms anionic species capable to be held on the strong alkaline resin (Amberlite 400), while Fe forms such species to a lower extent and Al to negligible amounts. Then Co was quantitatively and selectively eluted by using 4M HCl. The Co collected was 99.46% purity with only 0.54% Fe.

Conclusions

The anion exchange method was adopted to produce Co from the spent CoMo catalyst, 80 grams Co per batch, with 99.46% purity and only 0.54% Fe. Kilograms quantities werequantitively collected by using this method.

For a less pure Co with more than 20% loss of Co, the precipitation method may be adopted.

References

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Table (1): The composition of dissolution solution of CoMo spent catalyst

Component	Percentage
Al	1.80
Co	1.83
Fe	0.073

Table (2): The percentage of Co in CoMo spent catalyst by fussion experiments

Sample Number	%Co
1	2.51
2	1.80
3	2.08
4	2.25

Table (3): The percentage of Co dissolved with time and temp.

Temp. ^{o}C	Time in hours	% Co
25	1	0.82
25	2	0.84
80	1	1.21
80	2	1.33
100	1	1.62
100	2	2.41

Table (4): Seperation of Co by precipitation technique at different pH values

pH	% of Al remaining with Co after precipitation	% of Fe remaining with Co after precipitation	% Co lost
3	90.4%	40.9%	20.8%
4	13%	9.9%	27%
5	0.46%	1.4%	24%

Table (5): Separation of Co using Amberlite 400 resin

	Co	Al	Fe	Molarity	Flowrate
Composition of solution before percolating on col.	0.165g	0.148g	11.13mg	9M	
Composition of solution after percolating on col.	Nil	0.148g	0.16mg	9M	0.5 mL/min
Composition of solution after washing col. With 4M HCl.	0.1645g	Nil	0.9mg	4M	1 mL/min
Composition of solution after washing col. With 0.1M HCl.	-	-	10.01 mg	0.1M	1 mL/min

% Recovery of Co	99.69%
Purity of Co	99.4%
% Fe in Co	0.547%
% Al in Co	Nil

فصل الكوبلت من العامل المساعد المستهلك CoMo بتقنية الترسيب والتبادل الايوني

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الخلاصة

انجزت طريقتان لفصل الكوبلت من العامل المساعد المستهلك والحاوي فضلاً عن الكوبلت كل من الالمونيوم والحديد. الطريقة الاولى هي تقنية الترسيب، اذ وجد ان قيمة دالة الحامضية pH المساوية الى 5 هي الافضل اذ يتم استرداد 76% من الكوبلت مع شوائب الالمونيوم بمقدار 1.4% والحديد 0.5%. أما الطريقة الثانية فهي تقنية التبادل الايوني باستخدام راتنج الامبرلايت 400 اذ تم الحصول على 100% من الكوبلت النقي (99.46%) مع تلوث بمقدار 0.54% من الحديد فقط من دون أي كمية للالمونيوم.

للانتاج على مستوى واسع تم اعتماد تقنية التبادل الايوني للحصول على 80 غرام للوجبة الواحدة وتم تكرار العملية للحصول على كيلوغرامات من الكوبلت.