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Recovery of molybdenum from spent hydro-refining catalysts by soda ash roasting - A statistical approach

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ABSTRACT

In the present study, a hydro-refining spent catalyst with an alumina base has been taken into consideration. It is mostly used for the recovery of molybdenum. The spent catalyst constitutes around 21 pct of molybdenum as molybdenum oxide. The study has revealed that at temperature lower than 600ºC, it is possible to recover an appreciable quantity of molybdenum from the spent catalyst. The statistical experiments have been designed for the study to optimize the process parameters during soda ash roasting, i.e. roasting temperature, reaction time and percentage soda ash addition. In the trial run, it has been found to extract about 81% of molybdenum with temperature 500ºC, soda ash 20wt% when roasted for 20 minutes. The process has further been optimized and it has been possible to recover about 94% of Mo as its oxide, from the spent hydro-refining catalyst, under the optimum condition of reaction temperature 575ºC with 10wt. pct. soda ash addition and 45 minutes roasting time. © 2005 SDU. All rights reserved.

Keywords: Roasting; Molybdenum; Soda ash; Statistical designing

1. INTRODUCTION

Molybdenum has got wide application as an alloying agent in steel, cast irons and super alloys. It has a typical property to enhance the hardness, strength of the lost material and also has a greater importance as a corrosion resistant (Daone *et al.*, 1995). It equally has wide application in the field of catalysis, i.e. compounds of Mo is mostly used as petroleum hydro-refining catalysts, lubricant, etc.

The main source of molybdenum is molybdenite, fenite, etc. Extraction of molybdenum from these ores is mainly carried out by roasting the ore in multi-hearth furnaces (MHF) of Herroshoff type (Seryukov *et al.*, 1969). The MoO_3 produced after roasting contains plenty of impurities (Wilkomirshy, 1979). The impurities present in the sample such as copper, iron, nickel forms a non-volatile and insoluble molybdates during roasting (Dorfler and Laterly, 1980). Many processes have been developed by hydro as well as pyro-metallurgical routes to extract molybdenum from low grade resources (Bhappy 1979; Suri *et al.*, 1995). In the hydro metallurgical route nitric acid, sodium hydroxide leaching have got extensive uses to dissolve molybdenum from the concentrates. Processes like hypo-chlorite and electro-oxidation are also implemented for molybdenum recovery.

The pyro-metlalurgical routes are mainly implemented for the very low grade concentrate where chlorination and alkali roasting are two vital routes for molybdenum recovery. During chlorination, the medium is either chlorine or any chloride mixture which leads to form molybdenum chlorides in oxy-chlorides. This product again get treated using fractional distillation method, where molybdenum chloride get separated from its impurities (Mukherjee *et al.*, 1980; 1988).

Alkali roasting involves two processes i.e. lime roasting or soda ash roasting. The lime roasting process involves the formation of water insoluble molybdenates, which again leads to a subsequent leaching process to recovery molybdenum. The soda-ash roasting process has advantage over other processes is, as it is a single step operation to produce water soluble molybdate. In this process, the emission of SO_2 is completely restricted by the formation of subsequent sulfates (SO_4).

Soda-ash roasting has been undertaken by Wlodyka (1969). They carried out the roasting in presence of a mixture of soda ash and sodium nitrate of equal concentration. The reaction temperature was maintained to be 650ºC. In this study the roasted mass is water leached to recover the molybdenum as Na_2MoO_4.

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In another study, Mehra *et al.* (1973) have carried out the soda ash roasting of the molybdenum concentrate along with Fe_2O_3. Iron oxide in the presence of soda ash oxidize the concentrate to form a multi-variant compound i.e. Na_2MoO_4 as above. In this study, they converted sodium molybdate to calcium molybdate using $CaCl_2$ as a chlorinating agent.

Alper *et al.* (1977) have studied soda ash roasting in presence of Al_2O_3, aluminium, alike the Fe_2O_3, to produce sodium molybdate. The addition of Al_2O_3, simultaneously react with SiO_2 to convert it into aluminium silicate. Juneja (1991) had conducted the soda ash roasting of Jaduguda concentrate to recover 99% of the molybdenum present in the molybdate concentrate. In a similar study, Shah *et al.* (1997) have recovered around 98% of molybdenum, from Rakha molybdenite source, as molybdic oxide. They have implemented the soda ash roasting with changing various experimental parameters, so as to get a maximum recovery of 98% of molybdenum as its oxide.

In the present investigation, soda ash roasting process has been adopted to extract molybdenum from a hydro-refining spent catalyst. In order to get the optimum parameteric conditions, experiments have been carried out using 2^3 factorial designing method. The process has been optimised using steepest ascent method (Kafarov, 1976).

2. EXPERIMENTAL

The hydro-refining catalyst used in this investigation has the following chemical analysis, presented in Table 1.

Table 1
Chemical composition of the hydro-refining spent catalysts represented as wt%

Constituents	Al_2O_3	MoO	SO_3	SiO_2	MgO	Fe_2O_3	Co_3O_4	NiO	ZnO	CaO	Na_2O
% Wt	60.48	21.0	5.06	4.67	1.94	1.88	1.52	0.85	0.8	0.47	0.32

(All constituents are represented in their oxidic form)

The soda ash (Na_2CO_3) employed in the study was of BDH (Code.0222085) quality, with the following composition (Table 2).

Table 2
Chemical composition of the Soda ash (Loss at 300°C = 1.5%)

Elements	Chloride	Iron	Lead	Silicate	Sulphate	Na_2CO_3
% Wt	0.01	0.005	0.003	0.02	0.02	98.04

The soda ash roasting experiments were carried out with 50gms of spent catalyst as the charge. The charge mix containing a weighed quantity of catalyst and soda ash was held in a graphite crucible and heated gradually in a muffle furnace to the desire temperature. After cooling, the roasted mass was water-leached to recover molybdenum as sodium molybdate (Na_2MoO_4). The metal recovery was determined by analysing the molybdenum content with oxime method (Vogel, 1961).

3. RESULTS AND DISCUSSION

3.1. Factorial design

The reaction between spent catalyst's molybdenum oxide and soda ash in the presence of oxygen can be represented as

$$O_2(g) + MoO(s) + Na_2CO_3(s) \rightarrow Na_2MoO_4(s) + CO_2(g) \tag{1}$$
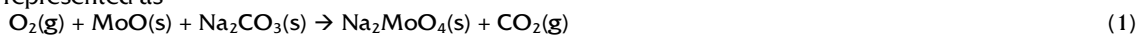
The heat of reaction at 298K (ΔH_{298K}) was found to be -1532.8 kJ/mole where the free energy change was found to be -1608.3 kJ/mole. The heat of reaction indicates that soda ash roasting is a highly exothermic reaction. Thus, it is required to heat the charge gradually to prevent sudden flaming up, which generally takes place at around 773K, when heated suddenly with a faster heating rate.

The experimental parameters affecting mostly the molybdenum recovery are temperature, roasting time and the percentage of the soda ash addition. Taking into consideration these three parameters design of experiments have been carried out.

To obtain the optimum condition for the soda ash roasting process a full factorial design of the type n^k has been used, where n = number of levels and k = number of factors under verification (here n = 2 and k = 3). Thus, with 2^3 factorial design, the total umber of trial runs become 8.

In general, for a 2^3 level full factorial design, with parameters x_1, x_2 and x_3, the regression equation becomes;

$$Y = b_o + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{23}x_2x_3 + b_{31}x_3x_1 + b_{123}x_1x_2x_3 \qquad (2)$$

where b_o, b_1, b_2 and b_3 are the interacting coefficients and Y represents the metal recovery.

The experiments were designed as below. Factor temperature varies between 400 to 600°C, retention time between 10 to 30mins and 15 to 25wt% soda ash addition. The variable parameters and their coded values are given in Table 3.

Table 3
Factorial variation intervals (X_1 = temperature in °C; X_2 = pct soda ash addition; X_3 = retension time in min)

Factors	-1	0	+1	Variation intervals
X_1	400	500	600	100
X_2	15	20	25	5
X_3	10	20	30	10

The study reveals that combined parameters have different effects on metal recovery. The results obtained from the trial runs (Table 4) are incorporated in the regression equation and the equation becomes;

$$Y_{Mo}(\%) = 57.15 + 11.34x_1 - 1.37x_2 + 9.46x_3 - 5.35x_1x_2 + 1.69x_2x_3 - 0.03x_3x_1 + 2.84\ x_1x_2x_3 \qquad (3)$$

Table 4
Design of trial experiments (coded values) and relative metal recovery

Trial No.	x_1	x_2	x_3	x_1x_2	x_2x_3	x_3x_1	x_1x_{23}	$Y_{Mo}(\%)$
1	+1	+1	+1	+1	+1	+1	+1	75.74
2	-1	+1	+1	-1	+1	-1	-1	58.13
3	+1	-1	+1	-1	-1	+1	-1	80.12
4	-1	-1	+1	+1	-1	-1	+1	62.46
5	+1	+1	-1	+1	-1	-1	-1	47.79
6	-1	+1	-1	-1	-1	+1	+	41.44
7	+1	-1	-1	-1	+1	-1	+1	70.33
8	-1	-1	-1	+1	+1	+1	-1	31.19
9	0	0	0	0	0	0	0	80.43
10	0	0	0	0	0	0	0	81.39
11	0	0	0	0	0	0	0	81.08

Each of the coefficient is assessed using student 't' test and the significant terms are properly arranged. Using Fisher's adequacy test at 95% confidence level, the adequate equation obtained for the above study is;

$$Y_{Mo}(\%) = 57.15 + 11.34x_1 - 1.37x_2 + 9.46x_3 - 5.35x_1x_2 + 1.69x_2x_3 + 2.84\ x_1x_2x_3 \qquad (4)$$

The above modified equation reveals that among all three parameters, temperature has higher unitary coefficient, followed by retention time where as the percentage soda ash addition has a negative unitary coefficient to effect the overall extraction of molybdenum. The binary parametric effect is found to be pronounced in case of x_1x_2 i.e., the combined effect of temperature and soda ash addition to the charge. The interacting parameter x_2x_3 shows some effect on molybdenum recovery, where as the coefficient x_1x_3 having no effect on recovery.

It has also been seen that the ternary coefficient has significant role on the yield, i.e., $x_1x_2x_3$ parametric effect in combination, plays a vital role for the appreciable extraction of molybdenum. The process has further been optimised to obtain the parametric values, that render the maximum molybdenum recovery.

3.2. Optimisation of the process parameters

The process optimisation has been carried out using steepest ascent method. The adopted regression equation reveals positive gradient for temperature and retention time. Thus, during optimization the step size has to be added up to the base level, for temperature and retention time to achieve the optimum. Similarly, percentage soda ash addition showing a negative gradient indicates decrease in percentage addition to optimize the condition. Thus, the step size has to be deduced from the base level. Keeping in view the above observations the step size is determined accordingly and the experimental parameters are tabulated in Table 5.

The normal step was added to the base level parameters in case of positive coefficients (i.e., temperature 500°C, retention time 20 minutes) whereas normal step is deduced from the base level for a negative coefficient (i.e., soda ash, 20wt%). The optimum conditions obtained from the base level by steepest ascent method are shown in Table 6. Molybdenum extraction shows a higher selectivity when roasted under the optimum experimental conditions.

Table 5
Steepest ascent optimisation

Incremental change	Temperature, °C (x_1)	%Na$_2$CO$_3$ addition (x_2)	Time, min (x_3)
Δbj (coeff)	11.3	-1.37	9.46
Z (step size)	100	5	10
Δbj x Z	1100	5	90.46
Normal Step	15	2	5

Table 6
Optimisation experiments

Temp., °C	Na$_2$CO$_3$, wt%	Time, mins	Yield, Mo%
500	20	20	82.76
515	18	25	88.21
530	16	30	90.97
545	14	35	92.01
560	12	40	95.98
575	10	45	98.03

The above optimization study reveals a nearly linear equation for the molybdenum recovery, with the change in experimental parameters. At temperature 575°C with 10wt% soda ash and 45min roasting time, it is possible to extract around 98% of molybdenum from the spent catalyst.

4. CONCLUSIONS

Factorial designed experiments are proved to be an efficient technique to quantify the effect of each parameters separately as well as to understand the combined parametric effect.

Temperature is found to be the most effecting parameter playing a vital role in molybdenum extraction. It is observed that around 82% of molybdenum could be extracted selectively from the spent catalyst at temperature of 500°C, with 20 wt% soda ash addition, when roasted for a period of 45min.

For molybdenum extraction is still proved that at an optimum condition of 575°C temperature and 10wt pct soda ash addition, it is possible to extract 98% of molybdenum as its oxide from a hydro-refining spent catalyst, with 45min roasting time.

REFERENCES

Alper, A.M., Boyer, C.W., Martin, B.E., U.S. Patent, 4, 006, 212, 21 Feb, 1977.
Bhappy, R.B., Hydrometallurgy, 2A., ed. Sutulov, Santiago de Chile, 1979, 316p.
Daone, D.V., Timuons, G.A., Hallada, C.J., Molybdenum and molbdenum alloys. In Kirk Othmer encyclopedia of chemical technology, 16, ed. M.H. Grant. New York, John Wiley and Sons, 1995, pp. 925-938.
Dorfler, R.R., Laterly, J.M., Review of molybdenum recovery process. In Extractive Metallurgy of Refractory Metals, eds. H.Y. Sohn, O.N. Catclson, J.M. Smith, Warrendale, The Metallurgical Society of AIME, 1980, 11 p.
Juneja, J.M., Studies on processing of low grade molybdenite concentrate by soda ash roasting. In Proc. Sundaram Symposium on thermochemistry and chemical processing, ed. C.K. Mathews, Kalpakkam, India, Calcutta, Indian Institute of Metals, 1991, pp. 389-394.
Kafarov, V., Cybernetic methods in chemistry and chemical engineering. MIR Publishers, Moscow, 1976.
Mehra, O.K., Bose, D.K., Gupta, C.K., Studies on processing of molybdenite concentrate. Trans. Ind. Inst. Metals., 1973, 26, 1-7.
Mukherjee, T.K., Bose, D.K., Gupta, C.K., Studies on molybdenum extraction. In Extractive Metallurgy of Refractory Metals, eds. H.Y. Sohn, O.N. Carlson, J.M. Smith, Warrendale, The Metallurgical Society of AIME, 1980, 25p.
Mukherjee, T.K., Saha, S., Rakha, S., Recovery of molybdenum metal powder from low grade molybdenite concentrate. Paper presented at CHEMECA-88, Sydney, August 28-31, 1988.
Seryukov, N., Kuzmin, B., Chelishcher, Y., The metallurgy of molybdenum. In General Metallurgy, Moscow, Mir Publishers, 1969, 523p.
Shah, V.D. *et al.*, Recovery of molybdenum as molybdic oxide from Rakha molybdenite, India, by soda ash roasting, Trans. Instn. Min. Metall. (Sect – C), 108, Sept-Dec 1997.

Suri, A.K., Sehra, J.C., Gupta, C.K., Studies on processing of low grade Indian molybdenum sulphide concentrate. J. Min. Process and Extractive Metallurgy Review, 1995, 15, 23-29.

Vogel, A.I., A text book of quantitative inorganic analysis, 3rd edn. London, English Language Book Society, 1961, 508 p.

Wilkomirshy, I., Roasting of molybdenite. In International Molybdenum Encyclopedia, 2A, ed. Sutulov, Santiago de Chile, 1979, 316 p.

Wlodyka, J., Possibility of producing molybdenum trioxide by alkali fusion of calcined molybdenite concentrate. Pr. Inst. Hum. Inst. Met. Niezelaznych, Poland, 1969, 21, 17-22.