JME

***J**ournal of **M**ining & **E**nvironment,*
Vol.4, No.2, 2013, 77-82.

Investigation on selective rhenium leaching from molybdenite roasting flue dusts

A. Entezari Zarandi[1], M. Karamoozian[1*], M. Eskandari Nasab[2]

1. Faculty of Mining, Petroleum and Geophysics, Shahrood University of Technology; Shahrood, Iran
2. Zarand institute of higher education, Shahid Bahonar University of Kerman

Received 18 December 2012; received in revised form 30 March 2013; accepted 10 April 2013
**Corresponding author: m.karamoozian@shahroodut.ac.ir (M. Karamoozian).*

Abstract

The possibility of selective leaching process was investigated during molybdenite flue dust leaching to recover its rhenium content. The results show that addition of alcohols to water makes the medium less favorable for molybdenum transfer into aqueous phase. On the other hand, addition of small amounts of alcohols (5-15%) makes a noticeable separation of rhenium over molybdenum, but by increasing the alcohol content recovery of both metals decreases. More than 90% of Re transferred into leach solution but the corresponding amount for Mo was only about 0.5%.

Keywords: *leaching, flue dust, molybdenum, rhenium, selectivity.*

1. Introduction

Rhenium is a less common metal, characterized by its high melting point and its important role in petrochemical, aerospace and metallurgical industries. It does not form its own minerals but exists in trace amounts associated with molybdenite in porphyry copper ores. Molybdenite veins in quartz are rhenium free. At present, rhenium is mainly recovered from the dust collected during the roasting of molybdenite concentrate associated with porphyry copper ores. The dust contains considerable amounts of Re_2O_7, which is solubilized in water [1]. The separation of rhenium from molybdenum in aqueous solution has always been a problem in hydrometallurgy and many technologies has been developed for this reason [2– 5].

Leaching is the starting point of separation in almost every hydrometallurgical process, but little information can be found in literature regarding molybdenite flue dust leaching, maybe because its rhenium content is in the form of Re_2O_7, which is readily soluble in water [6]. Yousefi et al, have recommended using solely deionized water as the leach medium instead of adding any acids, because in this way less molybdenum would transfer to aqueous phase. However, they have calculated the activation energy for the leaching of molybdenite to be 19.53 kJ/mol, and that for the rhenium to be 20.36 kJ/mol. The proposed leaching condition has a pulp density of 20%, temperatures as high as 80 °C, agitation speed of 480 rpm and 90 minutes for leaching time [6]. Leach solution obtained from this kind of operations has a typical Mo and Re content of 5–8 g/L and 250–400 ppm respectively.

During roasting of molybdenite concentrate rhenium sublimes in form of Re_2O_7, part of which traps in the filters but most of which (85% and more) runs away with off gases. The Re_2O_7 compound is readily soluble in water which forms HReO4, so the recovery of rhenium from the flue gases is more than 90%. Multistage pressure jet (venturi) scrubbers enable high rhenium recovery efficiencies to be achieved. They effectively remove the finest dust fractions and cause rhenium oxides to be absorbed [7]. Unfortunately, in none of the 17 Ferromolybdenum plants in Iran, venturi gas scrubber or even electrostatic filters are installed and bag filter used in these plants has low efficiency in recovering rhenium oxide formed during roasting. These systems would only trap up to 10% of rhenium, which is not recovered either. The obtained flue dust, is the sole source of rhenium in Iran, which would return to furnace to produce the possible MoO_3 product and again Re_2O_7 would waste to the air.

There are literatures on alcohol aided leaching process: Trifoni et al., processed manganiferous ores by reductive leaching with glucose and acid sulfuric and studied the effect of methanol, ethanol, and n-butanol. The experimental results of Mn, Ca, and Fe dissolution showed that methyl alcohol gave better results compared to ethyl and n-butyl alcohol [8]. Habib et al., studied addition of methanol to HCl-H_2O mixture for leaching of non-treated ilmenite and found that addition of little amounts of methanol enhances the reaction. A recovery of 91% Ti and 95% Fe was achieved using 6M HCL and 0.5M methanol in comparison with 53% Ti and 60% Fe recovery using only 6M HCl [9]. Jana et al., (1995) used Alcohol-modified hydrochloric acid for leaching of Cu, Fe, Mn, Ni and Co from sea nodules. They found that little propanol and butanoladditions in dilute hydrochloric acid was sufficient to achieve about 90% recovery of each of the metals [10].

The aim of present research is to study the influence of alcohols on the recovery and separation of rhenium and molybdenum into aqueous phase from molybdenite roasting flue dust.

2. Experiment

2.1. Materials and reagents

Molybdenite flue dust was kindly provided by Babakn ferromolybdenum company, Kerman, Iran. The chemical analyses of two samples are listed in Table 1. Deionized water was the main part of leachate, and all alcohols used in tests were of analytical grade.

Table 1. Chemical composition of molybdenite roasting flue dust (% w/w)

Element	Mo	Re	Cu	Fe	Se
Sample 1	36.44	0.135	0.51	0.91	0.22
Sample 2	37.83	0.128	0.42	0.88	0.2

2.2. Experimental procedure

Constant amounts of different alcohols (methanol, ethanol and *iso*-propanol) were added to deionized water. Solid to liquid ratio was kept as 1:4 (20%) and leaching continued for 30 minutes at different temperatures. Leaching process was made in a 150ml glass beaker and agitation action was done using magnetic stirrer and a cross shape magnet. After leaching, the aqueous phase was filtered and sent for Mo and Re was determined using atomic absorption spectroscopy. The results were compared with reference test which was leaching with pure deionized water.

3. Results and discussion

3.1. Effect of temperature

To investigate the effect of temperature on the selectivity of leaching process, three experiments were made in room (~25°C), cold (10°C) and hot (60°C) temperatures using deionized water as leachate. For these tests, 4000 g of flue dust and 16 L of deionized water were used in a 20 L reactor and small amount samples were taken out for analysis. Results are shown in Figures 1 and 2 for variation in recovery of rhenium and molybdenum with time.

Based on chemical analysis of dust, recovering 100% of Re in leaching process, would results a 300 ppm of rhenium leach solution content. Corresponding amount of Mo in solution would be obtained by modeling the curves fitted of data for Re and Mo recovery, and applying limiting condition of time required to bring all the Re in solution. The data for this modeling is presented in Table 2.

As shown in Table 2, the selectivity for rhenium recovery over Mo increases with the decrease of temperature, but the kinetics of reaction also drops significantly. As the flue dust is only semi roasted, some molybdenite particles had not enough time to be fully oxidized and roasted. Therefore the flue dust contains MoS_2 and both $MoO_2$and MoO_3 species. Figure 3 shows the variation of pure MoO_3 solubility in water at different temperatures. As shown in Figure 3, practically no molybdenum should be transferred into aqueous phase in temperatures less than 10°C. Based on this hypothesis and this fact that kinetics of leaching is very low at low temperatures, the effect of different types of water soluble alcohols on rhenium and molybdenum recovery was investigated.

3.2. Effect of addition of different Alcohols

The effect of different concentrations of Methanol (Figure 4), Ethanol (Figure 5) and 2-Propanol (Figure 6) on recovery of Mo and Re was studied at different temperatures for 15 minutes. Figure 4 presents the data obtained for leaching in room temperature (20°C). It can be seen that by increasing carbon chain in alcohols, less Mo has transferred into aqueous phase to check the reproducibility of results and follow the trend of leaching. The same experiments were done by increasing the time to 30 minutes.

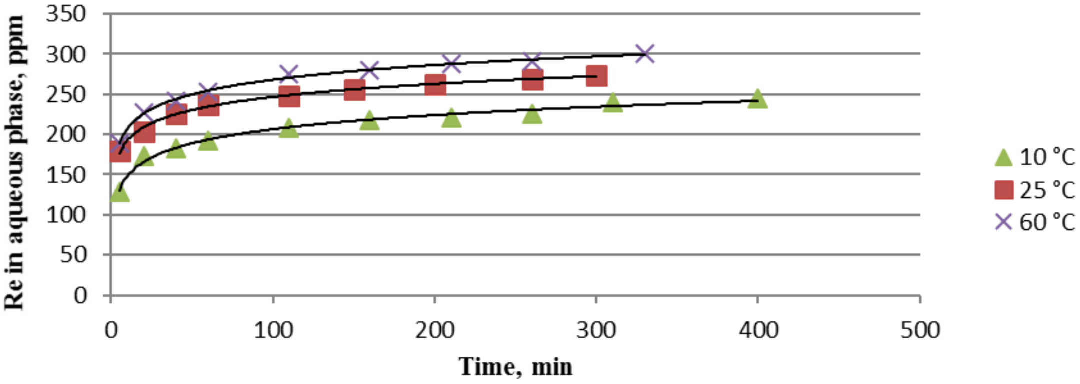

Figure 1. Variation of Re recovery (ppm) at different temperatures with time

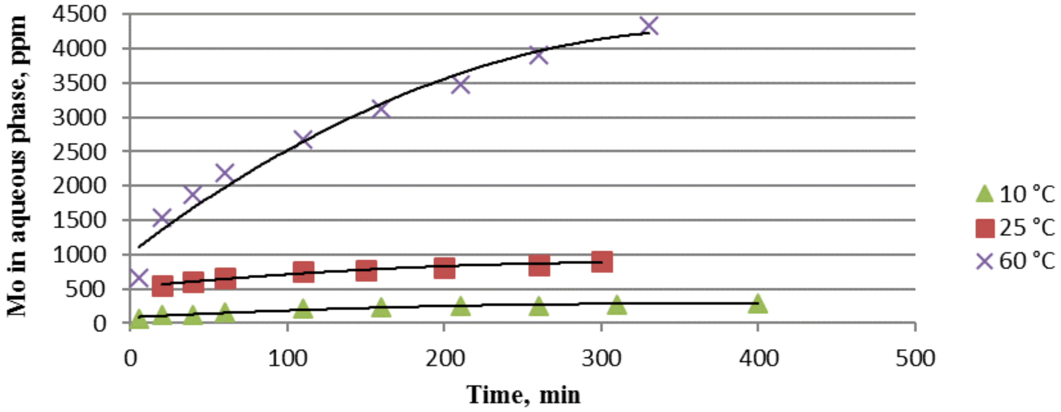

Figure 2. Variation of Mo recovery (ppm) at different temperatures with time

Table 2. Modeled Mo recovery based on data obtained of Figures 1 and 2.

Modeled Curve	Time needed to recover all Re content, min	Re in aqueous phase, ppm	Mo in aqueous phase, ppm
Leach at 10°C	1670	300	481
Leach at 25°C	1000	300	1025
Leach at 60°C	330	300	4330

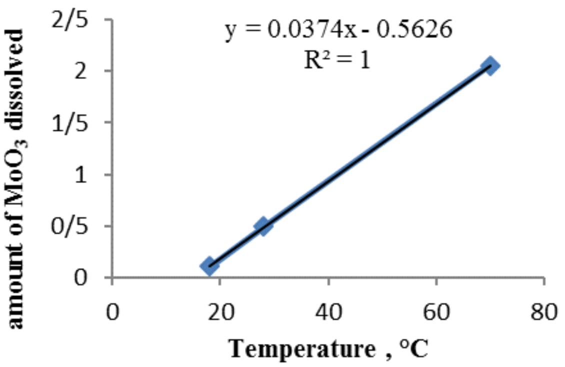

Figure 3. Variation of pure MoO3 solubility (gr/100ml) in water

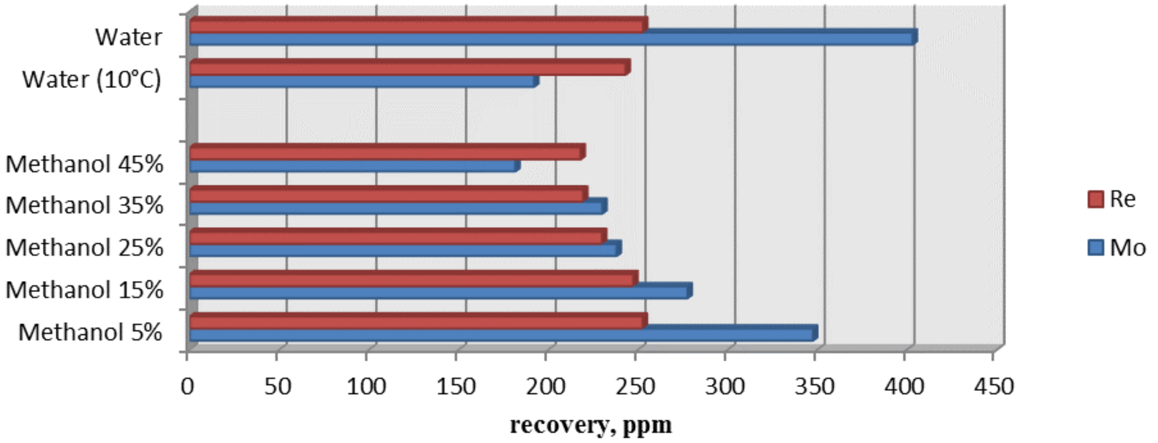

Figure 4. Effect of methanol addition to leachate

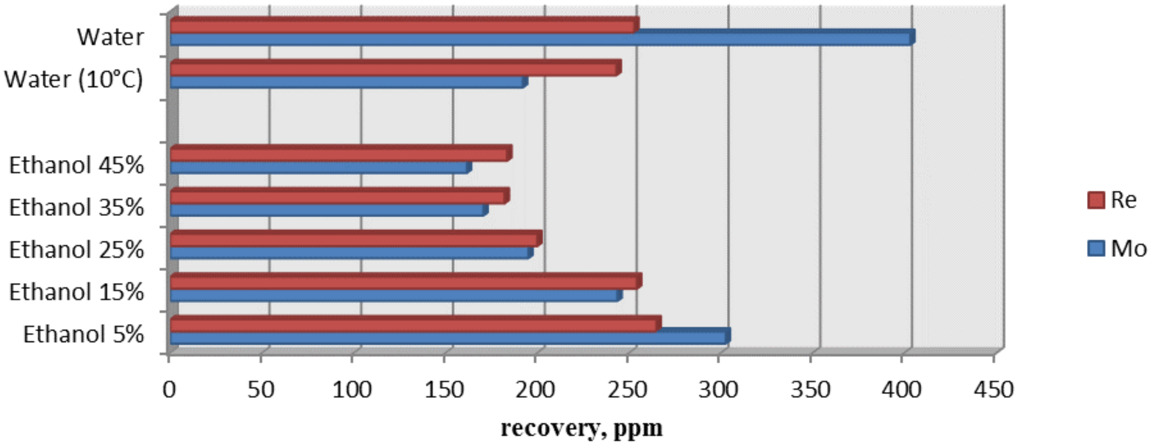

Figure 5. Effect of ethanol addition to leachate

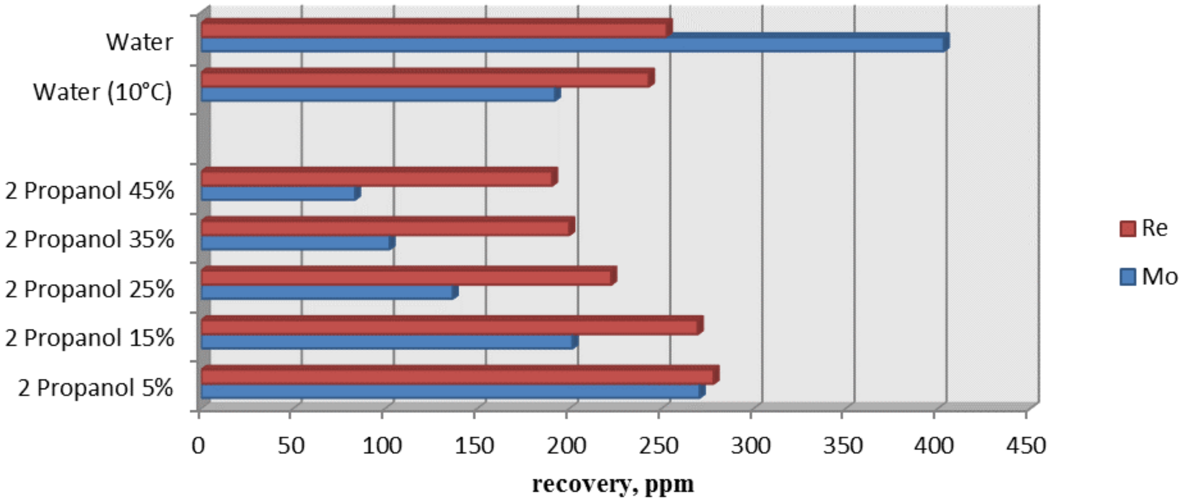

Figure 6. Effect of 2 propanol addition to leachate

However, actual mechanism of leaching by addition of alcohols has not been fully understood yet for rhenium and molybdenum, but I is obvious that addition of alcohols to water changes the dielectric constant. Also molybdenum and rhenium oxides have different solubility behavior. There is a great difference in solubility of different oxides present in flue dust and it could be shown as: Re_2O_7>> MoO_3>> MoO_2, while other species are insoluble or have very little solubility in water.

In inorganic chemistry handbooks it is stated that rhenium heptoxide has a good solubility in both water and alcohols while solubility of molybdenum trioxide is greatly limited to solvent temperature. MoO_2 has a very limited and low amount of solubility in water. By increasing the temperature, the possibility for its oxidation to MoO_3 and subsequent dissolution in water increases. But leaching with alcohol containing medium in room temperature, causes a reductive environment which is not suitable for molybdenum transfer into aqueous phase.

As seen in Figure 4, addition of methanol has caused less molybdenum transfer into solution and increasing of the alcohol content is unfavorable for both metals

Similarly to methanol, by addition of ethanol to leachate, less molybdenum is transferred into solution, but it has a positive effect for rhenium in low concentrations of ethanol (5-15%).

Figure 7 shows the overall diagrams of alcohol addition in a 30 minutes leaching. As it was said before, addition of alcohols is more suitable for rhenium recovery while it greatly decreases the molybdenum transfer into aqueous phase.

Comparison of graphs reveals that addition of 2 propanol makes the medium favorable for selective leaching of Re over Mo. It should be noted that these data are obtained from30 minutes leaching tests. Considering the maximum amount of rhenium and molybdenum that can be transferred into solution which are 335 ppm and 7.5 g/L respectively, over 90% of Re and at the same time less than 0.5% of Mo has recovered in these tests. This is important mainly because in the next operation, i.e. solvent extraction (preferably) or ion exchange, there is no need to remove part of molybdenum in advance as it is proposed in a technology developed by Keshavarz Alamdari [2], That is, two stages of Mo removal with 40% TBP, and the rhenium extraction could be done in a single stage extraction with the same organic phase after conditioning to pH equal to zero.

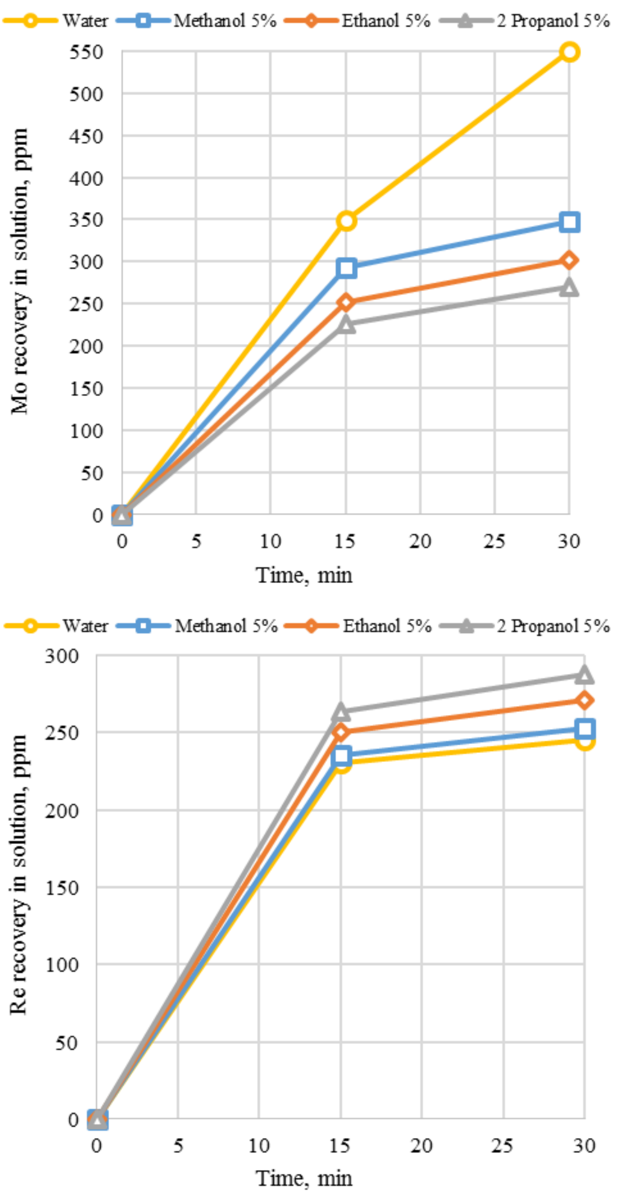

Figure 7. Effect of alcoholic leaching on transfer of Re and Mo into aqueous phase

4. Conclusions

Addition of small amounts of alcohols (5-10%) to leach solution makes the medium less favorable for molybdenum in aqueous phase but at the same time more rhenium would be brought to leachate. This phenomenon is mainly because of decreasing the di-electric constant of water and different solubility behavior of rhenium and molybdenum oxides. However, if the alcohol content will be more than 15%, solubility of both rhenium and molybdenum will be decreased, but this decrease is more significant for Mo. Also, by increasing carbon chain less Mo and Re are transferred in aqueous phase, but this is again more selective for Re over Mo.

Acknowledgments

With special thanks to Babakan ferromolybdenum plant for providing us with raw material. The authors are also thankful to Professor Fathi Habashi for his kindness and support.

References

[1]. Habashi, F. (2010). Rhenium, chemistry, metallurgy and history. Invest. Apl. Innov. 4(2).

[2]. KeshavarzAlamdari, E., Darvishi, D., Haghshenas, D.F., Yousefi, N., Sadrnezhaad, S.K. (2012). Separation of Re and Mo from roasting-dust leach-liquor using solvent extraction technique by TBP. Separation and Purification Technology. 86: 143–148.

[3]. Shariat, M.H., Hassani, M. (1998). Rhenium recovery from Sarcheshmeh molybdenite concentrate. Journal of Materials Processing Technology. 74:243–250.

[4]. Vartak, S. V., Shinde, V. M. (1996). Separation studies of molybdenum (VI) and rhenium (VII) using TPPO as an extractant. Talanla. 43:1465- 1470.

[5]. Zhan-fang, C., Hong, Z., Zhao-hui, Q. (2009). Solvent extraction of rhenium from molybdenum in alkaline solution. Hydrometallurgy. 97:153–157.

[6]. yousefi, E., Darvishi, D., Hagh-shenas, D., KeshavarzAlamdari, E., Sadrnezhaad, S.K. (2008). An investigation on the leaching of half roasted molybdenite dust. First Iranian conference on new materials. Tehran, Iran, 61-70 (in Farsi).

[7]. Nadler, H. G. (2012). Rhenium and Rhenium Compounds. Ullmann's encyclopedia of industrial chemistry. 527-537.

[8]. Trifoni, M., Toro, L., Veglio, F. (2001). Reductive leaching of manganiferous ores by glucose and H_2SO_4: effect of alcohols. Hydrometallurgy. 59:1–14.

[9]. Habib, M. A., Biswas, R. K., Ali, M. R., Hasan, A. K. M. (2006). Leaching of non-treated ilmenite by $HCl-CH_3OH-H_2O$ mixture and its kinetics. Indian Journal of Chemical Technology. 13: 53-56.

[10]. Jana, R. K., Singh, D. D. N., Roy, S. K. (1995). Alcohol-modified hydrochloric acid leaching of sea nodules. Hydrometallurgy. 38: 289-298.