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TITLE: Treatment of Molybdenite Ore Using a 2 kW Solar Furnace.*

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ABSTRACT

In the summer of 1977 several 10 g samples of molybdenite ore containing 5-6% Mo as MoS_2 were heated in one of the 2 kW solar furnaces at the Laboratoire des Ultra-Refractaires, Odeillo, France. The end products showed excellent separation with pure yellow acicular crystals of 99+% MoO_3 and pure white SiO_2 powder being the two major components. Impurity levels in the MoO_3 did not exceed 6000 ppm while only a small fraction of the molybdenite was entrained along with the SiO_2 . All treatment was done in a flowing oxygen atmosphere, and other elements condensed out at specific sites in the gas transport system. Analysis of the products was done by x-ray diffraction and x-ray fluorescence, emission spectroscopy, and wet chemical analysis. The ore was donated by Climax Molybdenum Co., Climax Co., and the work is a joint effort of LASL and CNRS Laboratoire des Ultra-Refractaires, Odeillo, France.

Work completed under the auspices of the Department of Energy.

Introduction

This paper describes the use of a 2 kW vertical axis solar furnace to treat small samples of molybdenite ore (MoS_2) concentrate. The original idea arose out of discussions with Coutures, Goldfarb, and Bezerra during a visit to Odeillo in the summer of 1976, and included the treatment of rare-earth containing minerals. A large fraction of the energy required to separate these minerals from their ores comes from fossil fuels. Conventional methods for preparing molybdenite concentrate from the ore utilize hydrometallurgical techniques and require an expenditure of about 25¢/lb of concentrate in electrical energy. Subsequently, the MoS_2 concentrate is roasted in an oxidizing atmosphere to make MoO_3 crystals with a considerable expenditure of fossil fuel energy usually in the form of natural gas. Initial examination of the thermodynamics suggested that a direct extraction process using a solar furnace as a heat source could conserve a considerable fraction of this energy. In the summer of 1977 the authors performed several experiments on small quantities of molybdenite concentrate in a flowing oxygen atmosphere. Subsequent analysis showed that excellent separation was achieved between the molybdenite and the gangue minerals. Results of these experiments are presented below.

Experimental Procedure

The solar furnace used in this experiment was described by Coutures et al (1) and is shown schematically in Fig. 1. The parabolic mirror is 2 m diam. with a focal length of 0.85 m, and it has a focal spot approximately 1 cm diam. The apparatus used was constructed by Goldfarb and Bezerra, (2) and is shown schematically in Fig. 2. It consisted of a

water cooled aluminum hearth surrounded by a 5 liter Pyrex globe with a vacuum tight seal. Sample material was placed on the hearth. The whole unit was evacuated and backfilled with an oxygen atmosphere, and then continuously flushed with gas. Other gases were tried but did not achieve separation of the minerals. The unit was pushed into and removed from the focus of the mirror on a small trolley.

Gas and particulates emitted from the sample during solar heating are carried by an excess flow of oxygen at 5 l/min through the top of the globe into a conductor pipe, thence to a cyclone separator. Condensate collects on the inside of the globe, in the pipe, and in the cyclone separator. That which does not collect in the cyclone separator by centrifugal action is subsequently filtered by a fine mesh stainless steel screen in the exhaust port. Non-condensable gaseous products, e.g. SO_2 , exhaust into the atmosphere.

The sample of molybdenite ore bearing rock furnished by Climax Molybdenum Corp. was ground to pass a 10 mesh screen. Without further treatment a 10 g amount was heaped onto the hearth of the furnace. The unit was moved to the focus of the furnace and the pile of powder was heated continuously for 10 min while the evolution of gases and smoke was observed visually. At the end of the heating period the hearth was removed from the focus, and samples were collected from six different locations in the system. The relative temperature of each sample decreases with distance from the hearth; the sample location 1 in Fig. 2 is the hottest and sample location 5 is the coolest.

PARABOLIC MIRROR - 2 KW

Fig. 1. Schematic of 2 kW vertical axis solar furnace.

Fig. 2. Schematic of apparatus used to treat molybdenite ore. Numbers are locations where samples were collected.

This experiment was conducted following an International Colloquium at Odeillo and was intended to be a scoping experiment only. A moderate attempt was made to do a mass balance, however because of several trials and the short time available this was not accomplished. Only rough analyses were performed at the time of the experiment; the more careful analyses had to wait for laboratory time. The results presented below are from the more careful analyses.

Results

At location 1 in Fig. 2 yellow crystals of vapor transported MoO_3 were observed to grow at the edge of the pile of powder. These crystals were collected carefully to avoid contamination by other products. The residue left behind after evaporation of the molybdenum oxide was the source of the second sample at the same location. A large fraction of the smoke from the evaporated rock was condensed as a white fluffy powder on the inside of the Pyrex globe. This powder from the surface of the globe formed the third sample, and is shown as location 2 in Fig. 2.

The fourth sample was material condensed as a grayish-white powder on the inside wall of the pipe connecting the globe to the cyclone separator. This is location 3 in Fig. 2. Smoke that condensed by centrifugal action was collected in the bottom of the cyclone separator at location 5 in Fig. 2. The sixth and last sample deposited on the fine mesh stainless steel screen in the exhaust port of the separator shown at location 4.

The samples were divided and a portion of each sample was submitted for the following analyses; x-ray diffraction, x-ray fluorescence, semi-quantitative spectrographic analysis, thermogravimetric analysis, and wet

chemical analysis. Wet chemistry was used to determine the Mo content in each sample except as noted later. Silica content was confirmed by x-ray fluorescence. Impurity content was determined by semi-quantitative spectrographic analysis, and is shown in Table 1. Stoichiometry of the molybdenum oxide was analyzed by thermogravimetric analysis.

The starting ore has a few strong lines in the forward direction which are characteristic of MoO_3 , however most of the x-ray diffraction lines are missing as would be expected with a sample as dilute as this ore. Semi-quantitative spectrographic analysis shows relatively high concentrations of Na, Mg, K, Ca, Ti, Mn, Fe, Zn, and Pb. The starting material is feldspathic in nature with occasional concentrations of molybdenite which appear as dark lines in the rock, and dark grains in the crushed ore.

Reagent grade molybdenum trioxide was used as the standard for comparison of x-ray diffraction patterns. The vapor grown crystals from sample 1 show an identical pattern with the standard material both for line position and intensity. Wet chemical analysis shows the sample contains 66% Mo which is stoichiometrically correct for MoO_3 . Spectrographic analysis shows this sample to be nearly as pure as the reagent grade MoO_3 used as the standard. Only Ca and Si were higher in the sample.

The crystalline material from sample 2, the residue from the rest of the pile, shows a very strong MoO_3 diffraction pattern also; however some of the intensities in the back reflection zone are reduced. This is consistent with the wet chemical analysis which shows 61% Mo present in this sample. Spectrographic analysis shows approximately the same relative distribution of elements in this sample as in the starting ore. It appears that a large fraction of the silica initially in the ore was

evaporated during the heating as it is reduced to 5% in this sample as compared with 30% in the starting ore.

The white powder collected as sample 3 from the inside of the globe yielded an amorphous x-ray diffraction pattern with four diffuse lines in the forward direction and no lines visible in the back reflection zone. X-ray fluorescence measurements on the powder indicated the major constituent was silica. Na, K, and Cr were concentrated in this sample, while Fe and Ti remained about the same concentration as the ore, and all other elements decreased in concentration. Some of this sample was subjected to thermogravimetric analysis. Very little weight was gained, and a large amount of gas was evolved.

The gray powder collected as sample 4 from the transfer pipe, location 3 in Fig. 2, has strong lines in the forward direction characteristic of molybdenum trioxide. Only a small amount of this sample was available for analysis so an exact determination of the amount of Mo was not made. Several of the transition metals concentrated in this region: Cr, Fe, Ni, Cu, Sn, and Bi.

Sample 5 was a gray powder collected from the cyclone cup, however its composition was considerably different than the gray powder in the transfer pipe. Wet chemical analysis on this sample shows 63% Mo present, and this is confirmed by the x-ray diffraction pattern which falls somewhere between sample 1 and sample 2 in intensity. It appears from the spectrographic analysis that this is very finely divided MoO_3 crystals which are relatively pure and are entrained in the gas stream. It is necessary to precipitate them from the gas stream by centrifugal action in the cyclone separator.

Sample 6 was collected from the stainless steel filter screen, and the x-ray diffraction film is similar in pattern and intensity to sample 4 from the transfer pipe. Very little material was collected at this stage as most of it had precipitated out earlier in the system. The spectrographic analysis shows it is still fairly rich in Na, K, Fe, Zn, and Pb. Both Cu and Sn have concentrated at this point in the system.

Thermogravimetric analysis was performed on samples at location 2 and 3 to determine the degree of stoichiometry by oxygen uptake. A large amount of gas was evolved rather than taken up. This coupled with the broad diffraction lines in the x-ray patterns indicate the powder is very finely divided.

Discussion

A mass balance was not performed on this experiment, however the qualitative results show that a very effective method of separating molybdenum as its oxide from the ore containing only a small amount of Mo has been found. Reference to Table I shows that the Mo was concentrated by a factor of 10 from the raw ore to the yellow MoO_3 crystals, and that fractionation of various elements occurred at different stages in the gas train. It also shows that Si was removed from the ore quite effectively by reducing the concentration of Si from 30% to about 4000 ppm in the MoO_3 crystals obtained. Examination of the silica powder from the inside of the Pyrex globe shows it to be relatively pure SiO_2 . This suggests that with further treatment in the same process the purity of MoO_3 could be improved, and very pure silica with high surface area could be prepared.

Semiquantitative Spectrographic Analysis of Samples by Location.
All Units Are ppm Unless Otherwise Indicated

	Mo	Si	Li	Be	B	Na	Mg	Al	Si	K	Ca	Ti	V	Cr
Standard	66%	10 ppm	< 10	< 1	< 3	40	6	< 30	10	200	5	< 3	< 10	< 3
Starting ore	6.5%	30%	200	4	30	400	2500	1.5%	30%	1%	6000	400	< 10	5
FeO ₃ yellow crystals (1)	66%	4000	< 10	< 1	< 3	< 30	8	50	4000	< 200	20	5	< 10	< 3
Residue from pile (1)	61%	5%	15	1	3	300	1000	1%	5%	3000	4000	200	< 10	5
Vapor from globe (2)	N/A	30%	300	1	150	2500	100	300	30%	3%	100	600	10	200
Vapor from transfer pile (3)	N/A	10%	< 10	3	< 6	250	500	800	10%	600	600	100	< 20	1000
Smoke from cyclone (5)	63%	5000	< 10	1	< 3	50	80	400	5000	200	150	15	< 10	3
Smoke from filter (4)	N/A	500	< 10	1	< 3	250	80	100	500	700	80	15	< 10	10

All Units Are ppm Unless Otherwise Indicated

	Mn	Fe	Co	Ni	Cu	Zn	Ge	Sr	Zr	Nb
Standard	1	< 10	< 100	< 30	40	< 300	< 10	< 1	< 50	< 100
Starting ore	600	5000	< 100	30	250	1500	< 10	25	< 50	< 100
MoO ₃ yellow xtals (1)	1	40	< 100	< 30	15	< 30	< 10	< 1	< 50	< 100
Residue from pit (1)	200	600	< 100	30	1500	1000	< 10	30	< 50	< 100
Vapor from globe (2)	60	5000	< 100	200	100	< 300	< 10	1	< 50	< 100
Vapor from transfer pile (3)	600	6000	< 100	400	500	< 600	< 10	< 2	< 100	< 100
Smoke from cyclone (5)	15	250	< 100	< 30	30	< 300	< 10	1	< 50	< 100
Smoke from filter (4)	50	1000	< 100	150	5000	400	< 10	1	< 50	< 100

Semiquantitative Spectrographic Analysis of Samples by Location.
All Units Are ppm Unless Otherwise Indicated

	Mo	Ag	Cd	In	Sn	Sb	Ba	Tl	Pb	Bi
Standard	66%	< 3	< 3	< 30	< 30	< 30	< 3	< 50	< 10	< 50
Starting ore	6.5%	6	10	< 30	< 30	< 30	80	< 50	1000	< 50
MoO ₃ yellow xtals (1)	66%	< 3	< 3	< 30	30	< 30	< 3	< 50	10	< 50
Residue from pile (1)	61%	30	3	< 30	400	< 30	80	< 50	500	150
Vapor from globe (2)	N/A	3	< 3	< 30	100	< 3	< 50	30	< 50	< 30
Vapor from transfer pile (3)	N/A	6	< 6	< 30	200	< 60	8	< 50	300	200
Smoke from cyclone (5)	63%	< 3	< 3	< 30	100	< 30	< 3	50	80	< 50
Smoke from filter (4)	N/A	8	10	< 30	1500	< 30	< 3	< 50	400	150

The silica may possibly be used in transistor manufacture or for catalysis. Table II shows the degree of separation between some of the important components in the ore and the crystals.

Table II.

Separation of Some Elements Between the Ore and the MoO_3 Crystals

<u>Element</u>	<u>Ore</u>	<u>Crystals</u>	<u>Separation Factor</u>
Mo	6%	66%	11
Si	30%	4000 ppm	75
Al	1.5%	50 ppm	30
K	1%	200 ppm	50

Although Nb and Zr were not present in large concentrations in the raw ore they seemed to follow through the process and remain in the same relative concentrations at each stage. The process may therefore also be useful for the beneficiation of ores of these two elements. Re was not found in the starting ore; and therefore no analysis was made for it in the products.

Fractions removed at different stages in the system showed widely varying concentrations of elements or groups of elements. For example, the vapor that condensed early in the gas train is high in Si, Ti, Mg, K, Na, and some of the transition elements. Other transition elements condensed later in the train; for example, Fe, Cr, Cu, and Ni are concentrated in the transfer pipe beyond the large surface area in the globe. The selective condensation suggests that it is possible to tap fractions of the

gas stream at various stages downstream, and to obtain enriched concentrations of specific elements,

Comparison of the analysis of MoO_3 yellow crystals made by vapor transport in the solar furnace with the analysis of the MoO_3 reagent grade standard shows that the impurity level for all elements in the crystals prepared by the solar furnace is at least as low as that in the standard except for Ca and Si. This suggests that reagent grade MoO_3 could be prepared rapidly and in quantity using the solar furnace method. It is also possible to reheat the MoO_3 crystals obtained from the initial heating to further refine it. This and subsequent heatings would not significantly increase the cost of the chemical because of the simplicity of the process.

Some elements were concentrated in the residue left behind during the evaporation of molybdenum. These are shown in Table III. The residue thus may be of some economic importance at some later time in the processing.

Table III.

Some Elements in the Ore and the Residue

<u>Element</u>	<u>Ore, ppm</u>	<u>Residue, ppm</u>	<u>Separation Fraction</u>
Cu	25 ppm	1500 ppm	60
Fe	5000 ppm	6000	~ 1
Sn	< 30	400	13
Ag	6	30	5
Bi	< 50	150	3

Examination of Table I shows some interesting results for fractions of the vapor that have condensed in different parts of the apparatus. The following pairs of elements behave quite similarly: Si and Al, Na and K, Mg and Ca, Cu and Sn, and the group Fe-Mn-Cr-Ni. Enrichment of these elements varied from a factor of 2 to about a factor of 5. This may not be of economic importance, however it does suggest that enriched vapor fractions might be removed from the vapor stream at various stages.

Conclusions

It is evident that excellent separation of MoO_3 from SiO_2 is achieved by the treatment of molybdenite ore in an O_2 atmosphere in a solar furnace, and that pure MoO_3 and SiO_2 products may be obtained. Increases or enrichment of many of the elements present in the samples are quite respectable, and this may be of some economic importance.

Niobium and zirconium follow the same path as molybdenum, but the concentration of these elements is low and the data on enrichment are inconclusive. Rhenium, which is almost always present in molybdenum ore, was not found in this material. An experiment should be conducted at some later date with rhenium ore to study its behavior. The vapor pressures of MoO_3 and Re_2O_7 differ widely thus one could expect an effective separation of these two materials in the vapor phase.

This experiment is an example of one that utilizes solar energy for process heat. It does not require a very high solar flux or very high temperatures to obtain results ($\sim 1400\text{--}1600^\circ\text{C}$). The oxidation of the MoS to MoO_3 is exothermic, and the kinetics appear to be rapid.

Future Work

The present work on ore refinement appears to yield good separation of molybdenum from its ore. The authors plan to examine the process using larger quantities in the batch mode. Two experiments are presently planned: 1) to treat kilogram quantities of the raw ore in the 1 MW facility at Odeillo to determine if MoO_3 can effectively be extracted from the raw ore which is very low grade MoS_2 ($\leq 1\%$ Mo), and 2) to roast MoS_2 concentrate in large quantities in the batch mode to make MoO_3 crystals of high purity. This latter product is used directly in steelmaking. A mass balance will be performed on both experiments. If the experiments are successful, economic and engineering analysis will be performed to determine if the process is adaptable on a continuous basis. Should this prove feasible, experiments could be prepared for the 5 MW Solar Thermal Test Facility when it is ready to commence operation.

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