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**CANADA**

**DEPARTMENT OF ENERGY, MINES AND RESOURCES**

**OTTAWA**

**MINES BRANCH INVESTIGATION REPORT 66-96**

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**DETERMINATION OF THE COMPOSITION OF  
A ROASTER STACK PRODUCT FROM A  
MOLYBDENITE ROASTING OPERATION AT  
THE MOLYBDENITE CORPORATION OF  
CANADA, LTD., VAL D'OR, P. Q.**

by

**J. C. INGLES AND J. B. ZIMMERMAN**

**EXTRACTION METALLURGY DIVISION**

**COPY NO. 5**

**DECEMBER 7, 1966**

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Mines Branch Investigation Report IR 66-96

DETERMINATION OF THE COMPOSITION OF A ROASTER STACK  
PRODUCT FROM A MOLYBDENITE ROASTING OPERATION AT THE  
MOLYBDENITE CORPORATION OF CANADA, LTD., VAL D'OR, P.Q.

by

J. C. Ingles\* and J. B. Zimmerman\*\*

SUMMARY

A sample of roaster stack product from the  
Molybdenite Corporation of Canada Ltd., plant at  
Val d'Or has been subjected to detailed chemical examination.  
No elements of economic significance other than molybdenum  
were found.

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## INTRODUCTION

Following a discussion between Mr. C. Marcoux, Mine Manager of the Molybdenite Corporation of Canada Ltd., and Mr. C. S. Stevens of this Division, a sample of product from the roaster stack at the Company's operation at Val d'Or, P. Q. was submitted for chemical examination. The accompanying letter, (Appendix 1 of this report) noted that the material, which accumulates at the rate of 500 lbs per month, is presently being discarded. The original sample was received September 8th and a second sample, which was required for additional analyses, was received October 3rd.

### Description of the Sample

The sample as received was a heavy blue-black paste, about the consistency of shoe polish, sparsely interspersed with hard, clear granules. It reacted strongly acid, avidly picked up moisture from the air and rapidly dissolved paper labels. Initial attempts to dry some of the material necessitated heating for several days at about 300°C and the dried material quickly regained its moisture on standing. Prolonged heating at higher temperatures resulted in the evolution of heavy white fumes. Preliminary examination indicated that the sample was a mixture of a water-insoluble portion resembling molybdenite in appearance, and a water-soluble portion which produced an opaque dark blue solution. This solution, on standing several weeks, deposited a small amount of a blue-black material, and the resulting clear supernatant solution was pale-yellow in colour.

## EXPERIMENTAL

Because of the wet condition of the material, and its extremely hygroscopic nature, it was not possible to cut out representative samples, or to obtain a dry weight datum. Accordingly, unweighed grab samples were used for determination of the relative proportions of the components in the water-insoluble and water-soluble fractions of the sample, and the balance of the sample was used to determine the relative amounts of these two components. A separate grab sample was used to determine the rhenium content directly, since this element is reported to be readily volatilized from strongly-acid solutions (1).

### Procedure

#### Grab sample No. 1

A sample of the paste weighing about 100 grams was slurried in about 150 ml of water, centrifuged and washed three times with 100 ml

portions of water. The filtrate and washings were combined and diluted to 500 ml. The solution was analyzed for molybdenum, sulphate, free acid and "fumed total solids". The "fumed total solids" determination consisted of evaporating an aliquot of the solution to dryness and fuming it over a gas burner until sulphur trioxide fumes were no longer evolved. The insoluble portion was dried at 110° C, weighed, and analyzed for molybdenum, total sulphur and silica. Both the insoluble material and the "fumed total solids" from the dissolved material were submitted for semi-quantitative spectrographic analysis and for examination by X-ray diffraction.

#### Grab Sample No. 2

A portion of the sample weighing about 5 grams was dissolved by alkaline fusion and its rhenium content determined by a combination ion exchange: X-ray fluorescence method. Details of the procedure employed are given in Appendix 2.

#### Main Bulk Sample

The main bulk of the sample was separated into a water-soluble fraction and a water-insoluble fraction. The former was evaporated to dryness, (finishing on a hot plate at about 500° C under infra-red lamps), transferred to a tared bottle, and weighed. The water-insoluble portion was dried at 110° C, transferred to a tared bottle, and weighed.

### RESULTS

#### Grab Sample No. 1

The water-insoluble portion of this sample weighed 27.20 g and had the composition recorded in Tables 1. and 2.(2). The X-ray diffraction examination (3) indicated that crystalline components of the sample consisted essentially of molybdenite and molybdenum trioxide.

TABLE 1

Composition of Water-insoluble Portion (27.20g)  
from Grab Sample No. 1 (Estimated Weight of Grab Sample -85g)  
from Wet Chemical Analyses

Component	Amount Present %
Molybdenum as Mo	42.7
Sulphur as S	21.8
SiO <sub>2</sub>	15.4

TABLE 2

Composition of Water-Insoluble Portion  
from Grab Sample No. 1 - Semi-Quantitative  
Spectrographic Values (Ref 21)

Component	Amount Present %
Si	1.79
Mn	.005
Mg	.18
Pb	.13
Fe	.49
Cr	.22
Bi	.11
Al	.21
V	.02
Cu	.04
Ag	.007
Na	.26
Ti	.04
Ni	.04
Co	.03
Sr	.15
Mo	Principal Constituent

The composition of the solution of the water-soluble portion, which had a volume of 500 ml, is given in Table 3. The results of the semi-quantitative spectrographic analysis of the "fumed total solids" from this solution (2) are given in Table 4. X-ray diffraction examination of the "fumed total solids" showed that the crystalline components were ferric sulphate and another crystalline constituent for which there is no published pattern (4).

TABLE 3

Composition of the Solution (volume 500 ml) of  
the Water Soluble Portion of Grab Sample No. 1  
(Estimated Weight of Grab Sample -85g)  
from Wet Chemical Analyses

Component	Amount Present	
	g/l	g in original sample
Molybdenum		
as Mo	22.0	11.0
as MoO <sub>3</sub>		<u>15.0</u>
Total Sulphur		
as S	26.6	13.3
as SO <sub>3</sub>		<u>33.3</u>
Free acid		
as H <sub>2</sub> SO <sub>4</sub>	82.0	
as S		13.4
as SO <sub>3</sub>		33.5
Iron		
as Fe	1.7	.85
as FeO		<u>1.09</u>
"Fumed Total Solids"	56.0	28.0
Sum of Assumed Major Components		49.39

TABLE 4

Composition of "Fumed Total Solids", from the  
Solution of the Water-Soluble Portion of Grab  
Sample No. 1 - Semi-Quantitative Spectrographic  
Values(2)

Component	Amount Present	
	in "Fumed Total Solids, "	in Water Soluble Portion of Grab Sample No. 1 Grams (calculated)
Si	0.53	.15
Mn	0.01	.003
Mg	2.04	.6
Pb	0.11	.03
Fe	5.11	1.4
Cr	.18	.05
Bi	.08	.02
Al	.30	.08
V	.02	.006
Cu	.06	.02
Ag	.003	.0008
Na	.02	.006
Ti	.08	.02
Ni	.09	.025
Co	.04	.011
Sr	.13	.04
Mo	PC	-

Grab Sample No. 2

Rhenium Content

The rhenium content of this sample was found to be less than  
 25 ppm.

Main Bulk Sample

The gross composition of the main bulk of the sample (that is, the relative proportions of water-insoluble material and water-soluble material) is given in Table 5. It should be noted that the bulk of the excess sulphur trioxide in the water soluble fraction was removed in the drying process used for the determination of the weight of this fraction.

TABLE 5

Gross Composition of Main Bulk Sample, dry basis

Component	dry weight, g	% of sample dry basis
Water insoluble fraction	1525	61.6
Water soluble fraction, dry (excess acid driven off)	530 g	21.4
Estimated Sulphur trioxide content driven off in drying the water-soluble fraction	<u>422</u>	<u>17.0</u>
Total	2477	100.0

Accordingly, the calculation of the sulphur trioxide content of the main bulk sample has been based on the assumption that the difference between "fumed total solids" and the sum of the major components of the soluble fraction (Table 3) represents sulphur trioxide in excess of that required to form the compound  $\text{MoO}_3 \text{SO}_3$ . On the basis of this assumption, and the assumption that the compositions of the water-soluble and water-insoluble fractions of the grab sample are the same as those of these fractions in the main bulk sample, a calculation of the relative proportions of the main bulk sample is given in Table 6. Table 7 summarizes the distribution of the molybdenum.



TABLE 6

Calculated Relative Proportions  
of Major Components in the Main Bulk Sample

Component	Fraction	Amount Present, %
MoS <sub>2</sub>	insoluble	23.2
MoO <sub>3</sub> SO <sub>3</sub>	insoluble	28.9
Si O <sub>2</sub>	insoluble	9.5
Total Insoluble		61.6
MoO <sub>3</sub> SO <sub>3</sub>	soluble	19.6
+ Excess SO <sub>3</sub>	soluble	17.0
Fe SO <sub>4</sub>	soluble	1.8
Total Soluble		38.4

TABLE 7

Distribution of Molybdenum  
in the Main Bulk Sample

Component	Fraction	Molybdenum Content, as Mo % of sample
Mo S <sub>2</sub>	insoluble	13.9
Mo O <sub>3</sub> SO <sub>3</sub>	insoluble	12.4
Mo O <sub>3</sub> (SO <sub>3</sub> ) <sub>3.6</sub>	soluble	<u>8.4</u>
Total		34.7

## DISCUSSION

On the basis of the samples examined, about a quarter of the molybdenum in the roaster stack dust is present in soluble form, accompanied by 3.6 moles of sulphur trioxide for each mole of molybdenum oxide. On water leaching, this sulphur trioxide is converted quantitatively to an equivalent amount of sulphuric acid i.e. about 3 grams of sulphuric acid are produced for each gram of molybdenum dissolved (Table 3). About half of the remainder of the molybdenum is apparently present as an oxide, but was not dissolved by the relatively mild water leach used in separating the components. It is possible that by suitable treatment this portion also could be dissolved, or it may represent material calcined at a higher temperature, which is reported to be difficultly soluble in some cases (5). Presumably, these fractions could be recovered for conversion to molybdenum chemicals if a suitable process could be worked out, and it were economically advantageous to do so. The "Molybdenum blue" colour, on the basis of visual observations, forms only a minor fraction of the sample and would be difficult to separate from the other components.

Rhenium, a valuable constituent that frequently reports in the volatile products from molybdenum roasters (1), is not present in economic amounts in this sample.

## CONCLUSIONS

Detailed chemical examination of the roaster stack dust failed to reveal any unsuspected values of obvious economic significance. In particular, no indication of commercial concentrations of rhenium was obtained.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge assistance provided by the Spectrographic Section of the Mineral Sciences Division and its head, Dr. A. H. Gillieson, by the Mineralogy Section, Extraction Metallurgy Division directed by Mr. S. Kaiman, and Mr. E. Kornelsen, Mr. D. J. Barkley and Mr. A. D. King of the Chemical Analysis Section.

APPENDIX 1

MOLYBDENITE CORPORATION OF CANADA LTD

2 September, 1966

Mr. John Ingles  
Extraction Metallurgy Division  
Mines Branch  
300 Lebreton St  
Ottawa, Ont.

Dear Sir,

During a recent telephone conversation that our mine manager Mr. C. Marcoux, had with Mr. C.S. Stevens, of your department, he mentioned that from the stack of our roaster we collect a product which is commonly known as "Molybdenum blue".

The amount collected is about 500 lbs per month.

Presently we discard this product, as we have no uses for it. But Mr. Stevens suggested that we send a sample to your attention, to investigate if this material has some possibilities as such (in pigments for instance) or if it can be transformed by chemical or metallurgical processes, in a valuable product.

In addition to that, although it was not mentioned between Mr. Marcoux and Mr. Stevens, we take the liberty to ask you to try to determine if there is some Rhenium in this product, and the quantity.

The sample is sent in a bottle, as this material is collected in a very wet form. We sent it to you "asis" to be sure that it represents well, the product we recover.

If more material or information are necessary regarding this project, please do not hesitate to ask for.

Thanking you for interest in our problems, we remain,

Yours very truly,

(Sgd) Florent Baril  
MOLYBDENITE CORP. OF CDA LTD.  
Florent Baril, Eng.,  
Chief Metallurgist.

## APPENDIX 2

### THE DETERMINATION OF RHENIUM IN MOLYBDENITE ROASTER STACK PRODUCT

#### Outline of the Method

The sample was taken into solution by alkaline fusion to avoid losses which might occur due to the volatility of perrhenic acid. The melt was dissolved, and concentrated hydrofluoric and hydrochloric acids were added so that the final solution was 20% HF, 25% HCl on a volume basis. This solution was then passed through a small column of Dowex 1 anion exchange resin to retain the rhenium (6). Most of the molybdenum and other elements present are not retained by the resin and were removed by passing an additional volume of the pure mixed acids. The resin containing the adsorbed rhenium was removed from the column, dried, powdered, and the intensity of the  $L\alpha_1$  -  $L\alpha_2$  rhenium lines ( $2\theta = 41.69^\circ$ ) were measured on a Philips type PW 1540 All Vacuum Universal X-ray Spectrograph.

To a second sample, rhenium equivalent to about 60 ppm was added and the spiked sample was carried through the entire procedure. The estimated rhenium content of the original sample was then based on the recovery of the spike.

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