AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT

LUCAS HEIGHTS RESEARCH LABORATORIES

DEVELOPMENT OF A PILOT PLANT FOR THE REMOVAL OF RHENIUM FROM MOLYBDENUM TRIOXIDE

by

E.J. LEE

P.J. SORBY

R.K. BARNES

R.E. BOYD

DECEMBER 1985

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT

LUCAS HEIGHTS RESEARCH LABORATORIES

DEVELOPMENT OF A PILOT PLANT FOR THE REMOVAL OF RHENIUM FROM MOLYBDENUM TRIOXIDE

by

E.J. LEE
P.J. SORBY
R.K. BARNES
R.E. BOYD

ABSTRACT

Reagent grade molybdenum trioxide used as a target material for the preparation of ^{99m}Tc pharmaceuticals contains trace amounts of rhenium. A simple charcoal adsorption process has been developed to remove rhenium selectively from molybdenum before neutron irradiation. Details are given of the design and operation of a pilot plant in which 17 kg of molybdenum trioxide was produced having a rhenium content of less than 1×10^{-6} μg g^{-1}. Although contamination of the ^{99m}Tc by inactive rhenium and [188]Re was effectively eliminated, [188]Re resulting from the irradiation of tungsten impurity in the molybdenum trioxide target was still present.

The following descriptors have been selected from the INIS Thesaurus to describe the subject content of this report for information retrieval purposes. For further details please refer to IAEA-INIS-12 (INIS: Manual for Indexing) and IAEA-INIS-13 (INIS: Thesaurus) published in Vienna by the International Atomic Energy Agency.

RHENIUM 188; TECHNETIUM 99; MOLYBDENUM OXIDES; PILOT PLANTS; ACTIVATED CAR-BON; CHARCOAL; DISSOLUTION; CRYSTALLIZATION; SEPARATION PROCESSES; SOLUTIONS; AMMONIUM COMPOUNDS; MOLYBDATES; ADSORPTION; CALCINATION; PURIFICATION

CONTENTS

1. INTRODUCTION

This report describes the following processes and operations for separating rhenium from molybdenum trioxide:

. Dissolution of molybdenum trioxide in ammonium hydroxide.

. Extraction of rhenium from ammonium molybdate solutions.

. Crystallisation of ammonium paramolybdate (APM).

. Calcination of ammonium paramolybdate.

In the dissolution process, a slurry of molybdenum trioxide powder is heated in dilute ammonium hydroxide solution. Rhenium is then extracted from the molybdate solution by adsorption on activated charcoal [Sorby 1984].

As the solubility of APM in ammonium hydroxide solution is little influenced by temperature [Funaki and Segawa 1950], the crystallisation process should allow evaporation. The recovery of ammonium paramolybdate crystals was described by Scheiner et al. [1976] as a process involving crystallisation after a solution containing 100 g L^{-1} molybdenum was reduced in volume to 1/26th of its initial volume.

Romanauski and Wladyslaw [1963] carried out a detailed thermogravimetric analysis on APM which indicated complete decomposition to molybdenum trioxide in 30 minutes at 500°C in air. However, as molybdenum reduces to lower valence state oxides by reaction with the gaseous biproduct gases, longer heating at higher temperatures is desirable.

2. THEORETICAL CONSIDERATIONS

The isotope molybdenum-99 (^{99}Mo) is produced by the neutron activation of either metallic molybdenum or molybdenum compounds, e.g. the trioxide

$$^{98}\text{Mo (24.4\% ab.)} \longrightarrow \ ^{99}Mo\,(t_{\frac{1}{2}} \ = \ 66 \text{ hours, } \sigma = 0.48 \ barns\,).$$
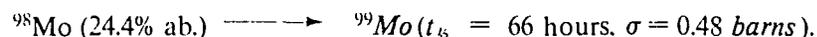
The radioactive ^{99}Mo decays to technetium-99m (^{99m}Tc), an isotope used widely in nuclear medicine.

Separation of ^{99m}Tc from its parent and the bulk inactive molybdenum is usually carried out using either sublimation of the more volatile technetium heptoxide from molybdenum trioxide or by selective solvent extraction of pertechnetate from a molybdate solution. However, in both of these processes, contamination of the ^{99m}Tc product with significant levels of chemical and radionuclidic impurities can occur. Consequently, for the production of ^{99m}Tc for use in nuclear medicine, the molybdenum feed material must be of high quality.

Rhenium is a common impurity in commercially prepared pure molybdenum trioxide. Because of the chemical similarity of technetium and rhenium, there is significant contamination of ^{99m}Tc with inactive rhenium and its radionuclides, regardless of the method used to separate ^{99m}Tc from the irradiated molybdenum. Given the high neutron cross sections of the rhenium isotopes ^{185}Re and ^{187}Re, significant contamination of ^{99m}Tc occurs with only trace amounts of rhenium in the molybdenum target material:

$$^{185}\text{Re} \longrightarrow \ ^{186}\text{Re}\,(t_{\frac{1}{2}} \ = \ 91 \ h, \quad \sigma = 310 \text{ barns})$$

$$^{187}\text{Re} \longrightarrow \ ^{188}\text{Re}\,(t_{\frac{1}{2}} = 17 \ h, \quad \sigma = 110 \text{ barns})$$
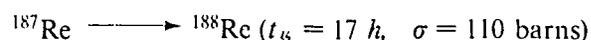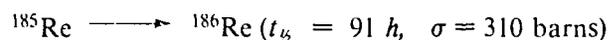
In addition, the contamination of molybdenum by tungsten (a common impurity in molybdenum ores) of the order of 500 μg g^{-1} also gives radioactive rhenium on irradiation:

$$^{186}\text{W} \longrightarrow \ ^{187}\text{W}\,(t_{\frac{1}{2}} = 24 \ h, \quad \sigma = 38 \text{ barns})$$

$$^{187}\text{W} \longrightarrow \ ^{188}\text{W}\,(t_{\frac{1}{2}} = 69 \ d, \quad \sigma = 70 \text{ barns})$$
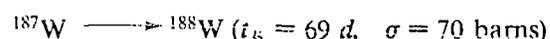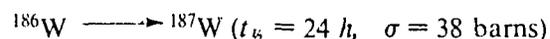
the ^{188}W decaying by β^- to ^{188}Re. Because of the double neutron capture reaction, the yield of ^{188}W is small, but it is still a significant long-term source of ^{188}Re.

The maximum allowable level of rhenium radionuclide contamination is determined from the British Pharmacopoeia specification of <0.01 per cent at the time of injection and the decay period between production and injection. At Lucas Heights, rhenium was removed from molybdenum trioxide by the selective sublimation of rhenium heptoxide. Although the process is simple (heating molybdenum trioxide

in an air stream to 500-600°C), it is slow and technically difficult. Molybdenum trioxide particles sinter at these temperatures, resulting in a significant reduction in the rate of rhenium oxide release from the molybdenum trioxide matrix after extended heating times. In addition, the containment of molybdenum trioxide vapour is extremely difficult as it is highly reactive to most commercial metallic and ceramic materials of construction. An extension of this process involving repeated sublimation and condensation of molybdenum trioxide at high temperatures (1000 to 1100°C) in an air stream [Toensing 1957], although practical on a large industrial scale, has similar corrosion difficulties on the smaller scale.

The commercial separation of rhenium from impure molybdate solutions using a simple charcoal adsorption process has been described by Lindstrom and Scheiner [1973] and Scheiner et al. [1973, 1976]. In pilot plant studies, the concentration of rhenium was reduced from 270-450 μg g^{-1} to less than 0.1 μg g^{-1} by passing an approximate molar ammonium molybdate solution through a bed of activated charcoal.

3. INITIAL SMALL-SCALE EXPERIMENTS

Fifty-gram batches of molybdenum trioxide were dissolved in 200 mL of 7.5 M ammonium hydroxide solution. After filtering, the solution of ammonium molybdate was passed through a packed column (10 mm diameter $\times$ 500 mm long) of granulated activated charcoal (Permutit 'Filtrasorb 200') at a flowrate of 1 L h^{-1}. The treated solution was refiltered and evaporated on a water bath to half volume and cooled to crystallise ammonium paramolybdate. The crystals were separated and calcined at 400°C for 16 h.

To enhance the rhenium activation, a reactor position having a low epithermal neutron flux was selected. Targets containing 5 g of molybdenum trioxide powder were irradiated for seven days at a thermal flux of 4 $\times$ 10^{13} neutrons cm^{-2} s^{-1}. For comparison, targets of untreated oxide were also irradiated concurrently. The irradiated molybdenum trioxide was dissolved in potassium hydroxide solution and the ^{99m}Tc extracted with 2-butanone (methylethylketone). Analysis of the extracted ^{99m}Tc on a 2000-channel gamma spectrometer indicated 13 μg g^{-1} of ^{186}Re in the extract from the untreated molybdenum trioxide, and 0.06 μg g^{-1} of ^{186}Re was detected in the ^{99m}Tc from the treated molybdenum trioxide.

4. PILOT PLANT STUDIES

An equipment flowsheet for the dissolution of molybdenum trioxide in ammonium hydroxide and for the crystallisation of ammonium paramolybdate is given in figure 1. All equipment which comes in contact with process solutions or slurries was constructed from 300 series stainless steels.

4.1 Molybdenum Trioxide Dissolver

The dissolver vessel was 300 mm diameter by 700 mm high and had a capacity of 50 L. Solution heating was carried out with a 6 kW, 3-phase immersion heater, the temperature being monitored by a sheathed chromel-alumel thermocouple. The dissolver contents were stirred with a 96 mm diameter by 100 mm pitch propeller, directly driven by an off-set, extended shaft, 1450 rev. min^{-1}, 0.2 kW electric motor. To avoid vortex formation, a 90 mm by 300 mm long baffle was placed on the inside wall, extending from the top of the heating coils to the top end of the dissolver.

Concentrated ammonium hydroxide ($\sim$ 15 M) was metered into the dissolver by a peristaltic pump, addition being made through the bottom outlet to avoid blockage by settled molybdenum trioxide powder.

4.1.1 Process operation

The dissolver was loaded with 30 L of demineralised water and 10 kg of molybdenum trioxide powder was then added slowly while stirring. The slurry was heated to 40°C (five minutes with 6 kW heating), the heaters were isolated and 4 L of concentrated ammonium hydroxide was slowly added at 300 mL min^{-1}. During addition, the slurry temperature rose from 40 to 60°C but, to ensure complete dissolution, the temperature of the solution was increased to and held at 70°C for a further 60 minutes. To prevent crystallisation of APM from the solution during cooling, demineralised water was added to give a total solution volume of 50 L (corresponding to 230 g L^{-1} of APM). The diluted ammonium molybdate solution was filtered through a Buchner funnel containing a nylon cloth. Three dissolution batches containing a total of 30 kg of molybdenum trioxide were bulked together as feed solution to the charcoal column.

4.2 Charcoal Adsorption Column

The adsorption column was constructed from a 3 m length of 18 mm diameter polyvinyl chloride (PVC) tube filled with Permutit 'Filtrasorb 200' charcoal. Ammonium molybdate solution was metered at 1.5 L h^{-1}

into the base of the column by a peristaltic pump, and the treated solution then filtered through a coarse 50 mm diameter by 2 mm thick polyester pad.

4.3 Ammonium Paramolybdate Crystallisation

The treated ammonium molybdate solution was returned to the dissolver vessel for evaporation and crystallisation. Initially, 50 L of solution was evaporated to 27.5 L. Further evaporation was carried out with the volume of solution being held approximately constant by continually adding dilute ammonium molybdate solution at 8.9 L h^{-1}. Constant volume evaporation was continued for 5.5 h with the addition of 50 L of dilute solution. During the last hour of evaporation, crystallisation of ammonium paramolybdate was noted. After the addition of dilute solution was complete, the crystal slurry was allowed to cool overnight ensuring continuous stirring to prevent crystal cake formation.

After cooling, the crystal slurry was drained into a plastic Buchner funnel, the crystals being retained on a multifilament 3/1 twill nylon cloth (Ermco Corp., ny-319F, 95 × 47 threads per cm), and the filtrate was collected in a 15 L industrial Pyrex receiver. Filtration was expedited by evacuating the filtrate receiver. After filtering, the crystals were drained on the filter. A futher evaporation and crystallisation run was carried out, the filtrate from the first crystallisation being recycled back to the dissolver vessel.

4.4 Ammonium Paramolybdate Crystal Drying

The crystal cake was placed on stainless steel trays, 500 mm by 450 mm by 45 mm deep, and dried in an electrically heated oven at 110°C for 24 hours.

4.5 Calcination of Ammonium Paramolybdate Crystals

The APM crystals were converted to molybdenum trioxide in a batch tray calcination furnace described by Alfredson and Janov [1975]. Although fourteen trays, each of 270 mm diameter by 32 mm depth, could be accommodated on the framework support, only the bottom six trays were used. To avoid reduction of molybdenum trioxide during calcination, a stream of air was introduced into the base of the calciner.

The dried ammonium paramolybdate crystals (weighing approximately 8 kg) were distributed evenly over the six trays; at this stage the material was free flowing with little lumping. The crystals were calcined by heating to 550°C over five hours, then holding at 550°C for 19 hours.

5. RESULTS AND DISCUSSION

5.1 Process Summary

Three 10 kg lots of molybdenum trioxide were dissolved in ammonium hydroxide solution and treated with charcoal. To simulate a semi-continuous crystallisation, 50 L of dilute ammonium molybdate solution was evaporated to 27.5 L and used as a simulated recycled filtrate in the first evaporation. The first evaporation was carried out over 5.5 h during which time 50 L of dilute ammonium molybdate solution was added. After the first evaporation, crystallisation from 32 L of concentrated solution containing 20 kg of dissolved molybdenum trioxide gave 8.7 kg of APM crystals (7.4 kg of molybdenum trioxide) and 33 L of saturated solution (12.6 kg of molybdenum trioxide).

A second evaporation was carried out using the first run filtrate and the remaining 50 L of dilute purified ammonium molybdate solution. Total evaporation time for this run was 5.5 h and crystallisation of the 27.5 L of concentrated solution (containing 22.6 kg of molybdenum trioxide) gave 11.3 kg of APM crystals (9.6 kg of molybdenum trioxide) and 26 L of filtrate (13.0 kg of molybdenum trioxide). Thus, from the 30 kg of molybdenum trioxide dissolved, 17.0 kg of purified molybdenum trioxide was obtained. However, in a semi-continuous process, the filtrate from each crystallisation batch would be used in further evaporation runs.

5.2 Product Purity

5.2.1 Rhenium estimation by gamma spectrometry

Because of the high ^{99}Mo activity, direct determination of the radioactive rhenium isotopes was not practical. However, the chemical similarity of rhenium and technetium permits selective extraction of these two elements from the bulk of the irradiated molybdenum. Extraction was carried out using methylethylketone (MEK) from potassium molybdate solutions.

The purified molybdenum trioxide was irradiated in a hollow fuel element rig in the AAEC materials testing reactor HIFAR for seven days at a neutron flux of 7.5×10^{13} neutrons cm^{-2} s^{-1} (epithermal flux index $= 0.119$) giving a ^{99}Mo activity of 55 GBq g^{-1}. The irradiated molybdenum trioxide was dissolved in potassium hydroxide solution and daily extractions with MEK were carried out. Concentrations of ^{186}Re and ^{188}Re in the extracted ^{99m}Tc were estimated using gamma spectrometry. Because ^{188}Re is derived from the activation of both ^{187}Re and ^{186}W, the exact proportion of ^{188}Re produced by the activation of rhenium cannot be estimated. However, as ^{186}Re is only produced from ^{185}Re in natural rhenium (having a 37.4 per cent abundance), the measured ^{186}Re activity in the pertechnetate extracts can be used to compute the level of rhenium in the molybdenum trioxide target material. The results of the extractions performed on three runs of purified and irradiated molybdenum trioxide are given in table 1.

In all samples analysed, ^{186}Re was not detected, the level being less than 300 Bq in 3.7 TBq. This corresponds to a rhenium content of less than 1×10^{-6} μg g^{-1} in the molybdenum trioxide target material.

TABLE 1
EXTRACTION RUNS ON PURIFIED AND
IRRADIATED MOLYBDENUM TRIOXIDE

Extraction Number	Percentage ^{188}Re in ^{99m}Tc		
	Run 1	Run 2	Run 3
1	0.01700	0.01000	0.0023
2	0.00190	0.00280	0.0014
3	-	0.00065	0.0023
4	0.00017	0.00032	0.0015
5	0.00015	-	0.0001
6	n.d.	-	0.00019
7	-	-	0.00006

Calculations show that the original rhenium in commercial pure molybdenum trioxide has been reduced from 3 μg g^{-1} to less than 10^{-6} μg g^{-1} by the charcoal absorption process. However, the process was not capable of removing tungsten from the molybdenum, as is evidenced by the presence of ^{188}Re in the ^{99m}Tc extractions.

5.3 Molybdenum Trioxide Powder Characteristics

Irradiations of target materials in hollow fuel element rigs of HIFAR are limited to an active volume of 120 cm^3 per rig position. Consequently, a high packing density for the molybdenum trioxide target material is important. Particle size distribution and tap densities were determined, both for the powders obtained in the initial small-scale and for the main pilot plant runs (table 2).

TABLE 2
PARTICLE SIZE DISTRIBUTION AND TAP DENSITIES

Particle Range μM	Small Scale Studies		Pilot Plant Studies	
	Fraction	Tap Density g cm^{-3}	Fraction	Tap Density g cm^{-3}
+300	0.140	1.55	0.268	n.a
212 to 300	0.080	1.61	0.216	n.a.
180-212	0.074	1.54	0.087	n.a.
150-180	0.286	1.56	0.030	n.a.
125-150	0.127	1.58	0.189	n.a.
106-125	0.057	1.55	0.028	n.a.
-106	0.236	1.64	0.182	n.a.
Overall	1.000	1.85	1.000	1.90

Tap density of molybdenum trioxide feed powder is 2.0 g cm^{-3}.
Tap densities were determined by the method described in ASTM: B527-70

Although the particle size distributions obtained for the products from the small-scale and pilot-plant studies were somewhat different, the tap densities were practically identical.

2. CONCLUSIONS

In the molybdenum purification process described here, trace levels of rhenium have been effectively removed. By the direct adsorption on activated charcoal, a solution of ammonium molybdate containing 3 $\mu g\ g^{-1}$ of rhenium was purified to less than $1 \times 10^{-6}\ \mu g\ g^{-1}$. The process is however ineffective in the removal of tungsten impurity and contamination by [188]Re in ^{99m}Tc produced from irradiated molybdenum trioxide. However, provided that the tungsten level in the molybdenum trioxide is no greater than 400 $\mu g\ g^{-1}$, this limitation on the usefulness of the process is not significant.

A pilot plant suitable for the production of 10 kg per day was tested. Molybdenum trioxide from this plant was suitable for use as target material in the HIFAR reactor and ^{99m}Tc extracted from the irradiated molybdenum trioxide was used in the routine production of technetium radiopharmaceuticals.

3. ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of Mr P.J.F. Newton in making this report intelligible, Dr R.J. Ring for the loan of laboratory facilities, Mr F.G. Geraedts for target canning and HIFAR Operations Section for target irradiation.

4. REFERENCES

Alfredson, P.G., Janov. J. [1975] - Batch tray calcination of ammonium diuranate to uranium dioxide . AAEC/TM559.

Funaki, K., Segawa, T. [1950] - Equilibrium of the system MoO_3-NH_3-H_2O at 25°C and 40°C. *J. Electrochem. Soc.*, Japan, 18:152-4.

Lindstrom R.E., Scheiner, B.J. [1973] - Extraction of molybdenum and rhenium from concentrates by electrooxidation. US Dept Interior, Bureau of Mines, RI-7802.

Romanauski, W. [1963] - Thermal decomposition of ammonium paramolybdate. *Chem. Stosowania*.7(1) 105-123.

Scheiner, B.J., Lindstrom, R.E., Pool, D.L. [1976] - Extraction and recovery of molybdenum and rhenium from molybdenite concentrates by electrooxidation: process demonstration. US Dept Interior, Bureau of Mines, RI-8145.

Sorby, P.J., Lee, E.J., Barnes, R.K., Boyd, R.E. [1983] - A simple method for purifying molybdenum trioxide prior to neutron activation. *Int. J. Appl. Radiat. Isot.*, 34(10)1486-7.

Toensing, C.H. [1957] - Molybdenum Metal Powder. The Metal Molybdenum. American Society for Metals, Cleveland, USA.

DISSOLUTION   RHENIUM EXTRACT   CRYSTALLISATION

NH₄OH SOLUTION
VOLUME : 4 L
CONC. : ~15 M
FLOWRATE=300mL min⁻¹

H₂O
AFTER DISSOLUTION
VOLUME : ~ 27 L

MoO₃ SLURRY
Wt. MoO₃ : 10 kg
VOL. H₂O : 30 L

CHARCOAL COLUMN

APM SOLUTION
FLOWRATE WHEN
BOILING : 8.9 L h⁻¹
TOTAL VOLUME 50 L
Wt. APM : 11.5 kg

APM SOLUTION RECYCLE
VOLUME : ~ 30 L
Wt. APM : ~15 kg
CONC.- SATURATED

APM SOLUTION
VOLUME : 50 L
Wt APM : ~11.5 kg

APM SOLUTION
FLOWRATE : 1.5 L h⁻¹

PUMP

PUMP

FILTRATE

CRYSTAL CAKE

APM BULK SOLUTION
DISSOLUTION BATCHES : 3
MoO₃ DISSOLVED : 30 kg
Wt-APM : ~35 kg
VOLUME : 150 L

APM BULK SOLUTION
DISSOLUTION BATCHES : 3
MoO₃ DISSOLVED : 30 kg
Wt APM : ~35 kg
VOLUME : 150 L

TRAY DRYER

CALCINER

PURIFIED MoO₃
BATCH Wt ~10 kg

FILTERING

CALCINATION

Figure 1   Flowsheet of the process