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LA-UR--84-3566

DE85 003747

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AUTHOR(S): K. Wolfsberg, G. A. Cowan, E. A. Bryant, K. S. Daniels,
S. W. Downey, W. C. Haxton,* V. G. Niesen, N. S. Nogar,
C. M. Miller, and D. J. Rokop

SUBMITTED TO: Proceedings of Conference on Solar Neutrinos and Neutrino Astronomy
Lead, SD, August 23-25, 1984

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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THE MOLYBDENUM SOLAR NEUTRINO EXPERIMENT

K. Wolfsberg, G. A. Cowan, E. A. Bryant, K. S. Daniels,
S. W. Downey, W. C. Haxton,^{*} V. G. Niesen, N. S. Nogar,
C. M. Miller, and D. J. Rokop

Los Alamos National Laboratory
Los Alamos, New Mexico 87544

The goal of the molybdenum solar neutrino experiment¹ is to deduce the ${}^8\text{B}$ solar neutrino flux, averaged over the past several million years, from the concentration of ${}^{98}\text{Tc}$ in a deeply buried molybdenum deposit. The experiment is important to an understanding of stellar processes because it will shed light on the reason for the discrepancy between theory and observation of the chlorine solar neutrino experiment. Possible reasons for the discrepancy may lie in the properties of neutrinos (neutrino oscillations or massive neutrinos) or in deficiencies of the standard solar model. The chlorine experiment only measures the ${}^8\text{B}$ neutrino flux in current times and does not address possible temporal variations in the interior of the sun,² which are also not considered in the standard model. In the molybdenum experiment, we plan to measure ${}^{98}\text{Tc}$ (4.2 Myr), also produced by ${}^8\text{B}$ neutrinos, and possibly ${}^{97}\text{Tc}$ (2.6 Myr), produced by lower energy neutrinos.

We anticipate (see below) a capability of measuring 10^7 atoms of ${}^{98}\text{Tc}$ by a mass spectrometric method. We will require about 2600 tons of ore, from a deeply buried deposit, which contain 13 tons of molybdenite, to obtain this number of atoms.¹ A problem, then, is how to chemically isolate a trace quantity of technetium for mass spectrometry from such a large quantity of material. Fortunately, some of the work is done for us in the commercial processing of molybdenum by the AMAX Corporation in the production of molybdenum oxide. Flotation separation at the Henderson molybdenum mine in Colorado produces a concentrate that is 90 to 99% molybdenite. The concentrate is shipped to the AMAX roasting plant at Ft. Madison, Iowa, for conversion of the MoS_2 to MoO_3 . There are two roasters at the plant, each with a capacity of roasting as up to 50 tons of concentrate per day. So, our experiment requires only part of a day's production. A schematic of the plant is presented in Fig. 1. The MoS_2 concentrate has a residency time of

about 8 hr in the roaster at temperatures from 740 to 815°C. The exhaust gas, containing principally SO₂ and SO₃, is treated for dust removal, cooled, scrubbed, and converted to sulfuric acid. The scrub operation removes fluorides, chlorides, some of the sulfur gases, selenium, and rhenium from the gas stream before it enters the sulfuric acid plant. In the scrub stream, the last traces of molybdenum dust are filtered out, selenium is precipitated with H₂S (probably as the metal) for environmental reasons, and lime is added to precipitate sulfates and sulfites.

To infer the fate of technetium in the process, we are currently relying largely on our measurements of its chemical homolog rhenium, which has similar properties. The boiling points of Re₂O₇ and Tc₂O₇ are 360 and 311°C, respectively; the redox potentials for the ReO₄⁻/ReO₂ and TcO₄⁻/TcO₂ couples are 0.510 and 0.738 volts, respectively. The MoS₂ concentrate fed into the roaster typically contains 7 ppm rhenium, whereas the MoO₃ product contains <0.1 ppm rhenium, indicating that rhenium is volatilized in the roaster. Molybdenum dust recycled from the precipitators contains about 6 ppm rhenium, indicating that there is no sink for that element in the hot gas exhaust line prior to the acid scrub (fluoride tower). Rhenium is condensed in the acid scrub and is found at concentrations of about 6 ppm both before and after the molybdenum dust filter and the selenium filter. Only about 10% of the rhenium is in the selenium filter; Re₂S₇ is not precipitated quantitatively because H₂S cannot be added in excess on account of the large amount of H₂SO₃ in the scrub stream. A process had to be developed for removing technetium and rhenium from this acid scrub stream, preferably ahead of the H₂S addition. It was also desirable that this process cause minimum disruption in the commercial operation of the plant.

Ion exchange appeared to be a good choice. Commercial columns of the type used for deionizing or softening water are rated for flow rates of up to 30 l/min. Perrhenate and pertechnetate are strongly absorbed on anion-exchange resin, and our experiments showed that many commercial resins work well. However, technetium does not sorb well out of H₂SO₃ solution, probably because it is reduced to a neutral or cationic species; rhenium still absorbs strongly. We solved the problem by oxidizing the solution with NaOCl, the addition of which is acceptable to the AMAX plant management.

Exploratory experiments were conducted with columns of Duolite A-162 resin, 0.7 cm diameter by 95 cm long, with flow rates of 25 ml/min; the

linear flow rate is equivalent to one of 26 l/min for a commercial 23-cm diameter column. Rhenium breakthrough curves and distribution on the column were measured. Technetium should be absorbed more strongly than rhenium. Laboratory experiments with $H_2SO_4-H_2SO_3$ solutions oxidized with NaOCl, indicated that 98% of the rhenium could be retained for a half-day run. We did a similar experiment at the plant, using actual plant-stream solution and found that 87% of the rhenium was captured on the column. The poorer, but acceptable, performance of the column under real conditions is caused by competition of molybdate for sorption sites and elution by molybdate. We have now designed the modifications at the plant required to remove technetium and rhenium from the acid scrub stream. These are indicated by the dashed lines in Fig. 1 for the addition of NaOCl to a storage tank already in the line and a by-pass loop to be constructed for the ion-exchange columns. The plan for this loop, shown in Fig. 2, allows for the interception of all or part of the stream through anion-exchange columns.

Our plan for a large-scale experiment is to return to Los Alamos with these columns to continue purification of the technetium. The next step is to recover the technetium from the ~100 l of resin in a relatively small volume. Pertechnetate has a very high distribution coefficient on anion-exchange resin, and we investigated methods for stripping technetium that involved reduction to non-sorbing species. It appears that once TcO_4^- sorbs on the resin it is very difficult to reduce, and none of the reducing agents we investigated was successful. The use of nitric acid as a stripping agent is hazardous on a large scale. At the present time we propose to ash the resin at 420°C for ~1 day. Tests have shown only ~10% loss of technetium, and the residue is soluble. Additional purification steps prior to mass-spectrometric measurement are being developed. We will still have to develop methods to separate the technetium, with high recovery, from rhenium (~100 g), molybdenum (~1 kg) (An overall decontamination factor of 10^{21} is required!), and other impurities such as arsenic.

We are pursuing the investigation of both thermal-ionization and laser resonance-ionization methods for mass spectrometric measurement of the technetium at the levels required. The principal problems are to achieve high ionization efficiencies and acceptably low levels of interference from molybdenum isobars.

For thermal ionization, we start with filaments made from zone-refined rhenium metal and heat them at 2300°C for 30 to 50 min. Filaments that exhibit low molybdenum signals at 1900°C are hand picked from these. To date the resin-bead method has given the best results both for high ionization efficiency and for low isobaric interference from the sample itself. In the last chemical manipulation, technetium is loaded from NH_4OH onto a single, $\sim 200\text{-}\mu\text{m}$ bead of anion-exchange resin bead that is subsequently washed with HCl . The bead is then put onto the rhenium canoe filament for mass spectroscopy in a tandem-magnet mass spectrometer. At the present time we can typically achieve ionization efficiencies of 8×10^{-5} for samples containing 50 pg (3×10^{11} atoms) of ^{99}Tc , although efficiencies as high as 7×10^{-2} have been achieved. To do the experiment, we will have to be able to routinely achieve an efficiency of about 5×10^{-4} to 10^{-3} ; this will give a count rate of 10 to 20 counts per second above a similar background. We are investigating the bead loading and filament parameters involved in this process and also schemes such as negative thermal ionization, which will produce TcO_4^- but no similar molybdenum ion.

Resonance ionization is a laser-based ionization technique that allows discrimination against unwanted atoms in the sample.³ For technetium, a variety of two-color, three-photon resonance ionization schemes have been explored that greatly reduce the problems associated with molybdenum contamination.⁴ To date, however, insufficient efficiency has been demonstrated for the solar neutrino measurements, efforts in this phase of the work are also presently centered on increasing the ion yields.

Technetium-99 will be present at several orders of magnitude greater than ^{98}Tc as a spontaneous fission product of the ^{238}U in the molybdenite. Demonstration of secular equilibrium is a requirement of the experiment. The ^{99}Tc will be traced for overall yield and mass spectrometry with artificially produced ^{97}Tc . The known concentration of ^{99}Tc can then be used as a tracer for ^{98}Tc in the large experiments.

Acknowledgement

This work is supported under the auspices of the U.S. Department of Energy.

The management of the AMAX Molybdenum Division of the Climax Molybdenum Company have been most gracious in allowing us to pursue the possibility of

this experiment. In particular we are indebted to T. Kearns, R. H. Cale, and their staff at the Ft. Madison, Iowa plant for much help and advise.

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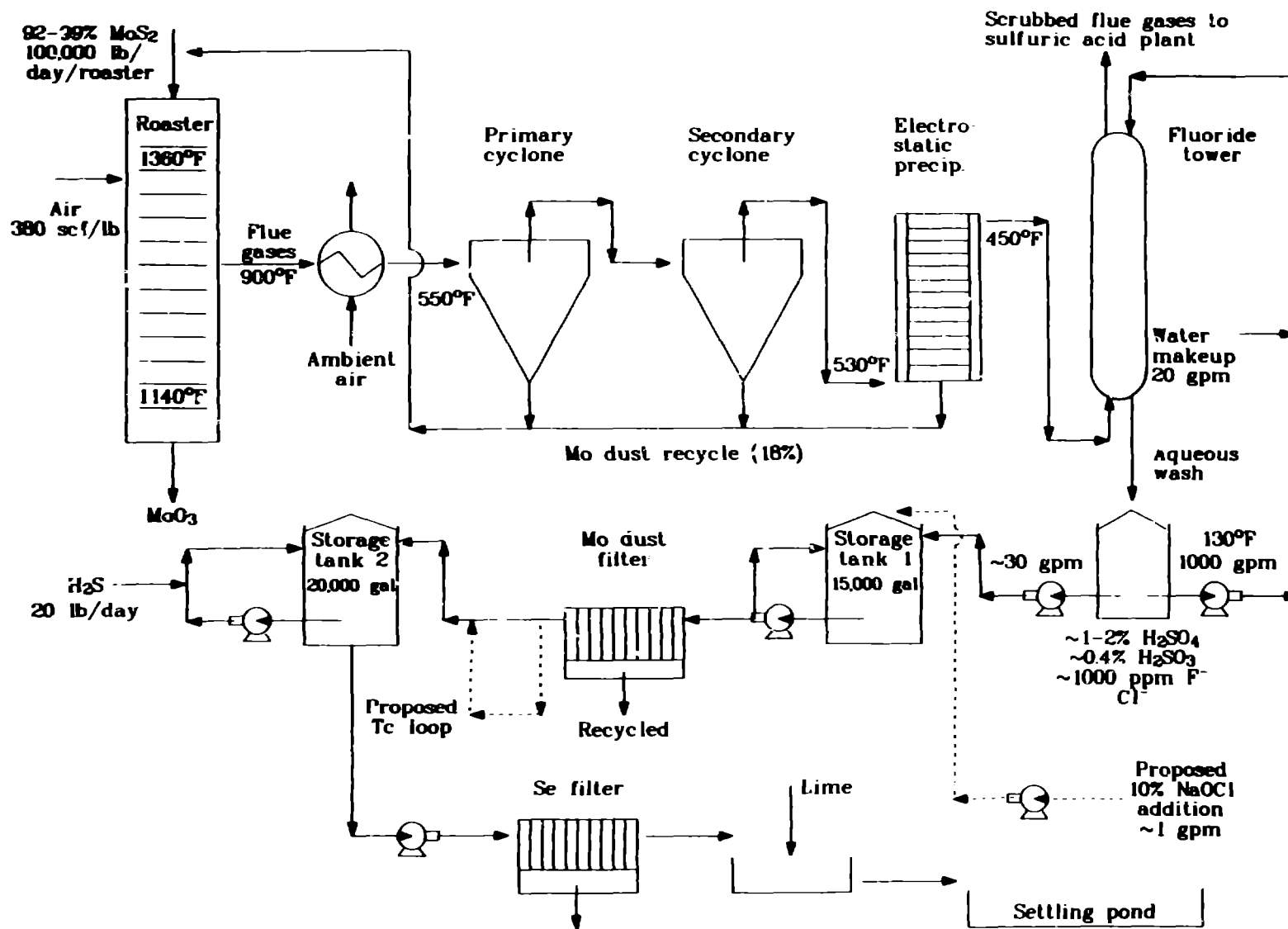
Figure Captions

Fig. 1. Schematic of AMAX molybdenum roasting plant. Dashed lines are modifications for the technetium experiment.

Fig. 2. Proposed technetium bypass loop.

Footnote

*Now at University of Washington, Seattle, consultant to Los Alamos National Laboratory.



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