

Chemical Technology Division

REMOVAL OF MERCURY AND TRITIUM FROM DOE WASTE OILS

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ABSTRACT

Experiments were performed at ORNL to determine whether tritium could be effectively stripped from samples of tritium-contaminated oil received from the Savannah River Site (SRS). This oil contained 0.72 TBq of tritium per 250 mL of oil, as well as 52-84 mg/kg mercury. Results indicate that the tritium could not be effectively stripped at either room temperature or elevated temperatures. However, an in-pump removal method was successfully demonstrated by using an SRS-type vacuum pump and hydrogen as a tritium surrogate.

Experiments were also performed to investigate the volatility of mercury species in the SRS oil. The results showed that vacuum extraction had little, if any, effect on removal of mercury species. In a subsequent study of the use of selective sorbents to solve this problem, the SAMMS sorbent outperformed all others. To determine the operating conditions for large-scale implementation, experiments were conducted with 16L of mercury-contaminated ORNL oil in a 55-gal system. Favorable results were obtained, and the demonstration was completed as an ORNL performance milestone.

1. INTRODUCTION

Tritium processing in the past at the Savannah River Site (SRS) has generated significant quantities of vacuum pump oil, which are contaminated with mercury (and tritium). Current operations generate 9,000 L of waste oil each year; the backlog for treatment is 78,000 L.¹ Mercury is present in the vacuum oil and despite cold traps and gold-amalgamation traps. This oil is designated as hazardous waste and is to be incinerated. The mercury and tritium are to be removed before this treatment.

The U.S. Department of Energy (DOE) Mound Plant (Miamisburg, Ohio) has the same type of waste (mercury and tritium contaminated vacuum pump oil), and will continue to generate this type of waste during decontamination and decommissioning activities. Los Alamos National Laboratory is generating a similar type of waste annually, and the total amount of organic liquids with mercury in inventory is 4100 kg.²

Tritium-contaminated SRS oil was received at ORNL on April 22, 1997. The shipping documentation indicated that approximately 7.2×10^{11} Bq of tritium was contained in approximately 250 mL of oil. Analytical results at ORNL indicated that the received oil contained approximately 4.4×10^9 Bq/g tritium and 84 mg/kg mercury. The shipment of contaminated oil was accomplished via the use of Viking containers. These containers, which were provided to the Savannah River Site (SRS) from Oak Ridge National Laboratory (ORNL), allowed shipment of oil both to ORNL and Ontario Hydro Technologies (Canada). The latter had been pursued without success for over a year prior to the initiation of this project.

A site visit to SRS was conducted in August 1997, and three vacuum pumps were identified in an area suitable for a demonstration. Later, during discussions with Efficient Separations and Processing Cross-cutting Program (ESP-CP) managers and SRS staff, it was concluded that the demonstration could not be performed at the SRS site, but would be done at ORNL instead.

2. EXPERIMENTAL METHODS

Studies conducted to investigate mercury and tritium volatility were performed by adding a small amount of oil to a 20-mL glass vial suspended in a partially water-filled vacuum flask (Fig. 1). The vial had a stirrer bar to allow for mixing with the magnetic stirrer hot plate.

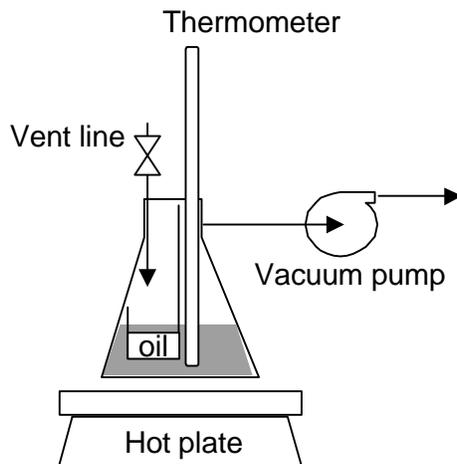


Fig. 1. Vacuum extraction setup in screening studies.

During the vacuum extraction, flask was evacuated to 24-in. of mercury below atmospheric pressure for 10 min at a pre-set temperature. After the vacuum extraction had been completed, the vent line was opened and the headspace was flushed for 10 minutes at a pressure of approximately 5-in of mercury below atmospheric. An aliquote of oil (0.1 mL) was added to a pre-weighed vial containing 9.9 mL of methylene chloride and mixed before filtration through a 0.45 μm syringe filter [Whatman (Clifton, NJ) Autovial with nylon membrane] and analysis.

Screening studies for mercury removal from the SRS and ORNL oil was conducted using 3 mL of oil in 10-mL glass vials and 50 mL of oil in 50-mL polypropylene centrifuge tubes, respectively. Intermittent agitation was used in experiments with the SRS oil and continuous agitation was used in sorbent screening experiments conducted with the ORNL oil.

Mercury removal experiments conducted with approximately 1 L of oil were carried out in a stainless steel vessel equipped with an overhead stirrer. In one of these experiments, intermittent samples of oil were taken and vacuum filtered through 0.45- μm -pore cellulose filters (Nalge Nunc International, Rochester, NY). In another experiments, the oil-sorbent mixture was pumped with a gear pump (Cole-Palmer, Vernon Hills, IL) through a commercial oil filter (Cim-Tech Filtration filter, Central Illinois Manufacturing Co., Bement, IL) before sample collection.

The largest scale mercury removal experiment was conducted in a large vessel equipped with an overhead stirrer and, after mixing, the oil-sorbent mixture was pumped with a gear pump through commercial oil filters (Hilco filter, Hillard Corp., Elmira, NY) before sample collection. Experiments conducted to study the accumulation of hydrogen (a tritium surrogate) in operating vacuum pumps are described in conjunction with experimental results.

Analysis of tritium in the SRS was determined using U.S. Environmental Protection Agency (EPA) Method 906 and total mercury was determined using EPA Method 7470A for all samples. Dissolved hydrogen was determined using American Society for Testing and Materials Method D3612-90.

3. EXPERIMENTAL RESULTS

3.1 VACUUM EXTRACTION OF TRITIUM

To investigate volatility of tritium species from the SRS oil, 2 mL of oil was containerized and placed under vacuum (24 in. mercury) for 10 min at both room temperature and 70°C, after which the headspace was vented for 10 min. Following treatment at the two temperatures, the oil contained 4.2×10^9 and 3.8×10^9 Bq/g tritium, respectively. Thus, it was concluded that vacuum extraction did not have much (if any) effect on the volatility of tritiated species. It is likely that the tritium, originally absorbed by the vacuum pump oil, reacted with the oil to produce low-volatility tritiated organics during extended storage at SRS.

3.2 IN-PUMP PURGING OF TRITIUM

To study prevention of tritium accumulation, “in-pump” removal of hydrogen (a tritium surrogate) was tested at ORNL in a vacuum pump similar to those used at SRS. If implemented, this approach would require very minor modifications of operational vacuum pumps at SRS, but would result in preventing the creation of highly contaminated oils in the future.

In the first set of experiments, hydrogen-containing nitrogen (2% H₂) was applied to the suction side of the vacuum pump (Fig. 2) for a 24-h period. This procedure did not accumulate measurable hydrogen levels in the pump oil. In subsequent experiments, pure hydrogen was introduced in the suction side of the pump for about 2 days. Several experiments were conducted; the results are listed in Table 1. Two strategies of hydrogen-accumulation preventive

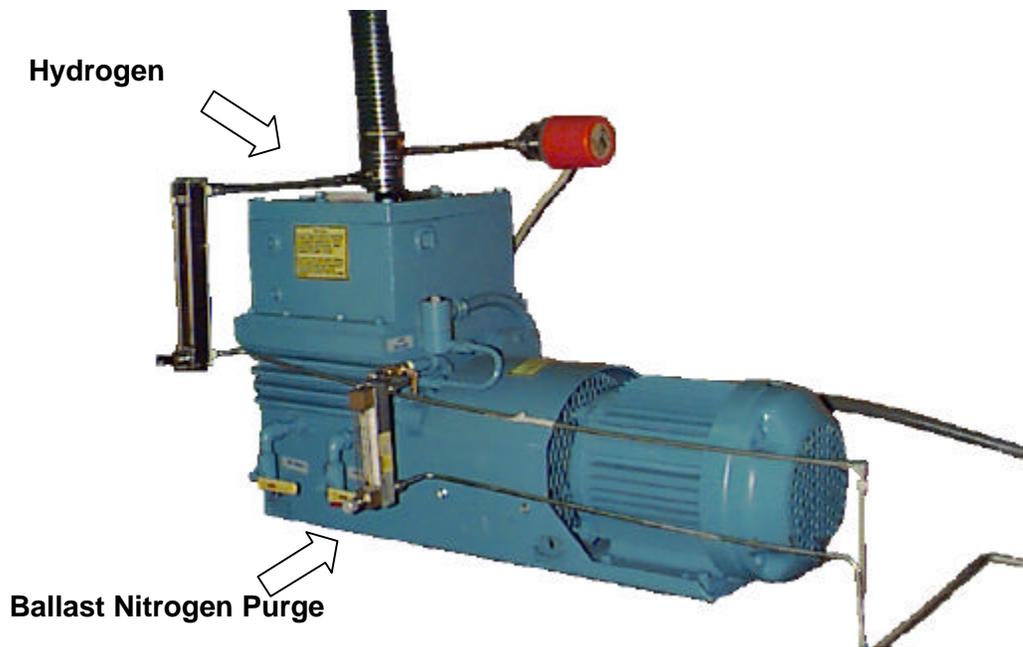


Fig. 2. Photograph of Kenny Model KTC-35 vacuum pump similar to pumps used at SRS tritium operation facilities.

Table 1. Design and results of experiments investigating “in-pump” methods for removing hydrogen (or tritium) during vacuum pump operation

Experiment	Suction-side condition	Accumulation prevention method	Results
1	Pure hydrogen for 2 days	None; study of accumulation during baseline operation	Hydrogen accumulations from nondetectable (ND ^a) level to 17 $\mu\text{mol/L}$
2	None	Nitrogen in ballast for 2 days; study of “in-pump” removal after the fact	Hydrogen stripping to levels of ND to 4 $\mu\text{mol/L}$
3	Pure hydrogen for 2 days	None; study of accumulation during baseline operation	Hydrogen accumulation reached 7 $\mu\text{mol/L}$
4	None	Nitrogen in sparging tube for 2 days; study of “in-pump” removal after the fact	Hydrogen stripping was noted to ND levels
5	Pure hydrogen for 2 days	Nitrogen in sparging tube; study of accumulation prevention	Dissolved hydrogen levels of ND to 4 $\mu\text{mol/L}$
6	Pure hydrogen for 2 days	Nitrogen in ballast; study of accumulation prevention	Dissolved hydrogen levels of 0.4 to 0.6 $\mu\text{mol/L}$

^aThe detection limit was 0.1 $\mu\text{mol/L}$.

methods were investigated. The first method is applicable to vacuum pumps that have a ballast configuration—a feature that is specifically designed for removal of gases from the oil during operation. The second method was to install a simple sparging device in the pump for continuous sparging of the oil during operation. This feature is applicable to those pumps that do not have a ballast.

As is noted from the results in Table 1, hydrogen accumulation in the oil was measurable when the pump was inducing a vacuum on a hydrogen stream. When the hydrogen was removed from the suction side of the pump, most of the dissolved hydrogen could be stripped from the oil by introducing nitrogen either in the standard ballast or in a sparging tube. When stripping was performed at the same time as hydrogen was introduced in the vacuum side, hydrogen was prevented from accumulating in the liquid to the levels seen in baseline operation. Based on the results obtained, it appears quite feasible to consider either of these methods for in-pump purging in order to obtain lower levels of tritium in the oil and to prolong the life expectancy of the oil and thus decrease the amount of waste generated. Only long-term studies during actual operation will determine the specific details of the improvement. From a practical standpoint, it was noted that the simple flow control (needle valve) used in the studies did not produce a constant gas flow. A more efficient flow controller is recommended for further work.

3.3 VACUUM EXTRACTION OF MERCURY

To investigate the volatility of mercury species from the SRS oil, 2 mL of oil containing 84.5 mg/kg mercury was containerized and placed under vacuum (24 in. mercury) for 10 min at room temperature and 70°C, after which the headspace was vented for 10 min. Following treatment at the two temperatures, the oil contained 83.9 and 84.6 mg/kg mercury, respectively. It was concluded that vacuum extraction did not have much (if any) effect on the removal of mercury species from the oil.

3.4 MERCURY ION-EXCHANGE SCREENING TESTS

The possibility of using selective sorbents for mercury removal was investigated using several materials [elemental sulfur; Mersorb LH (a sulfur-impregnated activated carbon) by Nucon International; Ionac SR-3 by Sybron Chemicals; Ionac SR-4; and Self-Assembled Mercaptan on Mesoporous Silica (SAMMS), produced by PNNL]. For each test, 0.2 g of sorbent was added to

3 mL of SRS oil and allowed to react for 48 h with intermittent shaking. The results may be seen in Fig. 3. As is noted, the SAMMS sorbent out-performed the others. The SAMMS material has been described in detail in Pacific Northwest National Laboratory Report PNNL-11691.³ Even the “blank” sample showed some removal of mercury. This is probably due to removal of particulate-bound mercury in the filtration procedure (see Section 2).

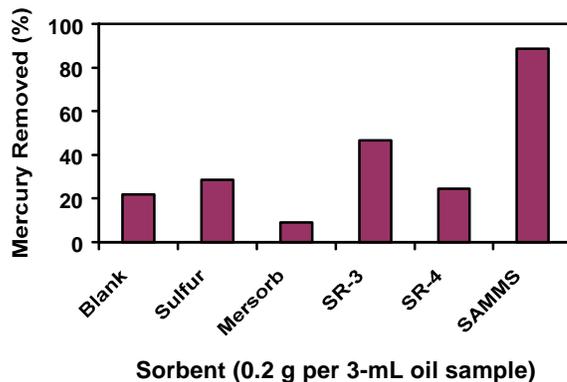


Fig. 3. Results from sorbent screening test performed with SRS oil.

Additional mercury sorption studies were performed with various amounts of SAMMS sorbent in 3-mL samples of SRS oil. The results are displayed in Fig. 4. As is noted, approximately 90% of the mercury was removed using the sorbent at dose rates of 0.2 to 0.3 g per 3 mL of oil.

To determine the operating conditions for the larger-scale implementation, treatability studies were performed on mercury-contaminated ORNL waste oil. In these studies, several sorbents [SAMMS, granular activated carbon (GAC) by Calgon, Mersorb LH, and SIR-400 by ResinTech] and sorbent doses were investigated over a 24-h contact time. The sorbents were sized (<10 μm) to reduce mass transfer effects and the SIR-400 resin was washed with an alcohol before use. The results showed that the SAMMS material was superior to other sorbents and that a dose rate of 0.1 g of SAMMS per 50 mL of ORNL oil was sufficient to remove the mercury to below 0.25 mg/kg. The raw waste oil contained 1.6 mg/kg mercury, and the samples (unless noted) were filtered through a 0.45- μm -pore filter prior to analysis (Fig. 5).

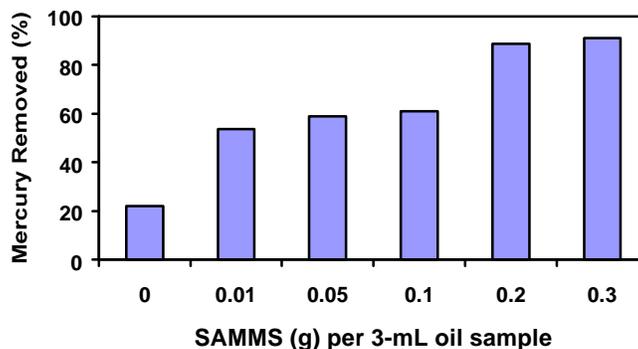


Fig. 4. Effect of sorbent loading using SAMMS sorbent and SRS oil.

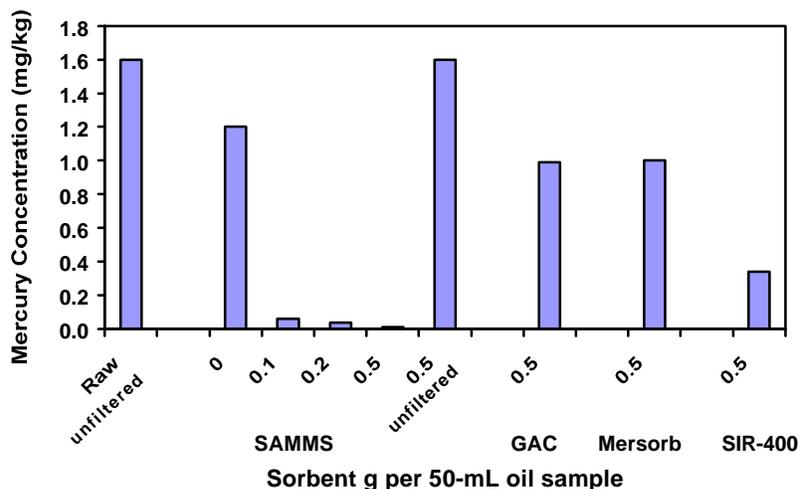


Fig. 5. Results from sorbent screening and sorbent loading experiments conducted with ORNL waste oil.

The necessary treatment time was studied by combining 2 g of SAMMS with 1 L of ORNL oil and taking periodic samples over a 24-h period, filtering each sample with a 0.45- μ m pore size filter. It was shown that a contact time of only 1 h was sufficient to reduce the mercury concentration to 0.25 mg/kg for this particular application (Fig. 6). It should, however, be noted that other oils might not respond to this short treatment period.

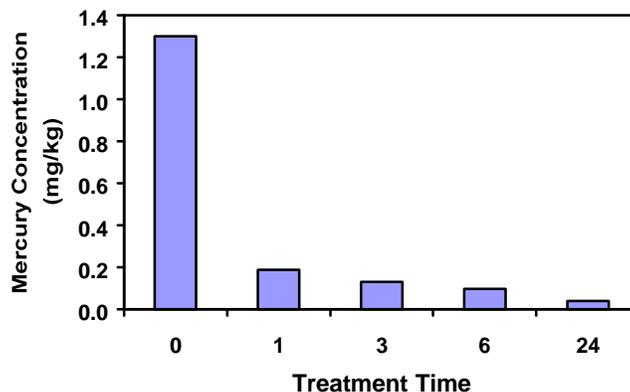


Fig. 6. Results from investigation of treatment time using SAMMS and ORNL waste oil.

Since it was clear from previous experiments that filtration was an important part of the process, the filtration requirements were studied in a separate experiment. In this experiment, 1 L of ORNL oil was mixed with 2 g of SAMMS for 24 h, after which the mixture was pumped through an oil filter cartridge containing a commercial oil filter (nominal 10- μm pore size). The oil was then filtered using a variety of filter pore sizes. The results indicated that a filter pore size of approximately 1 μm would be needed for effective separation of the SAMMS from the oil (Fig. 7). These results compare well with published information about the relative size of SAMMS particles.³

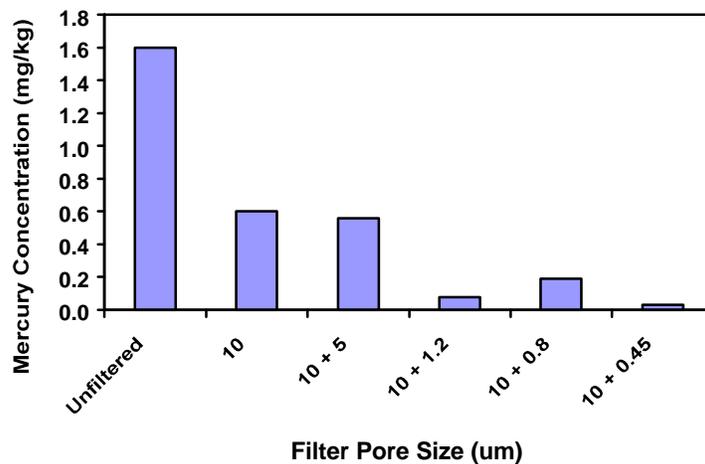


Fig. 7. Results from filter pore-size studies.

3.5 MERCURY ION-EXCHANGE FIELD TEST

The work with ORNL oil culminated in the treatment of 16 L of waste oil using the 55-gal demonstration-scale system shown in Figs. 8 and 9. In two batch-treatment operations, 8 L of oil was combined with 17 g of SAMMS material, mixed for 20–22 h, and then pumped through a filter cartridge with either a 0.5- or a 1.0- μm -pore filter. The filtration of each batch of oil was completed in approximately 15 min, and the treated oil contained 0.149 and 0.048 mg/kg mercury, respectively, indicating that a 1.0- μm filter was sufficient for the separation. It is interesting to note that the 1- μm filter actually performed better than the 0.5- μm filter. One possible explanation is that each of these filters is only nominal—and not absolute—in pore size. The treatment was successful, and the demonstration was completed as an ORNL performance milestone on schedule.

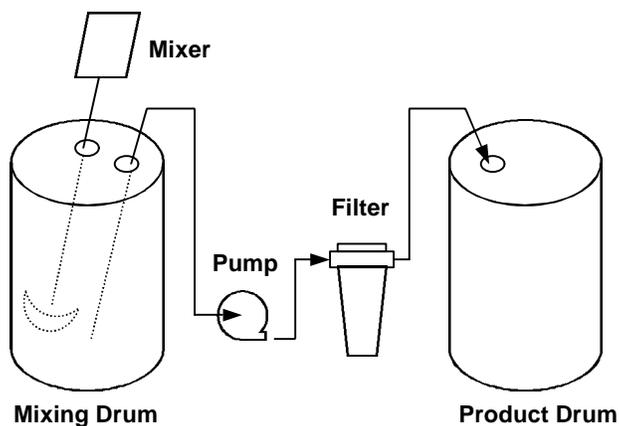


Fig. 8. Setup for large-scale (up to 55-gal) demonstration of the mercury-in-oil removal process (MORP).



Fig. 9. Photograph of setup for the mercury-in-oil removal process (MORP).

4. CONCLUSIONS

The following conclusions can be drawn from the results of the study described here:

1. Tritium could not be effectively stripped from the contaminated SRS oil at either room temperature or elevated temperatures under a moderately high vacuum. It is likely that tritium removal via stripping can only be accomplished with an on-line system at the SRS for “in-pump” removal. This method was demonstrated in a vacuum pump using hydrogen as a tritium surrogate.
2. Mercury was effectively removed from the oil via sorption using SAMMS material. The method was then demonstrated on a large scale using ORNL waste oil contaminated with mercury.⁴ This technology is now ready for further demonstration and implementation when the SAMMS sorbent becomes available in large quantities.

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