

DEVELOPMENT OF A ONE STEP DECONTAMINATION PROCESS FOR OILS CONTAINING BOTH PCBs AND RADIOACTIVE CONTAMINATION

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ABSTRACT

It is inevitable that lubricating, hydraulic and vacuum pump oil used in process industries become contaminated with process fluids and piping system corrosion products. When the process industry is associated with nuclear power production, the contaminants can also be radioactive. Good waste segregation practices are essential to keep certain hazardous contaminants such as PCB containing oils from mixing with radioactive waste oil. In the past these practices were not adequately followed and consequently Ontario Hydro has accumulated over the past 25 years of operations approximately 3m³ of lubricating oil that is both radioactive (>194pCi/kg beta/gamma activity, tritium>2uCi/kg) and contains >50ppm of PCB contamination.

Commercial waste disposal options exist for radioactive oil containing activity and <2ppm PCB. They also exist for insulating oils containing >50ppm PCB and no radioactivity. However for this mixed waste there are no available methods unless the waste oil is first treated to remove either the PCB or the radioactive contamination.

Ontario Hydro has decontaminated many thousands of liters of transformer insulating oil contaminated with PCBs over the past 10 years using metallic sodium to dechlorinate PCBs in insulating oil. Ontario Hydro Technologies has applied this technology as a potential one step process for treating radioactive lubricating oils. However this process, applied to lubricating oils is more complex. Whereas the radioactivity in lubricating oils is primarily associated with polar additives such as oxidation inhibitors, PCB contamination is associated with the non-polar species. A one step process based on metallic sodium requires therefore that there be sufficient sodium present to react with both the polar organics as well as the PCB contamination. The results to date have shown very effective destruction of PCBs and a conversion of the beta/gamma activity into a filterable phase. The resulting waste oil after filtration is non radioactive and has <2ppm of PCB contamination. It can easily be used as waste derived fuel in an industrial boiler. The secondary waste is a sludge containing sodium chloride, all of the activity but free of any PCB contamination. This waste stream can be immobilized and disposed of as low level waste.

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1.0 INTRODUCTION

It is inevitable that lubricating, hydraulic and vacuum pump oil used in process industries become contaminated with process fluids and piping system corrosion products. In nuclear power production, the contaminants can also be radioactive. Good waste segregation practices are needed to keep certain hazardous contaminants such as PCB containing oils from mixing with radioactive waste oil. In the past these practices were not adequately followed and consequently Ontario Hydro has accumulated over the past 25 years of operations approximately 3m³ of lubricating oil that is both radioactive (>194pCi/kg beta/gamma activity, tritium>2uCi/kg) and contains >50ppm of PCB contamination.

Commercial waste disposal options exist for radioactive oil containing activity and <2ppm PCB. They also exist for insulating oils containing >50ppm PCB and no radioactivity. However for this mixed waste there are no available methods unless the waste oil is first treated to remove either the PCB or the radioactive contamination.

Hydraulic and lubricating oils contain additive packages that are proprietary to the oil suppliers. These additives consist of antioxidants and corrosion inhibitors that preferentially degrade in the presence of oxygen and moisture thereby protecting the lubricating properties of the base oil and the component being lubricated. It has been shown in a number of studies/1,2/ that the radioactive contamination in lubricating oils is associated with the oil additives, which combine with the radioactive metal ions and form oil soluble organometallic complexes. It is for this reason that filtration was found to be ineffective in removing radioactive contamination from oil.

Ontario Hydro Technologies has patented/3/ a waste oil decontamination process that removes heavy metals (Pb/Cd) from oil as well as beta/gamma radioactive contamination. This process however is ineffective in destroying PCBs.

It uses oxidizing conditions at approximately 180°C in the presence of a catalyst to destroy the inhibitors. The method takes about 6 hours to complete and the additives produce a sludge containing the radioactive and heavy metal contamination that are easily separated from the oil mechanically. The kinetics of the reaction is believed to be dependent on the quantity and type of contaminants in the oil. At the end of the process the oil is free of contamination (Table 1 and 2) but the process also causes the oil to oxidize to some degree. In principle it is possible to remove all the oxidation products from the oil using activated alumina or Fuller's earth and restore the original

properties of the oil but the economics of doing this are not favorable. Furthermore there appears to be a great reluctance to use recycled/reconstituted oil instead of new oil in nuclear service.

TABLE 1
Radiochemical Characteristics of Oil Following Decontamination.

CONTAMINANT	Before (uCi/g)	After (uCi/g)	Decon Factor
Co-60 ($t_{1/2}$ 5.3y)	2.30E	1.1E-05	21
Sb-125 ($t_{1/2}$)	1.70E	8.00E-07	21
Cs-134 ($t_{1/2}$ 2y)	1.20E	3.00E-07	40
Cs-137 ($t_{1/2}$ 30y)	2.70E	4.30E-06	63
Ce-144 ($t_{1/2}$)	3.30E	4.00E-07	8
Eu-152 ($t_{1/2}$ 13y)	1.30E	3.00E-07	4
TOTAL	5.34E	1.71E-05	30
Tritium (uCi/kg)	148000	91	1626

Following decontamination the oil can be classified as conventional chemical waste, thereby allowing the oil to be either incinerated as waste derived fuel or recycled through a refining process.

TABLE 2
Chemical Characteristics of Oil Following Decontamination

CONTAMINANT	Before (uCi/g)	After (uCi/g)	Decon Factor
Total Chlorine (mg/kg)	3480	58	60
Lead (mg/kg)	21	<0.12	168
Cadmium (mg/kg)	0.12	<0.12	1
PCB (mg/kg)	8	7	1

The criterion for waste derived fuel however requires that the PCB contamination in the oil be less than 2ppm, which could not be achieved with this process. PCBs are very resistant to low temperature oxidation hence their former use as insulating fluids in transformers. To destroy them thermally requires very high temperatures in excess of 1200°C.

A PCB destruction process based on elemental sodium reaction with PCB in insulating oil has been extensively used /4/ on a commercial scale by Ontario Hydro to decontaminate transformer oils. Sodium metal is a very powerful reducing agent and is known to be an effective dechlorination agent. The sodium in turn forms sodium chloride, which can be mechanically separated from the oil. The reaction can be represented by equation 1.



It was assumed that in order to produce waste derived fuel from radioactive contaminated waste oils containing PCB contamination would require a two step process whereby radioactivity and heavy metals would be removed in the first step and PCB would be destroyed in the second step. A major disadvantage of this scheme is that a significant degree of oil oxidation takes place in the first step and this leads to a much greater amount of sodium required to destroy the PCBs in the second step.

A literature review of the mechanism of the two processes revealed that it is very likely that both the catalytic destruction of the antioxidants in lubricating oils and the dechlorination of hydrocarbons both proceed via radical intermediates. An obvious question was whether the sodium dechlorination reaction would also destroy the antioxidant in lubricating oil, which is associated with the radioactive and heavy metal contaminant. This would lead to a one step process for both radioactive and heavy metal decontamination as well as PCB destruction. Furthermore sodium consumption would be less than in a two step process.

2.0 EXPERIMENTAL

A one step process based on metallic sodium requires that there be sufficient sodium present to react with both the polar organics as well as the PCB contamination.

2.1 Apparatus

The laboratory scale reactor system consisted of a 1L three necked round bottomed flask equipped with a sealed mechanical impeller and a mantle heater. Nitrogen cover gas input and exit is through tubes in the central neck. The input tube is a dip tube, which extends to the bottom of the flask. A thermometer is also mounted in the central neck.

Sodium dispersion is added via a dropping funnel mounted on one of the side necks. The same funnel is used for quench water at the end of the reaction after first being flushed with oil.

2.2 Estimation of Sodium Requirements

Because oxidized hydrocarbon species in the waste oil compete for sodium during the PCB-sodium reaction, additional sodium is necessary to compensate for the sodium lost to these side reactions. This additional sodium must be added to that required to destroy the < 50 mg/kg PCB present in the oil.

The total quantity of sodium required for the reaction was estimated by assuming that the input oil contained about 0.5% (5000 mg/kg) reactive sludge, in addition to 50 mg/kg PCB, and that this sludge would consume sodium in the same mass ratio as an equivalent weight of Aroclor 1260 PCB. Under the above assumptions, the estimated sodium dispersion requirement is about 1% by weight of waste oil.

2.3 Procedure

A 500mL quantity of radioactive waste oil is added to the 1L flask, and the stirrer and 60mL/min nitrogen flow are started. The oil is heated to 100°C to drive off any water from the oil.

The sodium dispersion is added slowly to the oil and the temperature is raised to 130°C-150°C for 4.5 hours. At the end of the reaction period, the heater is turned off and the oil is allowed to cool overnight to ambient temperature.

About 10mL of quench water is slowly added through the dropping funnel to quench any unreacted sodium. The flask contents are subsequently transferred to a 1L separating funnel and the water and sludge phases are drawn off. The oil layer is filtered through a 0.45-micron filter and transferred to a 1L-polyethylene flask and submitted for chemical and radiochemical analysis.

3.0 RESULTS AND DISCUSSION

The results show that after reaction of approximately 4.5 hrs with sodium, (Table 3), a decontamination factor of 4 for the gamma emitting radionuclides is obtained. Ninety percent of the lead and 50% of the PCB content were removed following centrifugation and filtration (0.45mm) of the oil. There was no noticeable exotherm produced when water was added to the mixture for quenching any unreacted sodium. This was a clear indication that all the sodium had been consumed during the initial reaction.

The lack of excess sodium in the mixture after the reaction indicates that the reaction did not go to completion. Therefore, the filtered oil was subjected to a second exposure to a fresh charge of sodium. The contaminant concentrations in the oil after the subsequent filtration step through 0.45mm filter are shown in the fourth column of Table 3.

As noted in Table 3, the second exposure resulted in a further reduction of the gamma emitting radionuclides by a factor of 10 and reduced the PCB content to below the 2 mg/kg detection limit. It is interesting to note that the PCB concentration was reduced by a factor of only 2 after the first exposure showing that the dechlorination reaction is slower than the reaction of sodium with the polar additives in the oil which carry the radioactivity and the heavy metals.

There was essentially negligible removal of tritium in the oil. Past experience indicates that tritium does not become incorporated into the insoluble species formed in these reactions.

TABLE 3
Chemical/Radiochemical Characteristics of Oil
Following Reaction with Sodium.

CONTAMINANT	Before (uCi/g)	After (uCi/g) Exposure 1	After (uCi/g) Exposure 2	Decon. Factor
Co-60 ($t_{1/2}$ 5.3y)	2.97E-05	7.28E-06	6.95E-07	42
Sb-125 ($t_{1/2}$ 2.7y)	3.6E-06	7.00E-07	not detectable	
Cs-137 ($t_{1/2}$ 30y)	3.7E-06	2.70E-07	6.76E-08	55
Ce-144 ($t_{1/2}$ 285d)	1.20E-06	3.90E-07	not detectable	
Eu-152 ($t_{1/2}$ 13y)	1.50E-06	8.00E-07	not detectable	
Eu-154 ($t_{1/2}$ 16y)	9.00E-07	4.0E-07	1.99E-07	4.5
TOTAL Beta/Gamma	4.09E-05	1.03E-05	0.97E-06	42
Tritium (uCi/kg)	37	27	24	1.5
Lead (mg/kg)	12.9	1.32	0.4	32
Cadmium (mg/kg)	<0.2	<0.125	not measured	
PCB (mg/kg)	12	6	<2	

4.0 CONCLUSIONS

- (1) The sodium treatment method is effective for both PCB and radionuclide removal from active waste oils.
- (2) Sodium dispersion (40% w/w) consumption for effective treatment is estimated at between 1 and 2% by weight of waste oil, for oils containing oxidized oil components in the typical 0.5% by weight concentration range.
- (3) Based on the test results and previous experience with PCB destruction in multiple and single reactions, a reaction temperature in the range 130-150°C and a single reaction period of up to 5 hours appears to be sufficient for PCB dechlorination and activity reduction. This assumes that a 2% sodium charge is used.
- (4) As expected, tritium is not affected significantly by sodium treatment and would have to be removed from the oil matrix by other methods such as vacuum degassing at slightly elevated temperature.

- (5) Sodium is an expensive material. The cost effectiveness of this process can be greatly enhanced if slightly radioactive waste sodium is used to dechlorinate and decontaminate PCB contaminated waste oil. In such a case all the reactants are low cost waste materials.

REFERENCES.

1. Simiele, G.A., Fjeld, R.A and Robertson,C., "Radioactive Decontamination of Waste Oil by Filtration, Centrifugation and Chelation," Nuclear and Chemical Waste Management, 7, 257, 1987.
2. Brewer,K.M., and Fjeld, R.A., "Organic Phase Binding and Removal of Cobalt-60 in Turbine Lubricating Oil", Waste Management Vo.11, pp. 19-26, 1991.
3. Krasznai, J.P. and Janis, W.J., US Patent No: 5,516,969
4. Janis, W.J., "Dechlorination and Reclamation of PCB Contaminated Insulating Fluids". IEEE Transactions, PAS-102, 12, pp. 3928-3932 (Dec. 1983).