

# COBALT-60 BINDING AND DECONTAMINATION BEHAVIOR IN TURBINE LUBRICATING OIL

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## ABSTRACT

Experiments were performed to study the effect of oxidation on organic phase binding of cobalt-60 in turbine lubricating oil and its subsequent removal. A complete, commercial grade oil containing additives and the base oil without additives were spiked with cobalt-60 and heated in the presence of oxygen. Select samples were subjected to potential treatment processes. Binding behavior was inferred from measurements of the organic phase cobalt-60 concentration, operationally defined as that remaining following a water wash at 90° C. The effectiveness of each treatment process was based on measurements of cobalt-60 concentrations remaining in the oil following the process.

In the base oil, organic phase cobalt-60 concentrations increased monotonically with heating time. In the complete oil, the concentrations increased initially and subsequently declined. The differences in behavior are attributed to the presence in the oil of antioxidant and antiwear additives which bind with metals. Both oils were subjected to a variety of decontamination treatments including filtration, washing, and chelation. For the base oil, the treatments were generally less effective for the most highly oxidized samples. In contrast, for the complete oil there were dramatic improvements in treatment for the most highly oxidized samples. It is theorized that the improvement in decontamination for highly oxidized samples is due to the destruction or transformation of the additives responsible for cobalt binding and the formation of oil insoluble polymers that remove it from the oil phase. It is concluded that oxidation might be effectively employed as part of a scheme for decontaminating waste lubricating oils.

## INTRODUCTION

The disposal of waste oils contaminated with radioactivity is a problem faced by facilities throughout the nuclear industry, especially nuclear power plants. Bradley and Kirstein (1) and Siskind et al. (2) have conducted independent surveys of waste oil sources, characteristics, and management practices at nuclear power plants. Both surveys identify the principal radioactive constituents as cobalt-58, cobalt-60, cesium-134, and cesium-137; with radionuclide concentrations ranging from  $10^{-7}$  to  $10^{-3}$   $\mu\text{Ci/mL}$ . Although more than a dozen different types of oils are identified as being present in waste oils, the major component is reactor coolant pump lubricating oil at PWR's and turbine lubricating oil at BWR's. The principal management practices are storage, solidification and subsequent disposal as low-level radioactive waste, incineration, and decontamination. Storage is only a temporary measure, and solidification/burial is extremely expensive. Incineration is presently being employed at some locations and may be adopted at others as a result of proposed NRC rule making (3). However, due to economic or technical considerations at some sites and public opposition at others, it is doubtful that incineration will be used at all facilities. Decontamination, i.e. separation of the radioactive and non-radioactive components to allow independent disposal of each, has been used both as an adjunct to incineration to meet plant specific regulatory requirements and as a means of reducing radionuclide concentrations below detection limits to permit free release as industrial waste oil. Decontamination is likely to become

more important once below regulatory concern (BRC) regulations are promulgated or if a proposed rule (4) listing waste oil as hazardous is finalized.

Typical waste oils are a mixture consisting of particulate matter, water, and oil; and radioactivity may be associated in varying degrees with the particulate, aqueous, and organic phases of the mixture. In a previous study of contaminated turbine lubricating oil (5), conventional physical processes, specifically separation of the particulate component by filtration and separation of the aqueous component by centrifugation, were effective in removing over 95% of the total amount of radioactivity. The residual activity in the oil was dominated by cobalt-60. Results from this previous study are shown in Fig. 1. The initial concentration of almost  $10^{-3}$   $\mu\text{Ci/mL}$  was reduced to approximately  $10^{-6}$   $\mu\text{Ci/ml}$  following filtration, centrifugation, and washing with EDTA. Based on these results and on results of ultrafiltration research (6) in which measurable levels of cobalt-60 remained after essentially all particulate matter and water was removed, it was concluded that there is significant association of cobalt-60 with the organic phase. It was also hypothesized (5) that the cobalt-60 remaining following EDTA treatment might be in the +3 oxidation state, which forms a nonhydrated complex with EDTA and thus prefers the organic phase. It was suggested that removal might be enhanced by reduction of cobalt to the +2 state, which forms a hydrated complex with EDTA that associates with the aqueous phase.

Presented here are results of a follow-up study on the binding and decontamination behavior of cobalt-60 in tur-

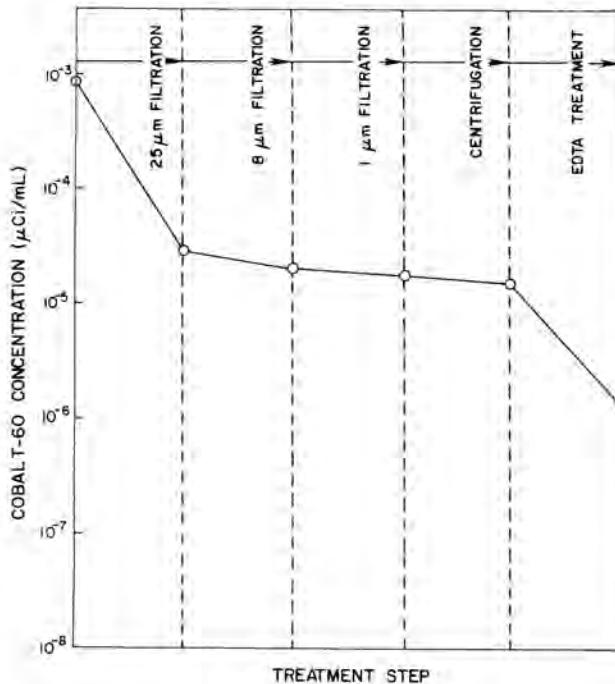


Fig. 1. Cobalt-60 Concentrations Following Treatment Processes (from 5).

bine lubricating oil. The specific objectives of the study were as follows:

#### 1. Organic phase binding

- To determine the effect of thermal oxidation on organic phase concentrations of cobalt-60.
- To determine the effect of additives on organic phase concentrations of cobalt-60.

#### 2. Organic phase removal

- To determine the effectiveness of chemical treatment with EDTA under various binding conditions.
- To determine if a reducing agent enhances the effectiveness of treatment with EDTA.

### EXPERIMENT

The experimental program basically consisted of three tasks. The first was laboratory generation and characterization of turbine lubricating oil contaminated under oxidizing conditions similar to those that might occur in practice. The second was measurement of organically bound cobalt-60 as a function of oxidation. The third was application of various treatment processes to the contaminated oil.

A commercial grade turbine oil, Mobil DTE-797, was used in this study. It contains a chain breaking antioxidant and zinc dithiophosphate, a mild antiwear agent. It is re-

ferred to here as the complete oil. Tests were also performed on the base oil, Mobil XMTL-401, without additives.

Contaminated oil samples were generated according to the following procedure. A two to three liter volume of oil was mixed with  $0.5 \mu\text{Ci}$  of cobalt-60 ( $2.5 \text{ mL}$  of a  $0.2 \mu\text{Ci/mL}$   $\text{CoCl}_2$  solution) in a three liter round bottom flask. The flask was equipped with a heating mantle, rheostat, thermometer, motor driven stirrer, and an air diffuser connected to a laboratory air source and flow meter. The mixture of oil and cobalt-60 were stirred for 20 minutes prior to the start of heating, and a  $100 \text{ mL}$  sample was withdrawn for sampling using a volumetric pipette. The oil was heated to  $200^\circ\text{C}$  using a uniform temperature ramp of  $3^\circ\text{C/minute}$ , and  $100 \text{ mL}$  samples were taken at regular intervals for six hours. This procedure was followed for both the complete oil and for the base oil.

Samples were allowed to sit for a minimum of fifteen hours in closed containers to allow oxidation reactions to reach equilibrium (7). Each sample was then washed. The washing procedure involved mixing with  $10 \text{ mL}$  of distilled water for 15 minutes at room temperature. The resulting emulsion was centrifuged for one hour at  $10,000 \text{ rpm}$  to separate the oil and water. A portion of the washed oil was removed and analyzed by gamma spectrometry for cobalt-60. This residual cobalt-60 remaining following the water wash was operationally defined as the organic phase concentration.

The results of the organic phase binding experiments suggested the existence of different binding conditions depending on the degree of heating. Based on these results, three batches of oil with heating times of 40, 220, and 360 minutes were prepared for treatment tests. Each batch of oil was washed with the following solutions: (1) water, (2)  $0.130 \text{ M}$  EDTA, (3) 40% hydrazine followed by  $0.130 \text{ M}$  EDTA ("sequential" treatment), and (4) 40% hydrazine combined with  $0.130 \text{ M}$  EDTA ("simultaneous" treatment). The water treatment was included to distinguish between simple partitioning of cobalt-60 between the aqueous and organic phases and active removal from the organic phase by chelation or reduction. Hydrazine was selected as a reducing agent because of its strong reducing capacity and its wide use in industry. The water, EDTA, and combined hydrazine-EDTA solutions were adjusted to a pH of 11 with 50% NaOH. At a pH of 11, the EDTA molecule is fully deprotonated and best able to complex metals (8). The pH of the 40% hydrazine solution was approximately equal to 11 without adjustment. To ensure adequate mixing, the ratio of treatment volume to solution volume was 10%. The EDTA concentration, pH, and volume ratio were based on the previous work of Simiele et al (5).

Each treatment, except for the one involving sequential hydrazine and EDTA, was performed on  $100 \text{ mL}$  volumes

of oil. The oil was placed in a 500 mL reaction vessel equipped with a motor driven stirrer, heating mantle, rheostat, and thermometer and was heated to 90°C before the treatment solution was added. The oil and treatment solution were mixed for 15 minutes while maintaining the temperature between 80°C and 90°C, and the resulting emulsion was centrifuged for one hour at 10,000 rpm. The treated oil was analyzed to determine the organic phase cobalt-60 concentration. The procedure for sequential hydrazine and EDTA treatment was identical except the initial oil volume was increased to 200 mL to allow for separate EDTA treatment. After the hydrazine treated oil was centrifuged and 50 mL removed for analysis, a 100 mL sample was transferred to the reaction vessel and treated with EDTA.

## RESULTS

Presented in Fig. 2 is the organic phase cobalt-60 concentration as a function of heating time for both the base oil and the complete oil. The two oils demonstrated very different cobalt-60 binding behaviors. Following mixing at room temperature, no organic phase binding was observed in the base oil. However, as heating of the oil progressed, the organic phase concentration in the oil increased from  $8.1 \text{ E-}8 \text{ mCi/mL}$  after 15 minutes to  $3.2 \text{ E-}6 \text{ mCi/mL}$  after 120 minutes. A rapid rise in the degree of binding began after about 120 minutes, resulting in organic phase cobalt-60 concentrations of  $1.1 \text{ E-}4 \text{ mCi/mL}$  after six hours of heating.

In contrast to the base oil, the complete oil exhibited the highest organic phase concentrations in the earliest stages of heating. The concentration was approximately  $8.0 \text{ E-}6 \text{ mCi/mL}$  following mixing at room temperature, but prior to heating. The concentration rose rapidly during the first 30 minutes of heating to reach a maximum of approximately  $9.0 \text{ E-}5 \text{ } \mu\text{Ci/mL}$ . It then decreased sharply and fluctuated around  $1.0 \text{ E-}5$  in the 2-5 hour time period reached a local maximum of  $3.5 \text{ E-}5 \text{ } \mu\text{Ci/mL}$  at five to six hours.

From the data presented in Fig. 2, it is clear that the high organic phase concentrations observed in the early stages of heating for the complete oil are due to the additives, since no binding was observed in the base oil during the same time period. The reason for the subsequent decrease in binding in the complete oil is not known. It may be that the antioxidants that are present initially differ chemically from those present during later stages of oxidation and have a different affinity for cobalt-60. It is known that antioxidant and antiwear additives, such as those in the complete oil, are consumed during the early stages of oxidation, but that the oil interacts with the peroxy radicals to form new antioxidants (9). If these regenerated antioxidants are chemically different from those initially present, their

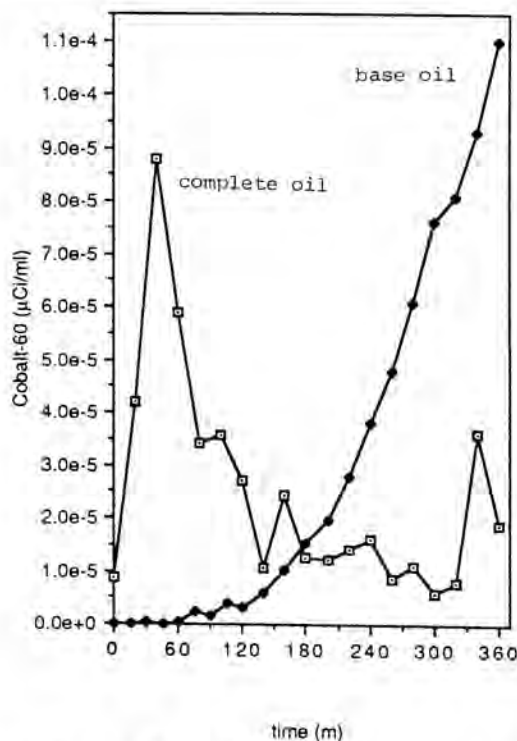


Fig. 2. Organic Phase Cobalt-60 Concentration in the Complete Oil and the Base Oil as a Function of Heating Time.

binding affinities for cobalt-60 could also be different, leading to the observed decrease in binding.

Results of treatment tests on the complete oil are presented in Fig. 3, where the organic phase concentration is given as a function of heating time. Hydrazine and sequential hydrazine-EDTA treatments were the least effective treatments, EDTA and simultaneous EDTA-hydrazine treatments were the most effective, and water was of intermediate effectiveness. There was a dramatic increase in the effectiveness of simultaneous hydrazine/EDTA and EDTA treatments for the long heating times. For the 360 minute heating time, EDTA reduced the organic phase cobalt-60 concentration to less than  $2 \text{ E-}7 \text{ } \mu\text{Ci/mL}$ . This behavior is the opposite of that observed in the base oil (Table I), where the treatments were less effective for oils subjected to longer heating times.

Probably the most important observation from Fig. 3 is the dramatic improvement in the effectiveness of EDTA treatment with increasing heating time. These results, which were not anticipated, prompted binding and treatment tests for an extended heating time of 17 hours. Organic phase concentrations from these tests are shown in Fig. 4. Results of the six hour test are repeated in this figure for comparison purposes. The binding behavior in the 0 to 6 hour time period was consistent for the two tests. After approximately seven hours of heating, the organic phase concentration

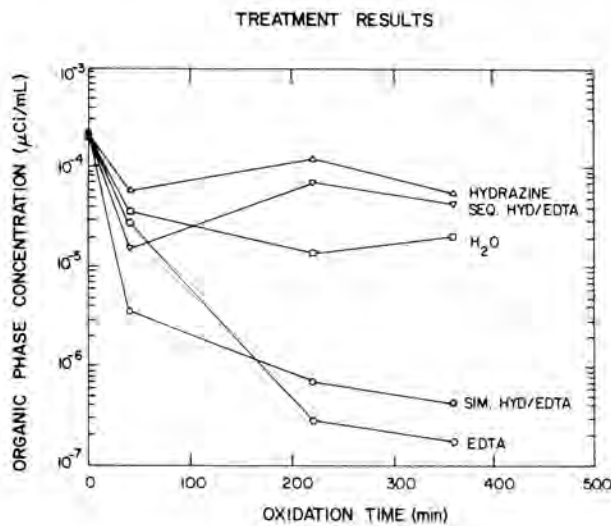


Fig. 3. Results of Treatment Tests for the Complete Oil.

TABLE I  
Treatment Results for the Base Oil

	Heating Time	
	180 min	300 min
Initial Concentration (µCi/mL)	1.4 E-4	1.8 E-4
Concentration after treatment		
Water Wash	4.4 E-6	5.0 E-5
EDTA	5.1 E-6	9.2 E-6
Hydrazine	1.3 E-4	1.4 E-4
Sequential EDTA/ Hydrazine	2.9 E-5	3.8 E-5
Simultaneous EDTA/Hydrazine	2.3 E-6	5.3 E-6

declined steadily. During this time, the oil darkened considerably in color, and particulate matter began to form. The change in color is due to the formation of oxidation products and the particulate matter is presumed to be composed of oxidation products that are insoluble in oil. The decrease in organic phase concentration during this time could be due

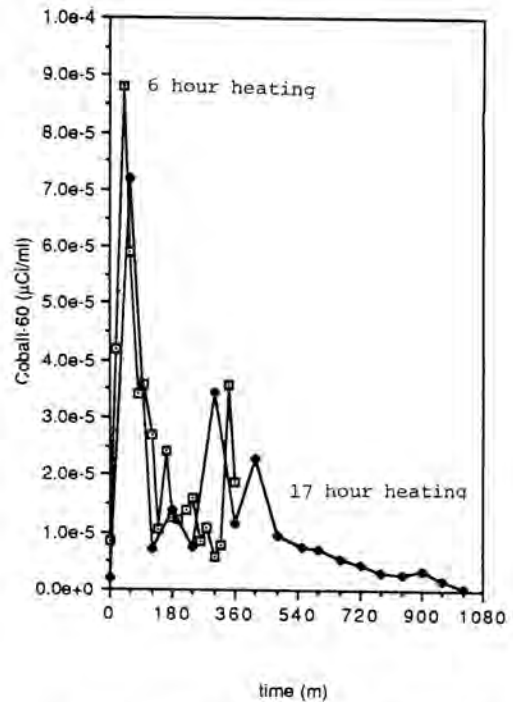


Fig. 4. Organic Phase Cobalt-60 Concentration in the Complete Oil for a 17 Hour Heating.

to the association of cobalt-60 with these particles, some of which were removed in the centrifugation step of the washing process. It could also be due to weakening or destruction of organo-metallic bonds, allowing a greater fraction to be removed in the water wash.

A single sequence of treatments consisting of filtration, water wash, and EDTA wash were applied to samples of the oil that were heated for 17 hours. Filtration was included because of the presence of particulate matter, a water wash was included because of the decrease in organic phase concentration observed in Fig.4, and the EDTA wash was included because of the results observed in Fig. 3. Results are presented in Table II. Filtration of the particulate matter produced during the long heating period reduced the cobalt-60 concentration from 2.4 E-4 µCi/mL to 3.7 E-7 µCi/mL. The water wash reduced the concentration to 1.2 E-7 µCi/mL, and treatment with EDTA reduced the concentration to below the detection limit of 5 E-8 µCi/mL. This improvement in decontamination can be attributed to two factors. As oxidation proceeds, the antioxidants and their derivatives that bind cobalt-60 are destroyed, decreasing the affinity of the oil for cobalt-60. Also, after extended oxidation (seven hours at 200°C), oil insoluble polymeric oxidation products begin to form. These products complex

**TABLE II**  
Treatment Results for Highly Oxidized Oil  
(17 hours at 200 °C)

	Cobalt-60 Concentration ( $\mu\text{Ci/ML}$ )
Initial	2.4 E-4
Filtration (1 $\mu\text{m}$ )	3.2 E-7
Water wash	1.2 E-7
EDTA	<5.0 E-8

or adsorb cobalt-60, thus transferring it from the oil phase to the particulate phase.

The results of treatment with the reducing agent hydrazine (Fig. 3) were ambiguous. In all cases, treatment with hydrazine by itself was less effective than the water wash. In the oil heated for 40 minutes, treatment with hydrazine appeared to improve the effectiveness of EDTA. However, for longer heating times, simultaneous EDTA and hydrazine treatments were less effective than EDTA by itself. Sequential treatment with hydrazine and EDTA was less effective than water for the 220 and 360 minute heating times, indicating that hydrazine may have been increasing, rather than decreasing, the affinity of the oil for cobalt-60.

The hydrazine results neither prove nor disprove Simiele's hypothesis regarding the aqueous solubility of EDTA-Co complexes. However, the use of a reducing agent in the treatment process does not appear to offer any advantages. The removal of organic phase cobalt-60 appears to be dominated by the affinity of the species in the oil for the metal. As these species change over the course of oxidation, so do the affinities for cobalt-60 and the effectiveness of decontamination.

### CONCLUSIONS

This research focused on organic phase binding and removal of cobalt-60 in turbine lubricating oil. The binding behavior of cobalt-60 in the complete oil differed significantly from that in the base oil without additives, suggesting that the additives play a major role in binding behavior. In the complete oil, organic phase concentrations increased dramatically in the early stages of oxidation and subsequently declined. In the base oil, organic phase concentrations showed a monotonic increase with increasing oxidation.

Initially, thermal oxidation was merely part of the experimental protocol for simulating the conditions under which contamination occurs. However, for an extended oxidation beyond that which would be expected to occur for oil in normal service, the following behavior was observed: (1) the organic phase concentration of cobalt-60 decreased, (2) filterable particulate matter containing cobalt-60 was

formed, and (3) the effectiveness of treatment with EDTA improved. Thus, a major finding of this study is that thermal oxidation may be effectively employed as part of a treatment scheme. However, turbine lubricating oil is only one component of a typical BWR waste oil, which is likely to be a mixture containing water, particulate matter, and other types of oil. The effect of these other constituents on oxidation processes and the behavior observed here in a pure lubricating oil is not known.

### ACKNOWLEDGEMENTS

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