REDUCTION OF ORGANICS IN RADWASTE PROCESSING:

WHY, WHAT, WHERE, HOW

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ABSTRACT

Natural and synthetic organic compounds enter power plant water systems and have been identified as causes of corrosion and water treatment system operating problems. In nuclear power stations, organics accumulate in the radwaste plant and can lead to increased radwaste treatment and disposal volumes. Ecosorb™-C, a recently developed precoat material containing powdered activated carbon, has been proven effective in removing organics from radwaste liquids during regular use on radwaste filters at two BWR stations. Results of field use and laboratory results on the physical and adsorptive properties of Ecosorb-C are presented and discussed.

WHY REMOVE ORGANICS

The removal of organic compounds from radwaste streams is essential to allow maximum reuse of processed radwaste liquids and to avoid the effects of organics in steam/water power cycles which tend to increase solid and liquid radwaste volumes. Some plants have already imposed limits on the allowable concentrations of organics in treated radwaste water prior to return to the condensate. As the awareness of the deleterious effects of these compounds increases, more plants can be expected to impose such limits. In the absence of any industry-wide specifications on organics, it has been recommended that the TOC (Total Organic Carbon) concentration of the final feedwater, steam, condensate and makeup be maintained below 0.5 ppm[1].

Organics Complicate Radwaste Treatment

A direct burden on the radwaste plant due to organics occurs when imposed TOC concentration limits are exceeded on treated water. Such water must undergo additional treatment to reduce TOC levels prior to return to the condensate system. If subsequent treatment is ineffective in removing TOC or if the option of subsequent treatment does not exist due to water management problems, some means of disposal must be implemented.

Ion Exchange Problems

The performance of water treatment systems is also hindered by the presence of organic impurities. Ion exchange resins, particularly the strong base anionic type commonly used in polishing applications, can become fouled by high molecular weight organic compounds, reducing the effectiveness of deep bed demineralizers[1,2]. Organic impurities can limit run lengths on Powdex® process precoat filter/demineralizers. A major undesirable effect of poor water treatment system performance is an increased burden on the radwaste treatment plant due to increased volumes of spent chemical regenerants and/or resins and precoat materials, leading also to increased radwaste burial costs.

Organics Cause Corrosion

The inflow of organic impurities to the feedwater of power systems has been identified as the cause of other operating problems. Steam turbine corrosion has been traced to localized condensation of steam containing volatile organic acids, which are thermal decomposition products of organic impurities entering the boiler[1,3,4]. In addition, organics are suspected contributors to corrosion at other points in the power cycle, including steam and condensate return lines and condenser tubes. Organics can also act as carriers of silica and metals which can eventually plate-out on turbine blades and foul heat transfer surfaces.

HOW ORGANICS ENTER THE SYSTEM

Organics can enter the condensate system with the make-up water, because they are only partially removed by make-up treatment processes, and with condenser cooling water in-leakage. These organics are primarily naturally occurring humic substances which can be soluble, insoluble or colloidal, and contain a wide variety of functional groups and complexed silica, iron, copper, manganese, sodium, potassium, calcium, and magnesium[1,5]. Such substances, generally referred to as humic and fulvic acids, are present in surface waters in a variety of molecular forms ranging in molecular weight from less than 1000 to between 1000 and 1,000,000[5]. In addition to these naturally occurring substances, surface waters can contain trace quantities of industrial solvents, pesticides, and detergents. Cooling water additives can also enter with condenser leaks and leakage of lubricating oils, such as turbine oils, into the water system can also occur.

However, at nuclear power stations, of equal or greater importance are the organics that can be carried in the treated radwaste water returned to the cycle. Radwaste sources include demineralizer backwash streams, equipment drains and floor drains. Besides naturally occurring organic matter, a variety of synthetic organic compounds find their way into the radwaste plant. These include industrial solvents, such as trichloroethylene, carbon tetrachloride and chloroform, detergents, and oils. TOC concentrations of 1 to 5 ppm or greater are not unusual in radwaste storage tanks. If these compounds are not effectively removed in radwaste treatment, they contribute significantly to the TOC levels of the condensate system to which the water is returned.

METHOD OF REMOVAL

Activated carbon treatment is an obvious choice for removal of organics from radwaste liquids. The effectiveness of activated carbon is expected based on the long list of published adsorption isotherms for natural and synthetic organic compounds. One reference gives adsorption isotherms for over 140 toxic organic compounds along with a summary of adsorption capacities at an equilibrium concentration of 1 mg/L at neutral pH[6]. Another presents a compilation of references to more than 100 detailed isotherm studies on a wide variety of organic compounds, including naturally occurring chemicals, industrial solvents and other compounds which have been found in surface waters and waste streams in the United States[7]. While activated carbon is effective in removing a broad range of organic compounds from aqueous solutions, the adsorption capacity of carbon for specific solutes is highly variable. Hexachlorobenzene, for example, has an equilibrium adsorption capacity (at 1 mg/L solution concentration) of 664 mg/g carbon compared to 1 mg/g carbon for benzene.

Several solute properties have been identified which influence adsorptive capacity. In general, the adscrptive capacity increases with increasing molecular weight within a class of organic compounds, decreases with increasing solute polarity and solubility, and decreases with increased branching[8]. There is, however, no generally accurate predictive correlation for activated carbon isotherms although methods useful in estimating relative equilibrium capacities of one compound to another are available[9]. In most cases, and especially where multiple solutes are present, field trials are required for performance evaluation.

While activated carbon can be applied in deep beds or as precoats, precoats are preferred in radwaste plants, which generally include precoat filters. A material has recently been produced that includes PAC (Powdered Activated Carbon) and which retains the adsorptive capacity of PAC and has a number of other advantageous properties for precoat filter applications. This patented precoat material, Ecosorb™-C, contains a flocculated mixture of PAC and inert fibers with minor amounts of ion exchange resins. The components of the precoat formulation are specially blended to produce aggregated PAC-containing floccules. This virtually eliminates the presence of individual fine particles, as evidenced by the clear supernatant of the settled precoat slurry. Ecosorb-C has a moisture content (about 70%) which avoids handling problems normally associated with PAC.

LABORATORY RESULTS

Physical Properties

Precoat tests were conducted on a precoat pilot plant system depicted in Fig. 1. The precoat was applied to the cylindrical septum surface by a recirculating flow from the precoat slurry tank, through the septum, and back to the precoat tank. The flow rate per unit septum area was 4.9 m/hr. (2.0 gpm/ft^2). The open area of the septum surface was 14%, the particle retention rating of the septum pores was 30 microns, and the septum outside diameter and length were 5.08 cm and 152.4 cm, respectively.

The duration of the precoat cycle was approximately 20 minutes and the Ecosorb-C precoat, applied at a dosage of 977 dry g/m^2(0.2 lb/ft^2), was uniformly distributed over the septum surface. To determine the degree to which Ecosorb-C was retained on the septum surface, two 4 liter samples from the precoat return

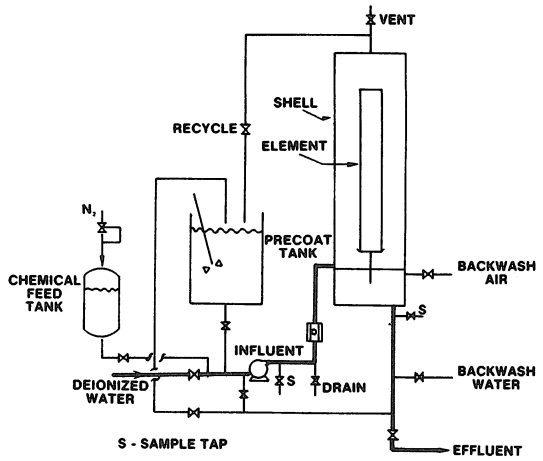

Fig. 1. Precoat pilot plant system.

were drawn through 0.45 micron Millipore filters, one during the first 10 minutes of the precoat cycle and the second during the final 10 minutes. The first filter had only a slight carbon stain and the second filter showed no staining, indicating virtually 100% retention of the precoat on the element surface. After precoating was complete, the flow rate was surged to 9.8 m/hr, simulating the start of a service run at twice the precoating area flow rate. Millipore filter sampling of the effluent during the flow surge revealed no bleedthrough of Ecosorb-C.

The hydraulic permeability of a precoat material is an important property in radwaste filter applications. Radwaste liquids contain suspended particles which must be removed along with dissolved organics and salts, and radwaste filters are normally run at a constant flow rate to a pressure endpoint. A precoat material with a high hydraulic permeability minimizes the initial pressure differential across the filter, maximizing the volume of liquid which can be treated per precoat.

Test results have shown that the hydraulic permeability of Ecosorb-C is much greater than that of PAC. These tests were performed at 20°C on a pressurized precoat filtration apparatus shown schematically in Fig. 2. Hydraulic permeability is expressed in terms of the Darcy unit, defined as follows: A material having a permeability of one Darcy unit passes one milliliter per second per square centimeter of liquid having a viscosity of one centipoise through a cake of one centimeter thickness at a pressure differential of one atmosphere. Individual tests were

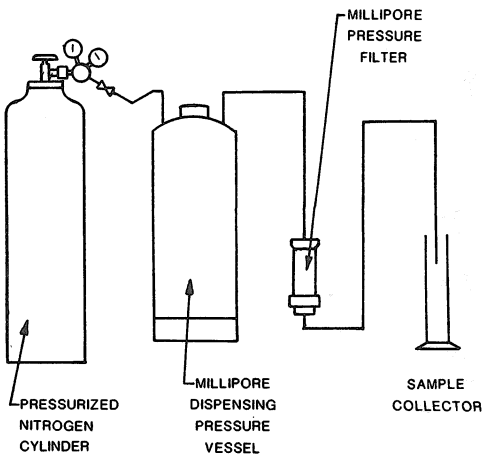

Fig. 2. Pressurized precoat filtration apparatus.

performed on PAC and Ecosorb-C at differential pressures of 0.176 kg/cm^2 and 1.055 kg/cm^2, and the results are given in Table I. As shown, the hydraulic permeability of Ecosorb-C is 10.0 and 7.7 times that of PAC alone at differential pressures of 0.176 kg/cm^2 and 1.055 kg/cm^2, respectively.

Table I. Hydraulic permeability of PAC and Ecosorb™ -C.

	Hydraulic Permeability (darcy)	
	0.176 kg/cm^2	1.055 kg/cm^2
PAC	0.14	0.11
Ecosorb™ – C	1.40	0.85

As mentioned previously, a precoat used in radwaste treatment must be efficient in removing suspended solids, or crud. To determine the crud holding capacity and removal efficiency of Ecosorb-C, a test was performed on a small precoat filter pilot plant. The test conditions included precoating a 0.036 m^2 cylindrical septum with Ecosorb-C at a dosage of 977 dry g/m^2. The influent area flow rate was 9.8 m/hr, into which iron oxide (Fe_2O_3), simulating crud, was injected to achieve an influent concentration of 0.5 mg/L. Over the course of the run, the differential pressure across the filter was measured and recorded, and effluent samples were drawn periodically through 0.45 micron Millipore filters to detect any iron or precoat leakage into the effluent.

A plot of differential pressure versus crud loading is shown in Fig. 3. The data indicate a crud holding capacity of about 0.28 g Fe_2O_3/dry g Ecosorb-C to a differential pressure end point of 1.0 kg/cm^2 (14.2 psi). The crud holding capacity of Ecosorb-C is several times greater than that of Solka-Floc and diatomaceous earth, and comparable to that of Ecodex®[10]. During the run, no leakage of iron or precoat material was detected on the effluent Millipore filters, indicating virtually 100% removal efficiency of iron oxide and that the integrity of the precoat was maintained.

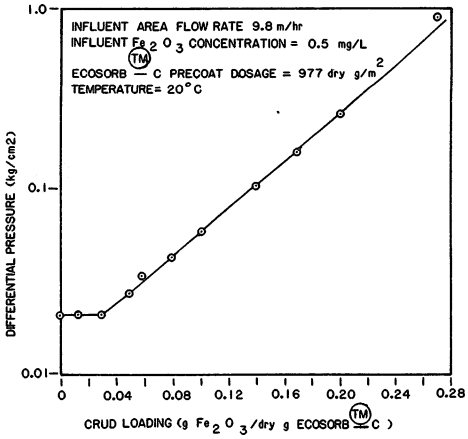

Fig. 3. Differential pressure response to crud loading on Ecosorb™-C.

Adsorptive Properties

The adsorption isotherm for o-chlorophenol on Aqua Nuchar® activated carbon at 25° C is shown in Fig. 4. Aqua Nuchar was also incorporated in an Ecosorb-C formulation (2/1 carbon/fiber dry weight ratio) which was used in a flow test. In the flow test, Ecosorb-C was applied to the septum at a dosage of 977 g/m^2, the influent area flow rate was 4.9 m/hr and o-chlorophenol was added to maintain an influent concentration of 1.0 mg/L. The results of the flow test are shown in Fig. 5.

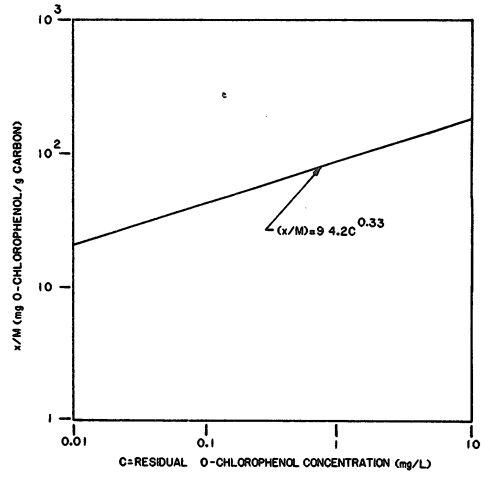

Fig. 4. Adsorption isotherm for o-chlorophenol on Aqua Nuchar carbon at 25° C.

A comparison of the o-chlorophenol adsorption isotherm and the flow test results reveal some important points about the performance of Ecosorb-C. One is that the adsorptive capacity of PAC is not diminished when used in the Ecosorb-C formulation. This can be seen from the results in Fig. 5, which show that as the effluent solute concentration approaches the influent concentration, the solute loading in the flow test approaches the isotherm value (Fig. 4) at 1 mg/L solution concentration.

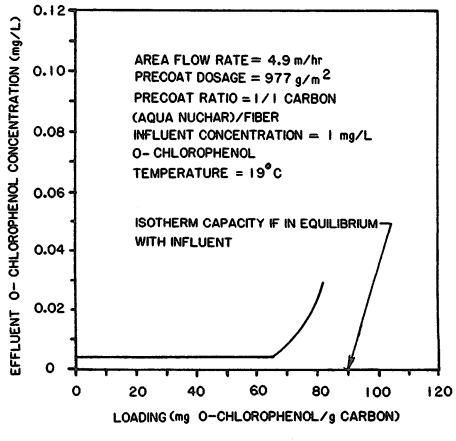

Fig. 5. O-Chlorophenol loading on Ecosorb™-C in a flow test.

Also, the PAC dosage required in an Ecosorb-C precoat to achieve a given effluent or final concentration is more closely represented by that of a multi-stage countercurrent contactor, where the

specific loading of solute on the carbon approaches the influent concentration equilibrium value, than that of a single batch system, where the specific loading is based on the effluent concentration equilibrium value. The equilibrium specific loading increases as the equilibrium solute concentration in solution increases for most solute-carbon systems, as is the case for o-chlorophenol-Aqua Nuchar (Fig. 4). The carbon dosage required can be estimated by use of the following equation:

$$M = \frac{C_i - C_f}{(x/M)} = \frac{C_i - C_f}{K\,C^{1/n}}$$

where,

C_i = initial or influent solute concentration (mg/L)
C_f = final or effluent solute concentration (mg/L)
x/M = specific loading of solute on carbon at equilibrium (mg solute/g carbon)
K = Freundlich coefficient
1/n = exponent
C = equilibrium solution concentration (mg/L)
C = C_f for equilibrium with the effluent
C = C_i for equilibrium with the influent
M = carbon dosage (g/L)

It is apparent from the above equation that the carbon dosage can be significantly less for a system where equilibrium with the influent is approached than where equilibrium with the effluent is attained. Using the results of Fig. 4 as an example, 3.8 times the carbon dosage would be required to reduce the solute concentration from 1 mg/L to 0.02 mg/L in a single batch than in a system where equilibrium with the influent is reached. The results in Fig. 5 show that for the Ecosorb-C precoat, 89% of the specific loading based on equilibrium with the influent was achieved at the 0.02 mg/L breakpoint.

The degree to which the adsorptive capacity of an Ecosorb-C precoat is utilized depends on the height of the mass transfer zone and the extent to which the available capacity within the mass transfer zone is utilized at the breakpoint. A representation of the mass transfer zone is provided in Fig. 6. A number of the experiments were performed on phenol and some phenolic compounds using the apparatus shown in Fig. 2 to determine mass transfer zone heights and the degree of utilization of the precoat adsorptive capacity. The tests were performed on an Ecosorb-C formulation incorporating Columbia LCK carbon in a 2/1 carbon/fiber ratio. The influent solute concentration was 10 mg/L, the area flow rate was 14.7 m/hr, the precoat depth was 19.0 mm and the temperature was 20° C. The

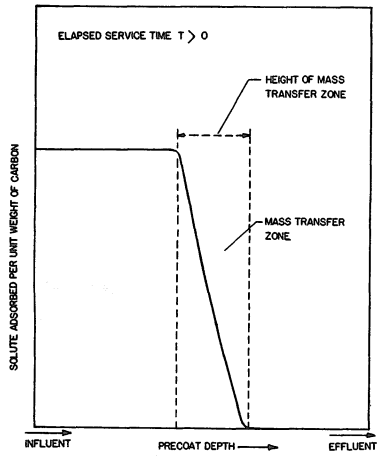

Fig. 6. *Mass transfer zone.*

results are summarized in Table II, where the following symbol definitions are used:

$(x/M)_b$ = the weight of solute adsorbed per unit weight of PAC at initial breakthrough (effluent concentration = 2% of influent concentration).
$(x/M)_e$ = the weight of solute adsorbed per unit weight of PAC at exhaustion (effluent concentration = 90% of influent concentration).
f = the remaining carbon capacity in the mass transfer zone at initial solute breakthrough expressed as a fraction of the capacity when in equilibrium with the influent.
Percent Efficiency = the solute adsorbed at initial solute breakthrough expressed as a percent of the solute adsorbed when in equilibrium with the influent.

Table II. Flow test results: Ecosorb™ - C adsorption efficiency for phenol and some phenolic compounds.

COMPOUND	(x/M)b (mg Solute/ dry g PAC)	(x/M)e (mg Solute/ dry g PAC)	Height of Mass Transfer Zone (mm)	f	Percent Efficiency
Phenol	37	47	7.4	0.57	77.8
2-Chlorophenol	75	101	8.9	0.55	74.2
O-Chlorophenol	77	101	8.4	0.54	76.1
2-4-Dichlorophenol	170	207	8.6	0.39	82.3
2-4-6-Trichlorophenol	180	253	9.1	0.60	71.3
2-Nitrochlorophenol	128	164	6.6	0.63	78.1

As shown, mass transfer zone heights for the compounds tested range from 6.6 mm to 9.1 mm, while the total precoat depth was 19 mm. In contrast, mass transfer zone heights for granular carbon beds typically range from 100 mm to 500 mm[11]. The percent efficiency values in Table II indicate the extent to which the adsorptive capacity, based on equilibrium with the influent, of the Ecosorb-C precoat is utilized and these values vary from 71.3% to 82.3% for the compounds tested. While these tests were performed at an area flow rate of 14.7 m/hr, most radwaste precoat filters operate in the range of 1.5 m/hr to 5.0 m/hr. At these more typical area flow rates, percent efficiency values in the range of 80% to 90% would be obtained for the compounds tested.

Effect of TOC on CF/D Run Length

Two tests were performed on a small precoat pilot plant to determine the effect of TOC in the condensate water on CF/D (condensate filter/demineralizer) run length to a pressure endpoint. Powdex resin precoats, containing a 3:1 dry weight mixture of hydrogen form cation resin and hydroxide form anion resin, were used and are typical of CF/D precoats applied in many BWR plants. In both tests, the precoat was applied at a dosage of 977 g/m^2, the area flow rate was 9.8 m/hr and iron oxide (Fe_2O_3) was injected to obtain an influent concentration of 0.5 mg/L as Fe_2O_3. To simulate condensate TOC, 1 mg/L humic acid was added to the influent in one test while none was added in the other.

The results of these tests, plotted in Fig. 7,

show a much greater rise in differential pressure across the precoat with increasing solids loading for the test where humic acid was added. It appears that organics, such as humic acid, cause the floc structure of the powdered resin precoat to break down, decreasing the precoat porosity and leading to decreased solids loading capacity to a differential pressure endpoint. Since the run lengths of many CF/D systems, especially in BWR stations, are terminated at differential pressure endpoints under normal operating conditions, the results indicating that the presence of TOC in the condensate can reduce CF/D run lengths are of practical significance. A direct consequence of this in nuclear plants is increased spent resin volumes which require treatment and subsequent burial.

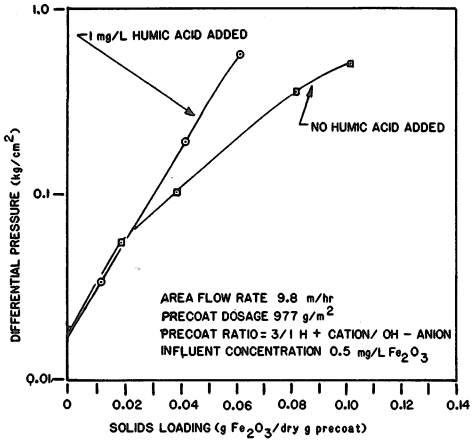

Fig. 7. Effect of humic acid on CF/D precoat crud loading capacity.

FIELD RESULTS

Ecosorb-C precoats have been applied on radwaste filters in a number of BWR stations, among which are Vermont Yankee and Northern States Power's Monticello station. These two stations were the first to try this precoat material and both now use it regularly on their waste collector filters. Regular field use has demonstrated that the waste sludges resulting from the Ecosorb-C can be handled in the same way as sludges of other filter aids and precoats currently used. The results of applying Ecosorb-C at both plants are discussed below.

Vermont Yankee

A flow diagram of Vermont Yankee's radwaste treatment system is provided in Fig. 8. As indicated, floor drain sources are treated through the floor drain filter, and equipment drains and regeneration/ rinse streams are treated through the waste collector filter. The floor drain filter and waste collector filter each have a precoatable surface area of 5.3 m^2. For simplicity, several cross-ties between the radwaste system and other plant water treatment systems are not shown since they are used infrequently.

Ecosorb-C is applied on the waste collector filter at a dosage of 977 dry g/m^2. The waste collector filter is operated at an area flow rate of 2.14 m/hr. Between 76,000 L/day and 102,000 L/day of radwaste liquids are treated by the waste collector filter. This includes about 11,000 L/day of floor drain waste initially treated on the floor drain filter, on which Ecodex precoats are applied, and subsequently pumped to the waste collector tanks.

All processed radwaste water is returned to the condensate storage tank (CST), where it is reused for make-up to the hotwell, backwashes, regenerations, rinses, etc. The make-up water rate from the river to the CST is normally less than 4000 L/month.

Water also flows constantly at about 76 L/min from the CST to the hotwell to satisfy the demands of the control rod drives. This flow provides another route for organics accumulated and not removed in the radwaste system to enter the feedwater. Removal of TOC in radwaste treatment should result in reduced feedwater TOC.

From May 28, 1982 through August 4, 1982, samples were taken from radwaste, the CST and the reactor, and TOC concentrations were measured. During this period, the waste collector tank TOC concentration varied from 0.42 ppm to 5.54 ppm, with an average value of 2.01 ppm. Ecosorb-C use began on June 17, 1982. Spot samples of the waste collector filter influent and effluent during different service runs with Ecosorb-C showed TOC removals of 97.2%, 91.0%, 56.1%, and 64.9% with influent TOC concentrations of 3.19 ppm, 5.54 ppm, 0.98 ppm and 1.88 ppm, respectively. The TOC concentrations of the condensate storage water and the reactor water were significantly reduced after the use of Ecosorb-C began, as shown in Fig. 9.

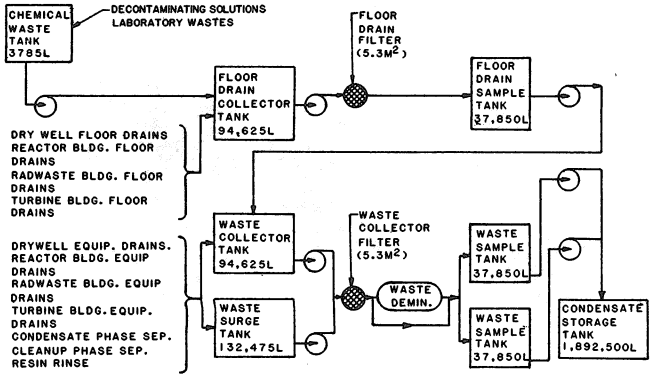

Fig. 8. Vermont Yankee radwaste treatment system.

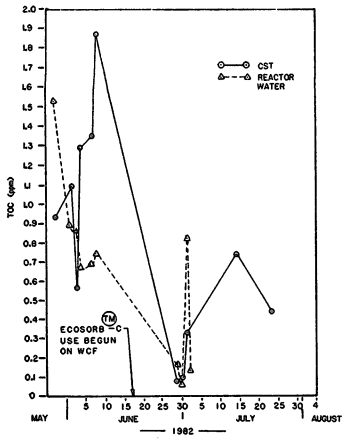

Fig. 9. Vermont Yankee condensate storage water and reactor water TOC.

The reactor water conductivity has also decreased from 0.2 μmho/cm to 0.16-0.18 μmho/cm since Ecosorb-C has been used. However, it is not possible at this time to confirm that the conductivity reduction is attributable to decreased concentrations of organics in the feedwater.

Monticello

Monticello's radwaste system is similar to Vermont Yankee's (Fig. 8). The waste collector filter, which has a precoatable surface area of 8.0 m^2, is normally used to treat all radwaste liquids (the floor drain filter is normally not used). The volumes of the waste collector tank and CST are 37,850 L and 870,550 L, respectively.

Approximately 37,850 L/day of radwaste liquids are treated on the waste collector filter, on which Ecosorb-C precoats are applied at a dosage of 977 g/m^2 and which is operated at an area flow rate of 1.57 m/hr. Regular use of Ecosorb-C began on March 1, 1982. Monticello recently obtained a TOC analyzer, but TOC measurement results were not available at the time of this writing. However, other results and observations indicate beneficial effects of Ecosorb-C use on plant operations.

In November, 1981, prior to regular Ecosorb-C use, a foaming problem occurred in the radwaste system due to detergents used to decontaminate the reactor cavity during a refueling outage. Ecosorb-C was applied to the waste collector filter and foaming was eliminated in the treated water. These detergents are still periodically used, but since Ecosorb-C precoats have been in regular use, foaming problems in treated radwaste water have not recurred.

An improvement occurred in CF/D run lengths to differential pressure endpoints during the period from May through August, 1982 while Ecosorb-C was in use. Run lengths averaged about 30 days during this period compared to 14-17 days previously. As a result, the number of spent CF/D precoats sent to radwaste during this period was approximately 37% lower than before Ecosorb-C was used. The plant was shut down for a refueling outage from September 2 through December 15, 1982. CF/D run lengths will again be followed in 1983 to determine whether this improvement continues.

Ecosorb-C precoats were also used during the 1982 refueling outage to clean up the hotwell, fuel pool and reactor, and the torus. On restarting in late December, 1982, it was found that the reactor water quality improved more rapidly than in previous restarts. The reactor water conductivity was reduced to 0.18 μmho/cm in one day, while in previous restarts it took at least three days to reach that quality.

CONCLUSION

Organic compounds enter nuclear water systems from several sources, and tend to accumulate in the radwaste plant. Removal of organics has several beneficial effects on plant operations, including reduced potential for corrosion and reduced radwaste disposal and treatment volumes. The use of Ecosorb-C precoats on radwaste filters has been proven to be an effective, easy and economical way of removing organics from radwaste liquids. Although radwaste is an important source of organics, there are still other sources. Studies are planned to evaluate side-stream treatment on the CST with Ecosorb-C precoats to reduce TOC levels in plant make-up from raw water sources. The use of these precoats on CF/D's to remove TOC is another possibility scheduled for investigation.

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