

# FULL-SCALE PERFORMANCE OF NEW ORGANIC RESIN RATIOS AND INORGANIC MATERIALS FOR PROCESSING LOW LEVEL LIQUIDS AT DIABLO CANYON POWER PLANT

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## ABSTRACT

This paper discusses Pacific Gas and Electric Company's full-scale operating experience using new ion exchange resins and ratios for processing radioactive liquids at Diablo Canyon Power Plant (DCPP). Previous tests investigated new organic resins, various resin ratios and several ion selective inorganic media for processing nonrecyclable and recyclable plant liquids (1). The data from those bench scale tests indicated how processing liquids at DCPP could be improved. Information obtained from the bench scale tests have been directly applied to full-scale operation throughout 1989.

Processing nonrecyclable and recyclable liquids prior to the bench scale tests utilized a 50:50 mixed bed (Amberlite IRN-150) ion exchange resin. The full-scale test of new media effectively processed more liquid at higher conductivities than previously experienced. Optimizing the cation and anion ratios has improved the removal of radionuclides and chemical species for specific liquid streams. The use of polyelectrolyte pretreatment in full-scale processing has enhanced the radionuclide decontamination for nonrecyclable liquids. The combination of these applications has improved the ion exchange process for treating nonrecyclable and recyclable liquids at DCPP.

## INTRODUCTION

Diablo Canyon Power Plant Units 1 & 2 are located on the Pacific coast in Avila Beach, California. Pacific Gas and Electric Company (PG&E) owns and operates the two unit Westinghouse 1100 MWe PWR units. The commercial operation dates for Units 1 & 2 were May 1985 and March 1986 respectively.

A previous paper discussed testing of organic and inorganic ion exchange media for liquid processing at DCPP (1). This testing determined optimum cation to anion ratios and media types for recyclable and nonrecyclable liquid processing.

A 4:1 ratio of cation to anion Dow resin was determined to be optimal for processing recyclable liquids (e.g., reactor coolant letdown, boron recycle and spent fuel pool). A 9:1 ratio of cation to anion media was found to be optimal for processing nonrecyclable liquids (e.g., equipment drain and floor drain liquids). Rohm and Haas IRN-77 cation resin and Clinoptilolite (a natural zeolite) were determined to be optimal for cesium removal. Duratek D-70 cation media and polyelectrolyte pretreatment with IRN-77 were best for cobalt removal. Sybron A-642 was determined to be the optimal anion media.

## RECYCLABLE LIQUID PROCESSING

Liquids recycled at DCPP are processed by ion exchange in the Chemical and Volume Control System (CVCS), the Boron Recycle System (BRS) and the Spent Fuel Pit Cleanup System (SFPS). The BRS at DCPP typically recovers over 2 million gallons of liquid annually. The use of ion exchange and evaporation in the BRS provides four major benefits. These are (1) reduced liquid processing load on the Liquid Radwaste System (LRW), (2) reduced

purchase of boric acid, (3) elimination of boric acid radwaste solidification, and (4) reduced makeup water requirements. The reduced makeup water is important because 60% of makeup water for DCPP is produced from the reverse osmosis of sea water. The cost of makeup water derived from seawater at DCPP is about \$8 per 1,000 gallons.

The Boron Recycle System consists of two trains of two demineralizers in series upstream of the boric acid evaporator. The spent Fuel Pit Cleanup System consists of a single 30-cubic-foot demineralizer vessel per unit. The CVCS letdown treatment train consists of five demineralizers in series (Fig. 1). The first two vessels contain lithiated mixed bed resin. Normally one of these vessels is aligned in service and the other is bypassed and held in reserve. The third vessel contains cation resin and is aligned intermittently to control reactor coolant chemistry. The last two vessels are designated as deborating beds. A deborating bed is aligned at the end of a fuel cycle to remove boron from RCS when evaporation becomes an inefficient removal process at low boron concentration levels. The concentration of dilute levels of borated RCS to 12% by weight for recycle results in the concentration of chemical contaminants (Cl, SO<sub>4</sub>, etc.) to unacceptable levels making the boric acid unable to be recycled.

The deborating vessels in the CVCS at DCPP can be regenerated. It has been demonstrated at DCPP that a single deborating vessel can be used to support the end of the fuel cycle with one regeneration. This has enabled an alternative use of one of these vessels. DCPP has utilized forced oxidation for every outage. The process of forced oxidation releases a large amount of radioactivity, enough to expend a bed due to radiation level. Due to the expense of the lithiated resin, cleanup of RCS during forced oxida-

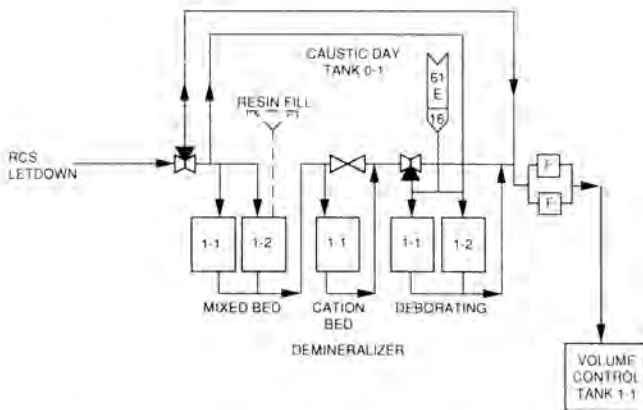


Fig. 1. Chemical and Volume Control System (CVCS) Letdown Treatment Train.

tion has been performed by less expensive mixed bed resin loaded into a deborating vessel.

This method of cleanup has proven to be effective for three reasons. First, by loading a mixed bed in a deborating vessel the anion capacity of the new bed can be utilized to remove boron. This may be required to support plant operation during the regeneration of the deborating demineralizer. Second, inexpensive resin is used in the throw away mode to remove the bulk of the activity released during forced oxidation. This allows the expensive lithiated resin to be conserved and utilized to support fuel cycle operation, perhaps enabling two fuel cycles per bed. Third, the extremely radioactive resin bed resulting from forced oxidation can be stored for a fuel cycle in the deborating vessel allowing decay to occur prior to waste packaging without impacting the spent resin storage tank capacity.

Prior to 1989, 30 cubic feet of 1:1 mixed bed Rohm and Haas IRN-150 had been loaded into deborating vessels for forced oxidation cleanup. The resin load to support forced oxidation for the Unit 1 third refueling outage in 1989 was selected as the first use of the optimized Dow 4:1 cation to anion resin ratio for processing recyclable liquids. This bed served to support boron removal prior to forced oxidation.

As a result of forced oxidation the top layer of the bed reached 4000 R/hr. The decontamination factors for

Co60, Co58, Cs137 ranged from 100 to 1600; I131 ranged from 100 to 500. This bed remained in service for the duration of the cleanup and was removed from service with a Co58 decontamination factor of 60. This Dow 4:1 bed allowed the cleanup of approximately 10 times more Cs137 activity and 3 times more Co58 activity than experienced in the previous Unit 1 second refueling outage where the resin bed reached 1200 R/hr. The Dow bed will be stored for Co58 decay until 1991 when it will then be transferred to a spent resin storage tank to enable the vessel to be reloaded to support another outage. Based on the performance of this bed, the Unit 2 Spent Fuel Pit demineralizer was loaded with a 4:1 Dow resin mix.

The Spent Fuel Pit Cleanup system is used to clarify and purify water from the spent fuel pit. Fuel pit water is pump through a filter or into the SFP demineralizer. Water from the demineralizer passes through a resin trap filter before returning to the spent fuel pool. In purifying the SFP water it is important that both radiochemical and chemical species are removed effectively.

The SFP demineralizer was loaded with the Dow 4:1 resins in December 1989. Two months of data have shown the Dow resin to perform as expected based on the information obtained from the bench tests. The radiochemical species (Co, Cs) have been sufficiently removed from the water. The chemical species (Cl, Na, F, Ca, Mg, and pH) are being maintained well below their limits. The performance of this demineralizer will be monitored closely to determine the full scale capacity and future use of this resin in the SFPS and BRS.

#### NONRECYCLABLE LIQUID PROCESSING

The liquid radwaste processing system (Fig. 2) at DCPD consists of a cartridge filter followed by four 30-cubic-foot vessels in series. The first two vessels, designated for filter media, discharge waste media directly out of the plant to mobile solidification/dewatering equipment. The two latter ion exchange vessels discharge waste resin to one of two spent resin storage tanks. The processed liquid is sent to collection tanks for analysis prior to discharge.

#### Organic Resin Full Scale Experience

The optimized 9:1 IRN-77 and Sybron A-642 mixed bed resin was loaded into the radwaste ion exchange vessels at Diablo Canyon in the fourth quarter of 1988. The liquid radwaste from floor and equipment drain receivers were pretreated with polyelectrolyte and salt and then processed through a cartridge filter and a single radwaste ion exchange vessel. The bed loaded in October 1988 remained in service through April 1989 and processed over 1 million gallons of liquid radwaste. The bed was taken out of service in April due to cesium breakthrough. The other ion exchanger was placed in-service. This second bed remained

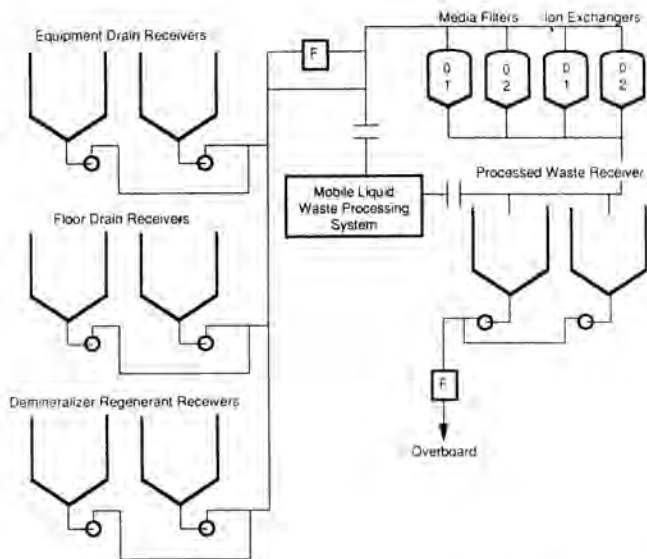


Fig. 2. DCPD Liquid Radwaste System.

in service until September 1989 and processed 850,000 gallons of equipment and floor drain waste. More floor drain liquids were processed through this resin bed than the previous bed. This bed was taken out of service due to cesium breakthrough. A third 9:1 ratio bed was placed in service in September 1981. This bed processed 430,000 gallons prior to being removed from service due to cesium breakthrough.

#### Cesium Removal Using Clinoptilolite Zeolite

Previous experience at DCPD indicated that the use of activated carbon in the media vessels was of no benefit. Due to the continued breakthrough of optimized organic resin by cesium, use of zeolite in the media vessels was proposed to counter this problem. Exhausted inorganic media can be discharged from these vessels directly to a mobile waste packaging system.

Prior to the use of inorganic media in full-scale service, the ability to package the exhausted media to federal, state, and disposal site criteria was required. The mobile wet waste packaging vendor at DCPD did not have procedures to solidify or dewater zeolite or D-70. Since these media will concentrate cesium or cobalt, a method to provide a stabilized waste form is required.

The development of a topical report to solidify varying mixtures of zeolite, D-70, and organic resin in cement was cost prohibitive. An alternative packaging method of dewatering waste media in an NRC approved HIC was

pursued. The vendor performed bench scale dewatering tests to determine whether clinoptilolite, D-70 or organic bead resin was more difficult to dewater. These tests demonstrated that the D-70 material was the most difficult media to dewater.

In order to ensure development of a procedure to repeatedly dewater combinations of organic and inorganic media, two full-scale dewatering campaigns of D-70 were performed. A dewatering test report was prepared by the vendor and approved by DCPD as part of the plant dewatering process control program.

A media filter vessel was loaded with inorganic media for the first time on December 1, 1989. This vessel contained 10 cubic feet of clinoptilolite (top layer), 12 cubic feet of IRN-77 cation resin, 3 cubic feet of Sybron A-642 anion resin, and 5 cubic feet of clinoptilolite below the outlet strainer of the vessel. The process pathway involved passing the waste through a 25 micron cartridge prefilter and then through the media vessel bed. The inlet Co58 activity ranged from  $1 \times 10^{-2}$  to  $1 \times 10^{-3}$   $\mu\text{Ci/ml}$ . Cesium activity averaged  $2 \times 10^{-4}$   $\mu\text{Ci/ml}$ .

The media filter effluent showed extremely poor decontamination for the cobalt species. Cesium was removed to the lower limits of detection or non-detectable levels for all the waste processed through this bed. This cleanup of cesium is attributable to clinoptilolite's high selectivity for cesium.

The poor decontamination of the cobalt species was suspected to be caused by the high concentration of submicron particulate material in the waste and not any adverse affect caused by the clinoptilolite. Cobalt removal was dealt with by improving the filtration and increasing pretreatment of the waste.

#### Economics

Significant cost savings have been achieved by using the optimized 9:1 organic resin for liquid radwaste treatment. There is virtually no cost penalty incurred by switching to a different type of resin. By changing the cation to anion ratio the cost of each bed is greatly reduced since cation resin is less expensive than anion resin. For a 30-cubic-foot demineralizer the savings is \$1,450 per bed used. Disposal of the organic resin can be accomplished by solidification or dewatering in an NRC approved HIC to achieve a stable waste form. Typical solidification and dewatering disposal costs for the 1:1 versus 9:1 resin ratio at US Ecologies' Richland, Washington site are shown in Table I. These data indicate that use of the 9:1 resin reduces disposal costs by a factor of 338 times. The data also indicate that dewatering is 1.4 times as expensive as solidification. Thus, the inorganic media, which must be dewatered to achieve stability, must demonstrate a throughput for high conduc-

TABLE I  
Organic Resin Disposal Cost

Resin Ratio Process	1:1		9:1	
	Solidification	Dewatering	Solidification	Dewatering
Container Delivery, Processing, Cask Shipment & Burial with 1990 Surcharge	\$24,931 per container	\$46,435 per container	\$24,931 per container	\$46,435 per container
Resin Volume per Container	120 ft <sup>3</sup>	158 ft <sup>3</sup>	120 ft <sup>3</sup>	158 ft <sup>3</sup>
Cost per ft <sup>3</sup>	\$207/ft <sup>3</sup>	\$293.9/ft <sup>3</sup>	\$207/ft <sup>3</sup>	\$293.9/ft <sup>3</sup>
Resin Throughput	3,000 gal/ft <sup>3</sup>	3,000 gal/ft <sup>3</sup>	1E6 gal/ft <sup>3</sup>	1E6 gal/ft <sup>3</sup>
Disposal Cost per Gallon	\$0.07/gal	\$0.10/gal	\$2.07 E <sup>-4</sup> /gal	\$2.94 E <sup>-4</sup> /gal

tivity liquids of 1.4 times greater than the 9:1 organic resin to be cost effective. Continued monitoring of the inorganic media will be conducted to determine the cost effectiveness of these media.

#### SUMMARY

The use of optimized ion exchange media at DCPD has improved the treatment of radioactive liquids. Increased activity removal has been achieved by the use of such media which has lowered releases to the environment and improved ALARA within the plant. The volume of solid radwaste generated has simultaneously been reduced which

lowered liquid waste processing costs and reduced the number of radioactive shipments from the plant. Monitoring of inorganic media for non-recyclable liquids and long term performance of organic media for recyclable liquids will continue.

#### REFERENCE

1. K.L. James and C.C. Miller, "Ion Exchange Media Testing For Processing Recyclable And Nonrecyclable Liquids At Diablo Canyon Power Plant," Waste Management '89 Proceedings, Vol. 2, p. 431, (1985).