THE IMPACT OF ION EXCHANGE MEDIA AND FILTERS ON LLW PROCESSING

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ABSTRACT

Optimized ion exchange media at Diablo Canyon have steadily improved the treatment of radioactive liquid waste. The activity released to the environment has been reduced while simultaneously reducing the volume of solid radwaste generated from processing radioactive liquids. This has lowered the liquid waste processing costs and reduced the number of radioactive shipments from the plant.

A cobalt treatment technique was identified and successfully implemented prior to reactor coolant chemistry alteration. A cesium treatment using zeolite has been successfully implemented. A cobalt removal treatment, combining series cation ion exchange with submicron filtration, has successfully removed cobalt after reactor coolant chemistry alteration. A new carbon-based material will be monitored to find a media to remove cobalt from high-conductivity liquids.

INTRODUCTION

Diablo Canyon Nuclear Power Plant (DCPP) Units 1 and 2 are located on the Pacific coast in Avila Beach, California. Pacific Gas and Electric Company (PG&E) owns and operates the two Westinghouse 1,070-MWe PWR units. Unit 1 began commercial operation in May 1985, and Unit 2 began in March 1986.

Testing of organic and inorganic ion exchange media for liquid processing at DCPP was previously presented (1). This testing determined optimum cation-to-anion ratios and media types for recyclable and nonrecyclable liquid treatment. A subsequent paper discussed the initial full-scale operating experience with inorganic ion exchange materials identified in testing (2).

This paper analyzes the two-year full-scale operating performance with optimized ion exchange media in the radwaste system, the experience with organic and inorganic ion exchange media in combination with cartridge filtration, and the impact on liquid effluents and solid radwaste packaging.

LIQUID WASTE PROCESSING

The liquid radwaste processing system (Fig. 1) at DCPP consists of a cartridge filter, four 30-ft^3 vessels in series, and a polishing filter that was added in January 1991. The two filter media vessels discharge waste media directly out of the plant to the mobile wet waste packaging system. The two ion exchange vessels discharge spent resin to one of two spent resin storage tanks.

Because of high cobalt activity during the first Unit 1 outage, we implemented a chemical pretreatment process developed by Duke Power to satisfy radioactive discharge requirements (3). This polyelectrolyte process successfully removed colloidal cobalt on organic cation resin during the Unit 1 refueling outage in 1986. The process remained effective for cobalt removal through the summer of 1989. During this period, organic cation resin in the liquid radwaste system was taken out of service due to cesium breakthrough, not colloidal cobalt. Resin throughputs of 4.5E6 l/m^3 (33,000 gal/ft^3) were achieved with the pretreatment technique.

To reduce solid radwaste generation, in 1989 we began cesium removal with zeolites, which were intended to prevent the organic cation resin from being prematurely removed from service due to cesium breakthrough. By removing cesium upstream of the organic bed, it was hoped that the life of the organic resin could be increased to an ultimate cobalt breakthrough.

Carbon-based ion exchange media for cobalt removal were also placed in service in 1989. Inorganic materials were used to determine their ability to remove cobalt from high-conductivity liquids such as floor drains, which were known to reduce the life of organic resin, even with pretreatment. It was hoped that the carbon media would remove cobalt without labor-intensive pretreatment. If inorganic media proved to have higher cobalt capacities than organic resin with pretreatment, then these expensive inorganic materials might be cost effective.

FULL-SCALE ZEOLITE EXPERIENCE

Bench tests at Diablo Canyon indicated that clinoptilolite was the optimal zeolite for cesium removal. This media has been loaded into the radwaste system's lead vessel, which was designed to hold activated carbon and has a conical bottom to facilitate media loadout. This material has been procured in a backwashed form. The media size was centered on 1 mm (16 Tyler mesh) based on the size of the activated carbon previously used in the vessel. The media is slurried into the vessel with a diaphragm pump.

A mixed bed of half zeolite and half cation resin was loaded in February 1990. Only 13 ft^3 of zeolite was in the active zone of the vessel. Although the resin depleted on cobalt within a few months, the zeolite continued to remove cesium and processed a total of 4.65E6 l (1.23 million gal) of radwaste. This bed processed liquids from the third Unit 2 refueling outage. The influent activity to this bed was about 37.6 Curie (Ci), excluding tritium and noble gas. In December 1990, the bed was taken off line due to sloughing of cobalt, not cesium breakthrough. This equated to a throughput of 1.26E7 l/m^3 (94,613 gal/ft^3).

The bed was reloaded with a full charge of zeolite. This bed processed liquids from the fourth Units 1 and 2 refueling outages in 1991. The total influent activity was about 34 Ci, excluding tritium and noble gas. In October 1991, this bed was taken off line due to cobalt sloughing after processing 5.33E6 l (1.41 million gal). This equates to a throughput of 6.28E6 l/m^3 (70,591 gal/ft^3).

A cesium breakthrough for zeolite has not been determined at DCPP. Duke Power's experience indicates that a

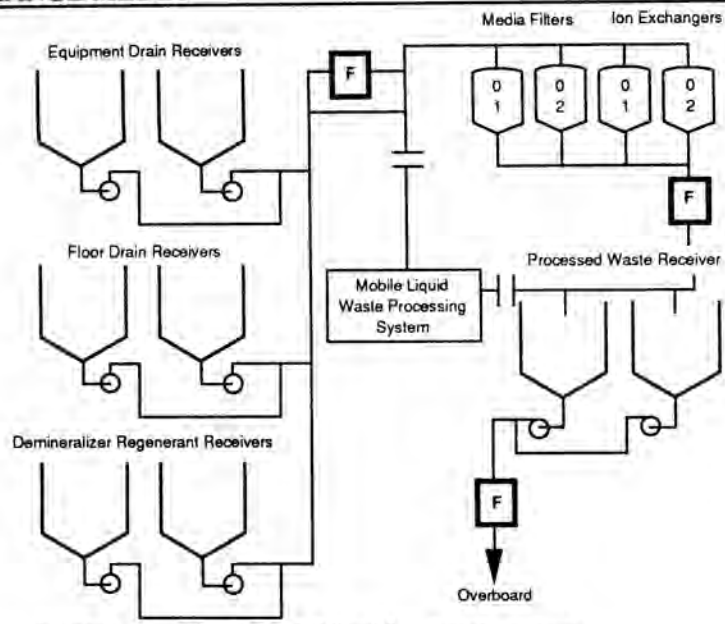

Fig. 1. DCPP liquid radwaste system.

graded, deep-bed prefilter upstream of the zeolite would prevent cobalt sloughing. Such a technique would be difficult at Diablo Canyon, which has only four vessels in its system. If one was loaded with filtration material, the capacity of a whole ion exchanger would be lost. In addition, the lead vessel has no capability to remove dirt from its top layer. Thus, an entire 30-ft^3 bed would be generated whenever the vessel achieved a high-differential pressure.

The lead vessel has been reloaded with a full charge of zeolite. In the future, the zeolite will not be removed from service due to cobalt sloughing. To use the zeolite cesium capacity to its fullest, downstream cation beds will be required to remove the cobalt. By retaining a full load of zeolite, a large cesium capacity is available to process liquids in case of fuel failures.

FULL-SCALE COBALT REMOVAL EXPERIENCE

We were able to remove cobalt with polyelectrolyte pretreatment and organic cation resin until the third Unit 1 refueling outage. Using inorganic selective ion exchange media for cobalt removal without pretreatment appeared desirable. The capacity of such media for high- and low-conductivity liquids has a great impact on the cost-effectiveness of the media. Organic resin throughputs in excess of 4.5E6 l/m^3 (33,000 gal/ft^3) had been achieved; resin costs about 15% of the inorganic media.

Durasil D-70

A mixed bed of zeolite and Durasil D-70 was loaded into the second vessel in January 1990. The first batch processed was high-conductivity regenerant waste of 800 μmho. The bed then processed liquids throughout the third Unit 2 refueling outage. This bed processed 2.1E6 l (555,738 gal) and exhausted on cobalt in June 1990, which equates to a throughput of 4.94E6 l/m^3 (37,049 gal/ft^3). The total influent activity to this bed was about 35 Ci, excluding tritium and noble gas.

The vessel was reloaded with a full charge of D-70 in August 1990. A high-conductivity batch (about 15,000 μmho) was, again, the first to be processed. Although the batch was discharged after treatment, the cobalt decontamination factor was only 5, and the D-70 was depleted.

A third bed of D-70, upstream of an organic cation bed, was reloaded in January 1991. The two beds aligned in series provided a large capacity for cobalt removal during the fourth Unit 1 refueling outage. This third bed processed 1.35E6 l (356,803 gal) of radwaste, with an average cobalt decontamination factor of 10. This equates to a throughput of only 1.91E6 l/m^3 (17,840 gal/ft^3). The total influent activity to this bed was only 1.9 Ci, excluding tritium and noble gas.

The vessel was again reloaded with D-70 to support the fourth Unit 2 refueling outage. This bed exhausted on cobalt after processing only 6.85E5 l (180,946 gal), which equates to 9.67E5 l/m^3 (9,000 gal/ft^3). The total influent activity to this bed was about 12.3 Ci, excluding tritium and noble gas.

The D-70 did not increase cobalt capacity compared to organic resin with pretreatment at Diablo Canyon. Although D-70 was able to remove cobalt from high-conductivity batches, the throughput for these batches was extremely low; however, the carbon material and downstream cation resin together produced acceptable effluent for discharge. A different carbon material will be used in the next reload. If this material does not improve treatment of high-conductivity liquids or increase capacity for colloidal cobalt, organic resin will be loaded into the second vessel. The continued use of carbon-based materials may be limited by waste packaging requirements or economics.

Cation Resin

Removal of colloidal cobalt using pretreatment with cation resin failed in 1989 during the third Unit 1 refueling outage. Prior to this, throughputs of 4.5E6 l/m^3 (33,000 gal/ft^3) were experienced without depletion on cobalt.

Using zeolite upstream of cation resin allowed improved throughput for the organic resin. A bed loaded into the third vessel in June 1990 remained in service until January 1991. This bed processed 5.68E6 l (1.5 million gal) prior to cobalt breakthrough, for a throughput of 6.68E6 l/m^3 (51,562 gal/ft^3). It did not process any refueling outage liquids or floor drains.

The total influent activity to this bed was about 12.8 Ci, excluding tritium and noble gas.

Another cation bed, downstream of a zeolite bed and a D-70 bed, supported the fourth Units 1 and 2 refueling outages. This cation resin processed 3.58E6 l (945,952 gal) of liquid before depletion on cobalt during the middle of the fourth Unit 2 refueling outage, equating to a throughput of 4.21E6 l/m^3 (37,531 gal/ft^3). The total influent activity to this bed was about 26.2 Ci, excluding tritium and noble gas.

This information shows improved organic resin throughput for cobalt removal by using zeolite for cesium removal, although this indication must be considered cautiously. First, the criteria for cation resin exhaustion due to cobalt exclude particulate cobalt greater than 0.22 μ. Previously, any cobalt less than 0.45 μ was thought to be soluble. Second, since 1990, the organic beds have not had to process high-conductivity floor drains during nonoutage periods; in prior years, the influent activity in floor drains, due to some fuel leaks, required processing. Cobalt capacity is depleted by processing these high-conductivity liquids.

The experience to date at DCPP indicates improved soluble cobalt treatment by using zeolite upstream of cation resin for cesium removal. This does not, however, assure production of dischargeable effluent when colloidal cobalt is present.

Colloidal Cobalt Removal

Pretreatment at DCPP enabled particulate cobalt to be removed by organic resin. In fall 1989, however, particulate cobalt from the Unit 1 refueling outage was not affected by the pretreatment. Inorganic carbon media used during the ensuing Unit 2 outage was unable to remove the particulate cobalt. It was later determined that the particulate cobalt activity would pass through a 0.45-μ milipore filter, but it could be removed by a 0.22-μ milipore filter. The species of particulate cobalt unleashed during the third refueling outage of each unit was unaffected by pretreatment, and it was smaller than any cartridge filters on site.

The source of the new species of cobalt particles is thought to be an alteration of reactor coolant chemistry. The Electric Power Research Institute (EPRI) reports that reduced lithium and corresponding pH resulted in an elevated generation of fine particulate activity at Doel 4 in Belgium (4). EPRI's experience also indicates that the size of the particles will increase (e.g., to 8 μ) by maintaining the coordinated chemistry for subsequent fuel cycles. It was confirmed that adding peroxide to the reactor coolant during shutdown was also a source of submicron particulate generation. Before peroxide addition, cobalt particulates in the reactor coolant could not pass through a 0.45-μ milipore filter. After peroxide addition, we identified particles that could only be removed by a 0.22-μ milipore filter.

Because mechanical filtration was the only means available to remove the new particles, we purchased submicron cartridge filters for use upstream of the radwaste system (5). An overboard filter was repiped to alter its function to that of a polishing filter in the radwaste treatment system downstream of the four demineralizer vessels. Submicron filter cartridges can be placed in this vessel to remove particulate matter that passes through the ion exchangers. This design change was completed prior to the fourth Unit 1 refueling outage. The generation of waste filters has been surprisingly low. Upwards of eight batches, 3.63E5 l (96,000 gal), have been processed by a single filter.

IODINE REMOVAL

The last vessel in the radwaste treatment train is loaded with anion resin for iodine and antimony removal. This vessel is usually bypassed, but it is aligned when iodine or antimony are identified in a batch that requires processing. In summer 1991, the vessel was aligned to process drains from a letdown line leak. This bed has yet to exhaust and has processed 1.74E6 l (459,597 gal).

SYSTEM PERFORMANCE

The performance of the liquid radwaste system has steadily improved despite the 1990 setback due to colloidal cobalt. The activity discharged from the plant, excluding tritium and noble gas, follows:

1987	2.86 Ci	single outage
1988	2.00 Ci	double outage
1989	1.61 Ci	single outage
1990	2.77 Ci	single outage
1991	>1.00 Ci	double outage

The conversion from mixed beds of resin to single-loaded vessels aligned in series has increased the system's ion exchange capacity and has allowed us to use the resin more effectively. By adding the polishing filter to the system in 1991, we were able to remove particulate cobalt and realize a continued reduction in effluent activity. The effluent activity of each component in the processing train for selected batches is shown in Table I.

SOLID WASTE GENERATION

The reduction in effluent activity has not substantially increased the solid radwaste generation. Spent media from the radwaste system have never exceeded 4.2 m^3 (150 ft^3) per year. The average spent media volume generation over four years is 2.5 m^3 (90 ft^3). By compacting spent filters, we have minimized the volume of cartridge filter generation. Up to 45 filters have been packaged in a drum for unstable waste disposal.

Inorganic media were expected to increase waste packaging costs per bed exhausted. Spent ion exchange media have always had to be disposed as a stable waste form at Diablo Canyon. Inexpensive cement stabilization was the common packaging method for spent resin. Packaging costs were expected to increase for the inorganic media because approved Nuclear Regulatory Commission (NRC) high-impact containers (HICs) are required to provide stability at the Richland, Washington, burial site. There were increases in waste packaging costs; however, cement solidification of resin ceased to be a viable option after the NRC issued Revision 1 of the Technical Position on Waste Form. All media, whether organic or inorganic, are currently dewatered in NRC-approved HICs at Diablo Canyon. Therefore, a waste packaging penalty is not incurred for inorganic or organic media.

There is a potential future waste packaging penalty for using carbon-based media at DCPP. The storage building can only hold 80-ft^3 containers, and the NRC has not approved 80-ft^3 HICs. The draft California disposal site license requires all media to be solidified. This requirement, if adopted, will stop continued use of HICs. It is anticipated that the NRC will

approve the vinyl ester styrene (VES) process for the stabilization of resin and zeolite without archive samples. Should this requirement be adopted, resin and zeolite will be solidified in VES at Diablo Canyon. This waste form will be convenient for storage, less expensive than HICs, and acceptable to the California site.

VES stabilization of carbon-based media has not been submitted to the NRC, although work is underway. Without an NRC-approved stabilization method for carbon, continued use of such media at DCPP may be halted.

ECONOMICS

NRC-approved HICs were required to stabilize waste media at DCPP. Media procurement and disposal costs at Richland, Washington, are summarized in Table II. The total cost for cesium removal with zeolite and cobalt removal with resin has been about a penny per gallon.

REFERENCES

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TABLE I

Effluent Activity (μCi/ml)
September 6, 1991

Nuclide	Process Tank Influent	M.F. 0-1 Effluent[1]	M.F. 0-2 Effluent	I.X. 0-1 Effluent[2]	I.X. 0-2 Effluent	
Co-58	3.98E-2	1.19E-2	2.05E-5	3.63E-6	≤1.03E-6	
Co-60	1.74E-3	3.07E-4	≤3.57E-6	≤2.66E-6	≤1.08E-6	
Cs-137	6.69E-5	≤2.42E-5	≤2.81E-6	≤2.81E-6	≤1.19E-6	
October 24, 1991						
Nuclide	Process Tank Influent (EDR-01)	M.F. 0-1 Effluent	M.F. 0-2 Effluent[3]	I.X. 0-1 Effluent	I.X. 0-2 Effluent	Filter 0-5 Effluent
Co-58	2.43E-3	6.89E-4	n.i.s.	1.95E-5	≤1.17E-6	2.71E-6
Co-60	3.67E-3	6.22E-5	n.i.s.	2.77E-6	≤1.12E-6	8.49E-6
Cs-137	≤1.86E-5	≤6.20E-6	n.i.s.	≤1.38E-6	≤1.04E-6	6.10E-7

[1] M.F. = media filter
[2] I.X. = ion exchanger
[3] n.i.s. = not in service

TABLE II

Media Procurement and Disposal Costs

	ZEOLITE[1]		CATION RESIN[2]		D-70[2]			
	1990 Bed	1991 Bed	1990 Nonoutage	1991 1R4 Outage	1990 2R3 Outage	High-activity Regenerant Treatment	1991 1R4 Outage[3]	1991 2R4 Outage[3]
Disposal Costs[4] ($)	47,335	46,920	46,920	46,920[5]	47,664	47,335	46,920	46,920[5]
Waste volume (ft^3)	114	114	114	114	158	114	114	114
Cost ($/ft^3$)	415	411	411	411	301	415	411	411
Media throughput (gal)	1.23E6	1.41E6	1.5E6	9.5E5	5.55E5	12,000	3.6E5	1.8E5
Media cost ($)	1,350	1,350	2,610	2,610	24,225	24,225	24,225	24,225
Cost ($/gal)	0.01	0.01	0.01	0.02	0.06	3.00	0.10	0.20

[1] cesium removal
[2] cobalt removal
[3] standard liquid waste
[4] 1990-1991 surcharges
[5] projected

Liquids at Diablo Canyon Power Plant," Waste Management '89 Proceeding, vol. 2:431 (1989).

2. K.L. JAMES and C.C. MILLER, "Full-Scale Performance of New Ion Exchange Materials for Processing Low-level Liquids at Diablo Canyon Power Plant," Waste Management '90 Proceedings, vol. 2:295 (1990).
3. R.M. PROPST, R.P. MICHAEL, G.T. HAMRICK, and G.L. WARD, "Use of Polyelectrolyte for Liquid Waste Processing," EPRI Seminar (1985).
4. AEA Technology, Winfrith, "The Nature and Behavior of Particulates in PWR Primary Coolant," EPRI NP-6640 (December 1989).
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