REDUCED PARTICULATE AND COLLOIDAL COBALT ACTIVITY IN LIQUID RADWASTE

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ABSTRACT

This paper discusses Pacific Gas and Electric Company's operating experiences with particulate and colloidal cobalt in liquid radwaste at Diablo Canyon Power Plant (DCPP). The adverse affect of particulate activity on radioactive liquid effluents and solid radwaste generation are described. Removal of particulates by polyelectrolyte pretreatment coupled with organic ion exchange resin in the liquid radwaste system had been successful from 1986 to 1989. During the fall outage of 1989 this treatment method was unsuccessful.

The use of mechanical filtration to remove particulate activity from liquids prior to entering the liquid radwaste system is discussed. The development of filter specifications, a program to decrease cartridge filter pore sizes and facilities to handle spent filters is also covered.

The addition of a polishing filter in the liquid radwaste system and future investigations into different pretreatment methods to enhance particulate removal are described.

INTRODUCTION

Diablo Canyon Power Plants 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 Westinghouse 1100 MWe PWR units. The commercial operation dates for Units 1 & 2 were May 1985 and March 1986 respectively.

Previous papers have discussed testing and full scale performance of selective organic and inorganic ion exchange media for radioactive liquid treatment at DCPP (1,2). Prior to the first outage at DCPP, the plant had conducted bench scale testing of a chemical pretreatment process developed by Duke Power(3,4). This process involved the addition of polyelectrolyte and salt to radwaste tanks which enabled the removal of particulate cobalt on organic resin which otherwise would pass through the resin.

RADIOACTIVE EFFLUENTS

High cobalt activity during the first Unit 1 outage required the implementation of the pretreatment method to satisfy radioactive discharge requirements. This process proved effective for colloidal cobalt removal during the Unit 1 refueling outage in 1986. The process remained effective for cobalt removal through the summer of 1989 up until the third Unit 1 refueling outage. During this period organic cation resin in the liquid radwaste system was taken out of service upon cesium breakthrough not colloidal cobalt problems. Throughputs of (4.5×10^6 L/m^3 33,000 gal/ft^3) of resin were achieved using of the pretreatment technique.

In order to reduce solid radwaste generation, cesium removal using zeolites versus cation organic resin began in 1989. Throughputs of 100,000 gal/ft^3 of zeolite have recently been achieved at DCPP for cesium removal.

The liquid radwaste system at DCPP is depicted in Fig. 1. The content of treatment media in the various vessels has changed during the operational life of the plant. Currently, the first vessel is loaded with clinoptilolyte zeolite for cesium removal. The second vessel is loaded with Durasil D-70 for cobalt removal. The third vessel is loaded with cation IRN-77 resin for cobalt removal. The fourth vessel is loaded with anion A-642 resin for iodine and antimony removal. The inorganic media are directly discharged from the first two vessels to a High Integrity Container (HIC). The resin from the last two vessels are discharged to the plants spent resin storage tanks.

DISCRETE HOT PARTICLES

Discrete hot particulates became a sensitive radiological concern in 1988. Upon investigation at DCPP Co-58 and Co-60 particles were identified. Strict radiological controls were implemented to prevent the spread and loss of control of such particles. Hot particle zones (HPZ) are required to be setup for any job which has the potential for releasing hot

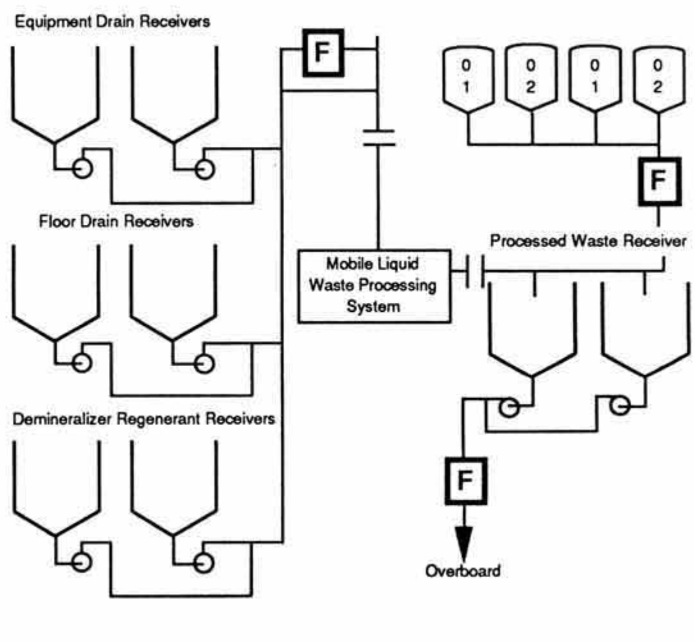

Fig. 1. DCPP Liquid Radwaste System.

particles. This includes all breaches of any system containing radioactive liquid.

Within an HPZ all personnel are required to wear an outer disposable set of paper coveralls, booties and gloves. In addition all zones with concrete floors are setup with disposable plastic sheeting. At DCPP work in HPZs constitutes 34% to 40% of the dry active waste (DAW) generated at the plant.

Several long range plans were developed to reduce the generation and migration of hot particles. Ultimately it is hoped that these plans will enable a reduction in HPZ DAW generation. Two plans involve source reduction of cobalt in the primary system. The first source reduction plan is the conversion to Westinghouse VANTAGE 5 fuel. The straps on this fuel are made of Zirconium rather than Inconel and therefore reduce the source of cobalt. The first load of new fuel was placed in service for cycle 4 of each unit.

The second cobalt reduction plan covers investigation into the use of valves that are made of non stellite, NoRem material. Such a valve is to be installed in a harsh duty non-safety related system during the forth Unit 1 refueling outage to obtain experience with these valves. Should the valve perform well, a program to replace specific valves in the primary system with NoRem valves will be initiated.

A third plan involves adopting coordinated reactor coolant chemistry. European experience has shown that such changes to reactor coolant chemistry can reduce out of core dose rates on system piping. This plan should ultimately reduce the generation and migration of hot particles in the primary system.

A forth plan involves the removal of particles from plant systems with existing cartridge filter vessels. This plan was implemented because a removal mechanism for hot particles is required whether cobalt source reduction plans succeed or fail. The institution of such a plan at the Obrigheim plant in Germany had been successful in reducing reactor coolant cobalt activity when coupled with coordinated chemistry and cobalt reduction. The benefits of removing particles within the system of generation include not only potential HPZ DAW reduction but also reduction of the input of particles into the Liquid Radwaste System and reduction of out of core dose rates.

The Chemical Volume Control System (CVCS) and Spent Fuel Pit (SFP) system are equipped with several filters, see Fig. 2 and 3. These filter vessels are housed in shielded cubicles. Shield plugs over each vessel are designed to enable remote opening of the vessel lids. Each vessel was adapted to house a single pleated filter cartridge element to facilitate remote removal of expended elements. A grapple "handle" on the end of each cartridge interfaces with the grapple of a spent filter transfer cask. The spent filter transfer cask is designed to mate with the filter cubicle shield lid when the plug is removed enabling remote

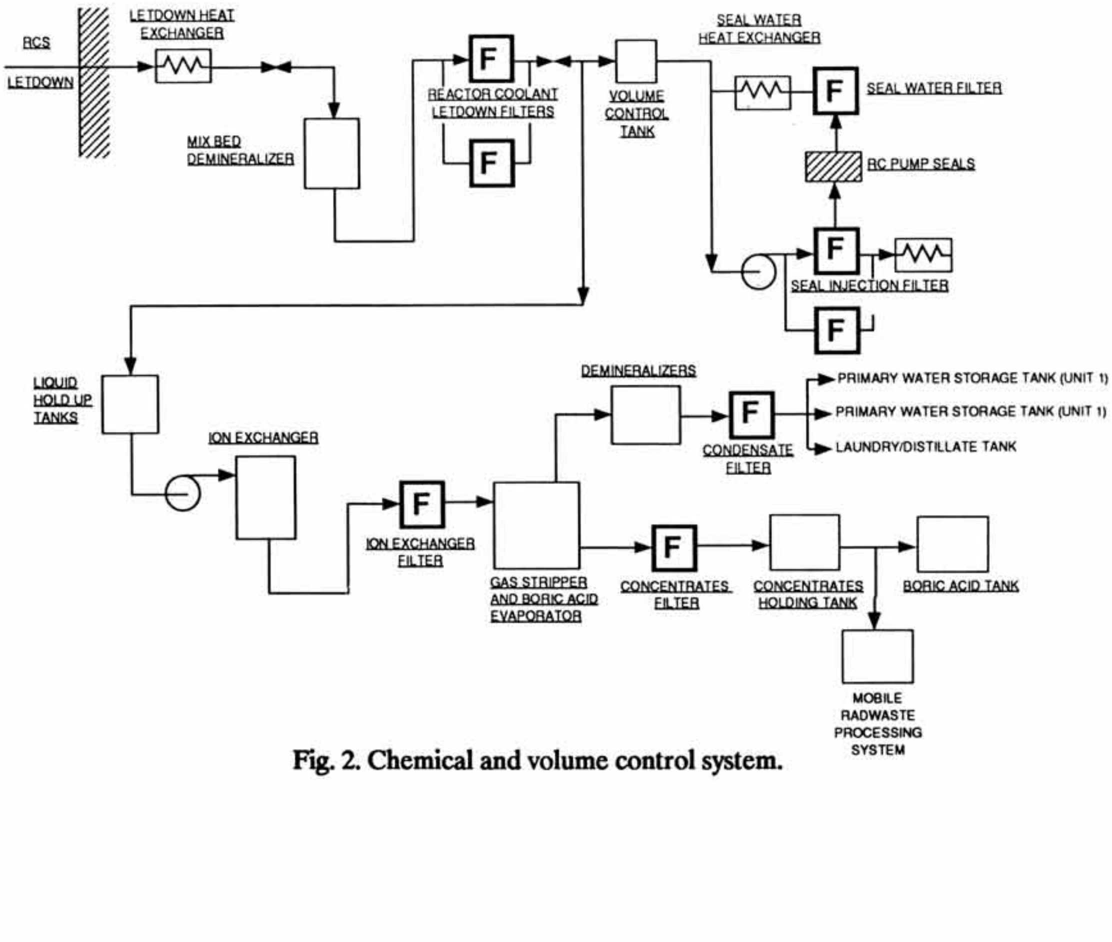

Fig. 2. Chemical and volume control system.

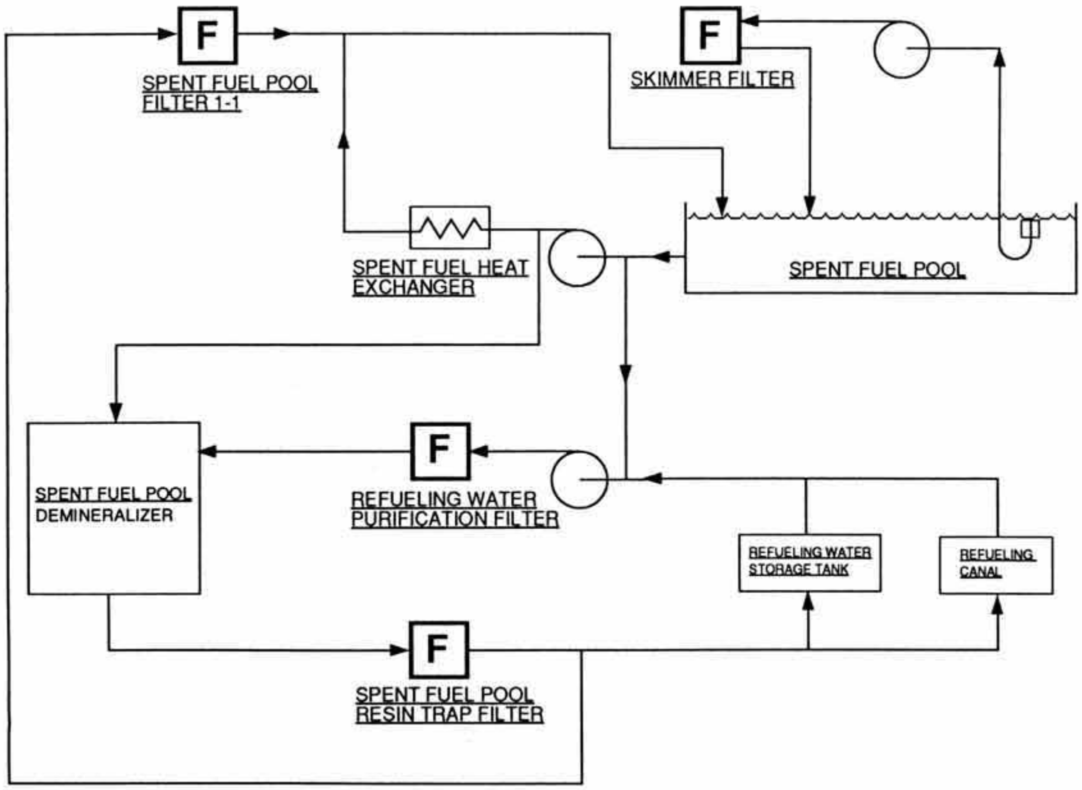

Fig. 3. Spent fuel pool system.

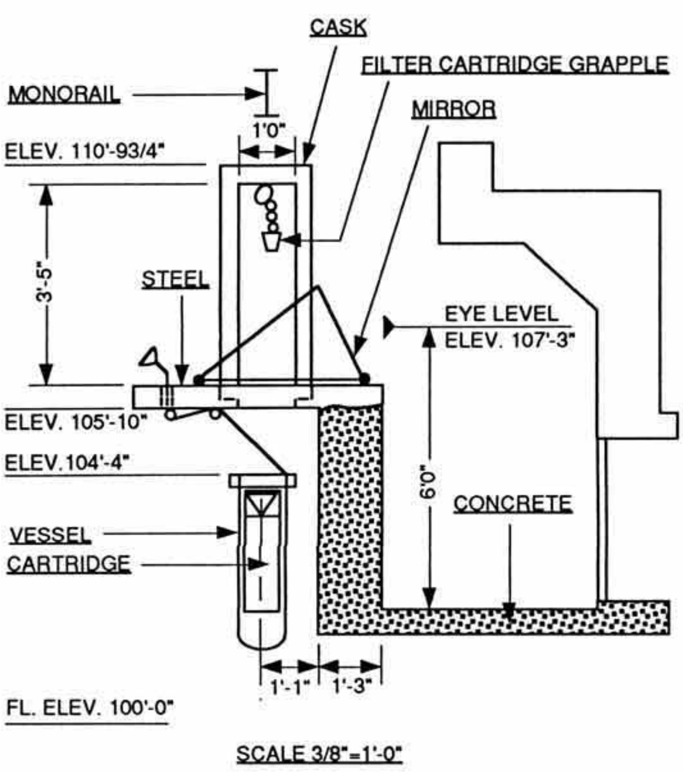

Fig. 4. Spent filter transfer system.

removal of the spent filter cartridge. The spent filter transfer cask is positioned over filter vessels by installed monorails see Fig. 4. The cask is provided with a cart to enable movement of the cask through the auxiliary building and to the Solid Radwaste Storage Facility (SRSF).

In the SRSF spent filters may be sampled for curie content determination, stored in either a storage cask or shielded drums and encapsulated for disposal as a stable waste form. Filters with radiation levels greater than 200 R/hr have been removed, transferred, sampled and stored with virtually no radiation exposure. Cartridge filters which do not require stability for disposal are compacted into drums with absorbent. Up to 45 filters can be packaged in a single drum by using the drum compactor in this manner.

The filters in the CVCS and SFP systems were originally specified to have 25 or 5 micron nominal filter cartridges. From plant operation in 1985 through 1987 very few CVCS filters required change out due to high differential pressure (D/P). Analysis of these filter media sizes by two different laboratories indicated that these cellulose based media were on the order of 50 micron absolute with little difference between the two size ratings.

Previous analysis of equipment and floor drain liquids identified particulate activity by size distribution, see Table I. Although particulate activity was a small portion of the total activity, a significant percentage of the particulate activity was below 5 micron. It was obvious that the filter media size in use was to course to effectively remove particulate activity.

CARTRIDGE FILTER MEDIA SIZE REDUCTION

In 1988 a program to reduce the filter media size was initiated. The program was fashioned to decrease media size incrementally so as not to generate large quantities of spent filters. To implement the program an action plan was developed to identify the various tasks which were required. These tasks included; design changes to revise documents to enable the reduction of filter media sizes, procedure development and revisions, filter cartridge procurement specification development and determining a reduced media size determination to start the program.

Four design changes were required to enable finer filters to be installed (a change for each system in each unit). Eight separate procedures were prepared to provide instructions for replacing the filter element in each of the various vessel types at DCPP. A procedure for handling the spent filter transfer cask was revised to interface with the filter replacement procedures.

In order to determine a starting point, a survey of U.S. operating plants designed in the late 1970s was conducted. Most of these plants had CVCS letdown filters rated at 3 micron. The Obrigheim plant in Germany was know to be using filters rated at 0.45 micron and were stepping down to 0.2 micron filters. At DCPP the letdown vessel was chosen as the first vessel for media size reduction. Since there are two letdown vessels in parallel a new cartridge could readily be bypassed by a valve manipulation upon high D/P. The letdown vessels at DCPP are also downstream of the demineralizers so the particulate loading was expected to be 8 microns or less.

In 1988 two filter cartridges were installed in the Unit 2-1 letdown vessel which were rated at 4 micron absolute. The first filter was expended during the Unit 2 refueling shutdown. Since this was the first letdown filter to D/P during shutdown, it did remove fine particulate activity which had not been previously removed by the larger media size filters. The spent filter had a radiation level of about 10 R/hr on contact. This cartridge was replaced in November 1988 by another 4 micron rated filter. This second 4 micron filter was placed in service following the Unit 2 second refueling outage and did not D/P after three months. Two 2 micron rated cartridges were obtained shortly after the 4 micron elements. A 2 micron cartridge was installed in March of 1989 in the Unit 2-1 letdown vessel. This element lasted about one month before D/P. This experience provided confidence in procurement of filter cartridges 2 micron and finer.

A procurement order was prepared for 100 cartridges. Twelve cartridges were to be 2 micron, twelve 1 micron and

TABLE I

Non-Outage LRW Particulate Activity Data

	Equipment Drains	Floor Drains
TSS	1560 ppm	510 mg/l
TSS> 25u	4.6E-6 g/cc	4.4E-6 g/cc
TSS 25u> >5u	6.3E-6 g/cc	5.6E-6 g/cc
Total Activity	3.03E-4 uCi/cc	1.72E-3 uCi/cc
Particulate % of Total Activity (>0.45u)	0.02%	0.4%
% Part. Act >25u	NA	8%
% Part. Act. 25u> >8u	NA	14%
% Part. ACt. 8u> >2.5u	NA	30.5%
% Part. Act. 2.5u> >1.2u	NA	23.5%
% Part. Act. >1.2u	95%	NA
% Part. Act. <1.2u	5%	23.5%

twelve 0.45 micron. The remaining 64 element sizes would be determined by PG&E at a later date base upon operational experience. A filter specification was developed to support the purchase order. The filter specification included limits on leachables from the media and adhesives of a cartridge to comply with Westinghouse primary system austenitic stainless steel specifications.

The filter specification also included a particle challenge test of each media size to ensure all vendor size ratings were placed on an equal footing. A particle challenge test was developed based upon the principle that 99% of all particles of the filter rating size should be removed from the fluid in a single pass from the beginning of filter use to the end of filter life. The material chosen for the challenge test was AC fine test dust. This material was selected based upon its common use for filter size testing by manufacturers and size distribution. The specification required laser particle counters to be utilized to determine the number of particles at the rated size to 1 micron larger in the influent and effluent of the media. The "differential efficiency" of each media at initial use and at a differential pressure near the end of life (ie., five times the initial D/P) were required to be reported.

With this specification bids from three vendors were reviewed and the purchase order awarded. Decreases in letdown filter sizes continued in 1989 upon delivery of the new cartridges. A 1 micron filter was installed in a letdown vessel in August 1989 prior to the third Unit 1 refueling outage. This cartridge was expended during the unit shut down and replaced with a 0.45 micron element. The 0.45 micron cartridge was aligned to support Unit 1 startup in November of 1989. This element was expended within two days due to the crud burst from hydrazine injection with a contact dose rate of 220 R/hr. The cartridge was replaced with a 2 micron filter to support startup. Once the unit was at 100% power the 2 micron cartridge was replaced with a 0.45 micron element.

During the first half of 1990, 0.45 micron cartridges were installed in all the letdown and seal water vessels of the CVCS in both units. Thirty two 0.45 micron cartridges were requested to be supplied on the open purchase ordered. None of the letdown filters exhausted during the fuel cycle for either unit. None of the seal water filters required change out due to high D/P during 1990 either.

1989 OUTAGE IMPACT ON EFFLUENTS

During the 1989 Unit 1 outage, high levels of activity were received in the liquid radwaste system. These first batches of liquid from the outage were pretreated with polyelectrolyte and salt and routed through the ion exchange media in the treatment system. The effluent from these batches had elevated levels of cobalt. The processed liquid was filtered in the lab through a standard 0.45 micron filter to determine if the activity was particulate. Virtually none of the activity was removed by the lab filter. Since the filter collected no activity it was initially thought that the activity was soluble and that the ion exchange media had depleted.

Similar results from subsequent batches processed through unused ion exchange media indicated that the activity in the processed liquid should be particulate. The processed liquid was filtered in the lab through a 0.2 micron filter and virtually all the activity was removed. The cobalt species which entered the liquid radwaste system during the Unit 1 third refueling outage was different than previous particulate cobalt species. This new species was not affected by pretreatment and was smaller than any cartridge filters on site. Since there was no immediate solution to this problem, batches from the Unit 1 outage were discharged with elevated cobalt concentrations. These discharges adversely affected DCPP discharge goals in the forth quarter of 1989 and the first quarter of 1990.

Several action plans were developed to combat the new particulate cobalt problem. The source of the new species of cobalt particles is thought to be the alteration in reactor coolant chemistry. EPRI report NP-6640 indicates that reducing lithium and correspondingly pH resulted in elevated generation of fine particulate activity at Doel 4 in Belgium (5). This experience also indicates that by maintaining the coordinated chemistry for subsequent fuel cycles the size of the particles will increase (eg., 8 micron). Since the altered reactor coolant chemistry has a positive effect on reducing out of core dose rates the practice will be continued at DCPP.

Removal of the new cobalt particles by mechanical filtration was the only mechanism known to work. The first action taken was to request the filter cartridge supplier to fulfill the remainder of the order with 0.2 micron rated filters. The vendors filter rating was accepted without a particle challenge test in order to obtain filters prior to the 1991 outages. Use of these filters will occur in 1991.

The second action was to implement a design change to alter the function of an existing overboard filter in the liquid radwaste system. The filter was repiped so that it would function as a polishing filter in the radwaste treatment system downstream of the four demineralizer vessels. This filter can be fitted with fine cartridges to enable removal of particulate matter which passes through the ion exchangers. In order to reduce solid radwaste volume, investigation into compacting filters which require stability into 30 gallon drums and overpacking the drums in HICs will be pursued in 1991.

Based upon the bid response for fine cartridge filters and the actual plant experience with submicron particulate problems, the filter specification for submicron filters was revised. Two problems with the original particle challenge test were: the average particle size of AC Fine test dust was too large for submicron media and not all vendors had laser counters capable of detecting submicron particles.

The new particle challenge test for submicron media has two parts. The first part is a latex bead test to assure all vendor size ratings are placed on an equal footing. The latex bead test does not require submicron laser counters but, more readily available optical instruments to determine the efficiency of a media. The latex bead test is a mechanical sieving test and does not take credit for particle removal by surface charge effects. Since the new particles at DCPP were unaffected by polyelectrolyte pretreatment, it is likely that they are not affected by charged filtration media.

The second part of the submicron filter specification is a particle challenge test using iron oxide versus AC Fine test dust as the material for the particle challenge test. This test is identical to previous particle challenge test except that the end of life D/P was increased to at least 40 psig. This test was retained to assure that the media will perform efficiently at the end of life in the removal of corrosion products.

The next order for submicron filters will employ the revised filtration specification. The results of future filter bids will be reviewed to determine if further changes to the specification are required.

The third action plan to enable removal of submicron particles is to retest polyelectrolytes and selective inorganic media. During the forth Unit 1 refueling outage samples of liquid radwaste will be collected. These samples will be analyzed for particulate activity and various molecular weight polyelectrolytes will be tested for enhancing the removal of the particles on ion exchange resin. Untreated liquid samples will also be applied to selective inorganic cationic media to determine particulate removal efficiencies. The use of different polymers or media will be pursued based upon successful test results.

CARTRIDGE FILTER MEDIA SIZE REDUCTION CONTINUED

In the second half of 1990, the reduction of cartridge filter media size was expanded to the SFP system and the Boron Recycle Subsystem (BRS) of the CVCS. Based upon the long life of 0.45 micron filters in the CVCS it was decided to install 0.45 micron filters into the various SFP filters and the BRS evaporator feed filter.

It was suspected that there might be a considerable amount of fine particulate in the fuel pools. This suspicion was based on the relatively high dose rates around the fuel pool. Selective resin had been loaded into the SFP demineralizers in the hope of reducing the surface dose rates from the pools. Although the selective resin has provided good effluent and removed an increased amount of radioactivity, as evidenced by higher vessel dose rates, the pool surface dose rates have not been affected. The source of this activity must be particulate matter in the pool water.

The first 0.45 micron filters installed downstream of the SFP demineralizers were expended on high D/P within a few days of alignment. Replacement 1 micron cartridges were installed to enable longer filter runs and reduce the quantity of large particles in the pools. Finer cartridges will be installed once the 1 micron filters are no longer effective (eg., do not D/P within 3 months).

The BRS recovers water and boric acid for reuse from the Liquid Hold Up Tanks (LHUTs). Like the fuel pool there were suspicions that a considerable amount of fine particulate activity might be in these tanks. Again, 0.45 micron filters were installed in the evaporator feed filter vessels. These filters exhausted on high D/P within a single day on line. Replacement 2 micron cartridges were installed to enable longer filter runs required to support plant operation. Finer filters will be installed incrementally upon loss of filter efficiency.

It is apparent that a large portion of the particulate activity which has been causing problems for the liquid radwaste system and requiring HPZs to be established, adversely affecting DAW generation rates, has been located. A program is now in place to remove this portion of the particulate activity problem within the BRS and SFP system.

SUMMARY

Historically, particulate activity of small micron size has rendered standard filtration and ion exchange systems ineffective in achieving effluent of discharge quality. Chemical pretreatment of radwaste tanks using polyelectrolytes and salt have been successful in removing such activity. The mechanism which enables this type of pretreatment to work is not well understood. Pretreatment can be subject to failure when changes in the particulate species occur.

Mechanical filtration is a proven method of removing particulate activity. The impact on solid radwaste generation from mechanical filtration can be problematic if not properly implemented. Large quantities of non radioactive suspended solids in radwaste floor drain systems inhibit the use of submicron filters in treatment systems for such liquids. The use of layered bed filtration media and/or series cartridge or bag filtration vessels is required.

Alternatively, removal of particulate matter within the systems upstream of the liquid radwaste system can reduce the input of particulate activity to liquid radwaste. Implementation of such a program also offers the benefit of reduced out of core dose rates and a reduction in the quantity of hot particles and the DAW generation which accompanies hot particle controls. Several prerequisites are required to implement a cartridge filter media size reduction program. These are as follows:

- A spent filter handling system must be available and functioning. Remote filter removal, transfer, sampling, storage and packaging equipment need to be in place or procured to enable timely filter replacement.
- Procedures covering filter replacement, spent filter handling equipment operation and spent filter disposal are required to support the program.
- Development of a filter media specification is critical to ensure that the filters procured will remove the particles of concern. Vendor particle size ratings should not be accepted at face value because there is no standard filtration efficiency definition. Filters should be tested to the requirements of ASTM F 795-88 as a minimum.

At DCPP, pretreatment was successful in removing particulate activity from liquid radwaste during from 1986 until 1989. Upon the failure of this treatment method, strategically applied mechanical filtration methods have and are being adapted. Submicron filters are in service upstream of the radwaste system and can be employed in the treatment of radwaste ion exchanger effluent. Further examination of pretreatment techniques and inorganic filtration/ion exchange deep bed media will be performed on particulate laden outage liquids in 1991.

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