

THE APPLICATION OF POLYELECTROLYTES TO IMPROVE LIQUID RADWASTE TREATMENT SYSTEM RADIONUCLIDE REMOVAL EFFICIENCY

W.A. Homyk and M.J. Spall
Consolidated Edison Company
J.N. Vance
Vance and Associates

ABSTRACT

At nuclear plants, miscellaneous waste water treated in the liquid radwaste processing system contains a significant fraction of suspended particulate materials ranging in size from a few microns down to the submicron region. The finer particles that typically exist as colloids are generally negatively charged by virtue of inorganic and organic anions absorbed onto the particle surfaces. Because many of the radionuclides exist as colloids and resist agglomeration and settling, they are not easily removed by mechanical filtration or ion exchange processes. The colloidal materials will easily pass through most filters with conventional pore size ratings and through most ion exchange media. This leads to poor decontamination Factors (dFs) and higher radionuclide releases to the environment.

A laboratory-scale testing program was conducted at Indian Point Unit #2 to determine the effectiveness of the use of organic polyelectrolytes to destabilize colloidal suspensions in liquid radwaste. Destabilizing colloidal suspensions will improve the removal efficiencies of the suspended material by typical filtration and ion exchange processes. The increased removal efficiencies will provide increased dFs in the liquid radwaste treatment system.

The testing focused on identifying the specific organic polyelectrolytes and the associated dosages which would be effective in destabilizing the colloidal suspensions on actual waste water samples. The testing also examined the filtration characteristics of the water source to determine filter parameters such as: body feed material, body feed dosages, specific flow rates, etc., which would provide the basis for the design of filtration systems for these applications.

Based on the testing effort described herein, the following are the major conclusions from this investigation:

- Two different cationic polyelectrolytes were found to destabilize colloidal suspensions of radionuclides such as: Cr-51, Mn-54 Co-60, and Fe-59.
- Increases in overall dFs across a simulated vendor ion exchange treatment system ranged from 5 to 300 depending of the colloidal fraction of the radionuclides in the waste stream sample.
- Each waste collection tank will have a different stream chemistry and corresponding differences in the colloidal fraction of the species and in the level of improvement in the dFs achieved by the use of a polymer.
- A limited correlation between polymer dosage and waste collection tank turbidity was found as follows: Based on the favorable lab scale tests, a full scale polymer addition skid was constructed onsite and placed into service in April 1989. This skid pumps a polymer mix directly into the influent line to the liquid radwaste ion exchange processing skid at the dosage levels previously listed. In the actual full scale field tests, the polymer improved average radionuclide removal efficiencies for colloidal cobalts by a factor of 10 for cobalt-58 and cobalt-60. All other nuclides were removed by improved factors of 2 to 200. These improved decontamination factors have been observed for a wide range of turbidity and activity levels.

<u>Turbidity (NTUs)</u>	<u>Polymer Dosage (PPM)</u>	
	<u>Betz 1153</u>	<u>Betz 1192</u>
1-5	5	1
6-10	10	2
10-15	15	5
20	20	10

INTRODUCTION

Indian Point Units 1 and 2 are located on the Hudson River in Buchanan, New York. Consolidated Edison Co. as owners and operators of the operating 900-Mwe PWR Unit #2 and the retired PWR Unit #1, has become increasingly interested in improving the performance of its radioactive waste water treatment system while reducing resulting waste volumes and discharges to the Hudson River.

The plant has used a variety of waste water treatment methodologies since startup in 1974. A waste evaporator package was used until 1981. The two units had numerous problems and never operated at their rated capacities of 25 gpm. Since 1981, all plant liquid radwaste has been processed by demineralization. First with disposable demineralization vessels until 1985, and then sluicable reusable stainless steel pressure vessels from 1985 to present (1). Demineralization has shown dramatic positive results when compared to evaporation.

In late 1988, Indian Point set a 1989 goal to reduce the amount of radioactivity discharged in its treated effluent by 75%, and to reduce the total liquid discharged by 10% while generating the same amount of waste water related resin and filters as in 1988. The 75% reduction in part was based on the desire by plant staff to eliminate differences in the Cesium-134, Cesium-137 and Co-60 treated effluent discharges from Indian Point Unit #2 as compared to the New York Power Authority's Unit #3. Total whole body doses due to effluent releases were well within effluent limits. In order to achieve these goals plant staff required the demineralizer vendor to use cobalt and cesium specific resin, use a 48" diameter deep bed filter vessel, and to closely monitor influent chemistry and activity to match vessel loadings and flow rates to produce the desired 5E-5 uci/cc effluent activity. In order to reduce input to the liquid radwaste system, plant staff used live load valve packings, eliminated non-radioactive inputs from steam, equipment, seal water and building leakage. These actions reduced waste water volumes from 3,500,000 gallons in 1987 to 2,226,600 gallons in 1989. Total resin and filters generated and shipped for treating water in 1988 was 499.8 ft³. In 1989, the volume of resin and filters generated was 598 ft³. Thus, although the waste generated was slightly higher in 1989 than 1988, the reduction in effluent radioactivity releases and the effects of refueling outage water treatment normalized the difference.

Concurrent to the implementation of these waste water treatment goals, Operations staff was having reactor cavity water clarity problems during fuel movement in scheduled outages. These problems resulted in critical path delays from several hours to more than one day. An investigation showed that suspended oxides of iron in the refuel-

ing cavity were reflecting and absorbing light resulting in poor visibility. These fine colloidal particles were not being removed by mechanical filters such as the reactor cavity skimmer and submersible filters.

Subsequent tests modifying the techniques used at Three Mile Island Unit #2 showed that the application of organic polyelectrolytes could destabilize colloidal materials and improve low clarity conditions (2). The results will be evaluated for possible full scale skid development and associated reactor coolant system chemistry system evaluation for the spring 1991 refueling outage. Results also indicated the possible use of polymer injection in the influent stream to waste water demineralizers which is the subject of this paper.

BACKGROUND

It is well known that many radionuclides in liquid waste streams in nuclear plants exist, in part, in a colloidal state. The fraction of the radionuclide that exists in the colloidal state as compared to an ionic state, or as larger particulate materials is a function of the waste stream chemistries and the particle characteristics. Colloids are extremely small particles suspended in the liquid waste stream. The particles have a surface electrical charge, either positive or negative. By virtue of the surface charge, the particles will repel each other and resist any natural agglomeration tendency to form larger particles. Hence, once formed, colloids tend to remain suspended over long periods of time and thus, the term "stable" is usually applied to the colloidal system. More importantly from a waste treatment point of view, the extremely small particles (unagglomerated) will pass easily through most conventional filters and ion exchange media. Consequently, dFs for the colloidal radionuclides are generally small because of little or no removal. In most natural waters and in typical plant waste streams, the colloidal particles have a negative charge. The negative charge results from the adsorption of anions, particularly, organic acids, onto the surface of the particles. The charge density on the particle surfaces varies with the waste stream chemistries, the anions involved and the particle characteristics. Recognizing that the existence of colloids in liquid waste streams pose potential treatment problems, EPRI sponsored research to investigate methods of deal with the colloids. In one EPRI research effort (3), organic polyelectrolytes were investigated as a pretreatment method to destabilize Co-58 and Co-60 colloids and, thereby, increase the dFs achieved in the liquid radwaste treatment system. In two other studies (2)(4) organic polyelectrolytes were investigated as a means of destabilizing the non-radioactive colloids to improve the filterability of the waste stream. This would, thereby, increase the filter run lengths and decrease waste volumes. Regardless, of the ultimate objective to be achieved (i.e., improved dFs or filterability), the organic polyelectrolyte works essentially

on the same principal in destabilizing both radioactive or non-radioactive colloids.

The organic polyelectrolytes are typically large, long chain polymeric molecules with either negative or positive charges at reaction sites along the long chain. Non-charged polymers are also available. The organic polymers act by absorbing onto the colloidal particle where the opposite charges on the polymer chain and the particle surface react to effectively neutralize the surface charge. This is illustrated in Fig. 1. Elimination of the surface charge then allows the particles to agglomerate to form larger particles that can be removed by filtration. Because of the negative surface charges in most waste waters, only cationic polymers are of interest in waste treatment.

The basic structure of the organic molecule in the polymer may be one of several types, such as: poly-vinyl alcohol, poly-acrylic acids, poly-acrylamides, metamine formaldehydes and quaternary ammonium polymers. Generally, the different polymer formulations have varying molecular weights ranging from a few hundred thousand up to several million. The charge densities are also varied in the formulations from low to high. One polymer formulation may be effective at destabilizing a colloidal suspension in a given waste stream and another may not be effective. The reasons for the differences in the effectiveness are not well known owing to the extremely complex field of surface

chemistry. As a consequence of the complexities, it is difficult to predict which polymer and at what dosage a particular polymer will be effective in a given waste stream. The effectiveness depends on the particle characteristics, the surface charge density, the waste stream chemistry, the molecular structure of the polymer, the charge density of the polymer and the dosage applied. Usually a dosage range is found that is effective below which the polymer is ineffective and above which may cause the system to restabilize. The restabilization is caused by an overdose of the polymer causing an excess positive surface charge which again will cause the particles to repel each other. The inability to predict which polymer will be effective and what the dosage range will be is the basis for "jar" or lab-scale screen testing of the polymers using the actual waste water.

LABORATORY TESTING GOALS AND METHODOLOGY

The objectives of the laboratory studies were to:

- Identify one or more organic cationic polymers which would effectively destabilize the radionuclide colloids which exist in the miscellaneous liquid radwaste stream at IP-2.
- Quantify the effectiveness of the polymer by comparisons of the radionuclide dFs with and without the polymer addition.
- Identify an operating range of polymer dosages which would be applied to the liquid radwaste stream.

The testing was conducted using actual radioactive influent samples. Typical influent characteristics are given in Table I.

The test program was conducted to evaluate a series of cationic organic polymers supplied by Betz Industrial Corporation. The polymers were screened for effectiveness over a range of dosage in combination with a body feed dosage level in a millipore filter test rig shown in Fig. 2. The filtration test parameters recorded for the screening were effluent turbidity and filter delta pressure. If the polymer(s) is effective in destabilizing the colloids in the waste water, the filter effluent turbidity will be lower than the effluent turbidity measured when no polymer is added. Also, the delta pressure rise across the filter will generally be lower if the polymer is effective in destabilizing the colloids as compared to filter runs with no polymer addition.

The testing method involved the addition of polymer and filter aid material at the test dosages to a beaker of waste water sample. The beaker was continuously stirred. The waste water was then pumped through a millipore filter which contained a 25 μm filter screen. The filter delta pressure was recorded as a function of filter run time and effluent samples were collected for turbidity measurements. It was assumed that if the non-radioactive (metal oxides)

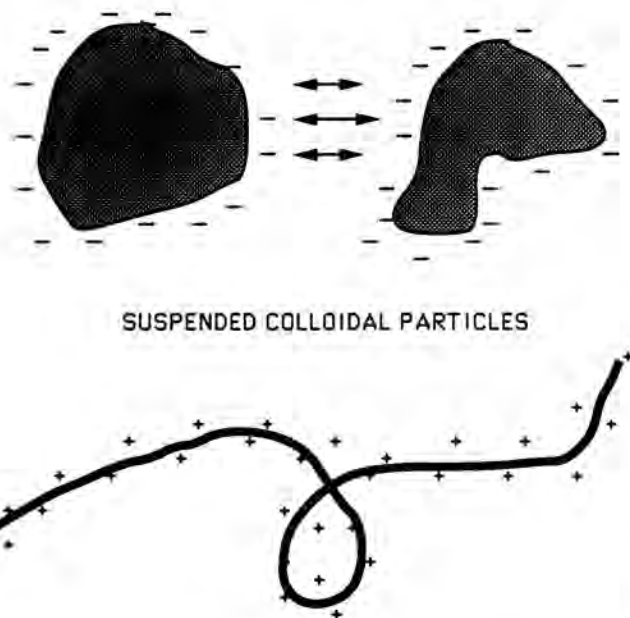


Fig. 1. Organic Polyelectrolyte Molecule.

TABLE I
1989 Average Indian Point Waste Water Influent Chemistry

<u>Parameter</u>	<u>Concentration/Units</u>		<u>Comment</u>
Radioactivity	Ag-110M	3.0E-5	Co-58 makes up 74.7% of all activity
	Co-57	8.0E-6	
	Co-58	5.0E-3	
	Co-60	1.0E-3	
	Cr-51	1.0E-4	
	Cs-134	2.0E-5	
	Cs-136	6.0E-5	
	Cs-137	3.0E-4	
	I-131	4.0E-6	
	La-140	5.0E-5	
	Mn-54	5.0E-5	
	Nb-95	2.0E-5	
	Sb-124	2.0E-5	
	Sb-125	3.0E-5	
Conductivity	116 uMHOS	Maximum 259 uMHOS	
pH	5.0 - 7.0	Average 6.03	
Turbidity	5.0 - 30.0 NTU	Average 14.0 NTU	

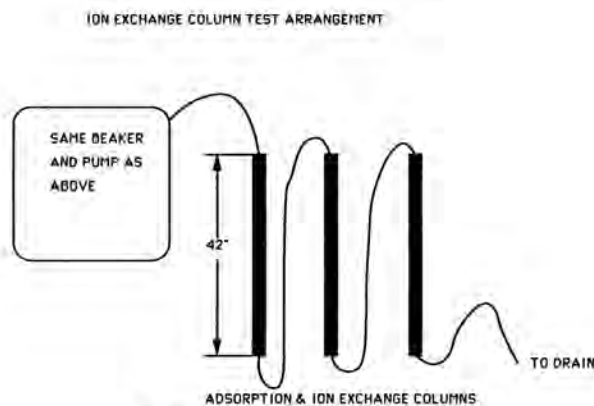
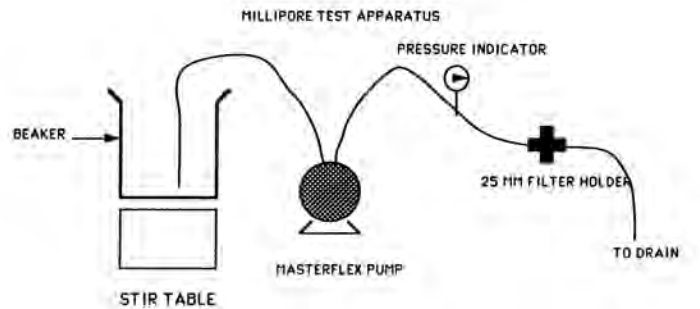


Fig. 2. Test Apparatus.

colloidal material, which controls the filterability of the waste, is destabilized then the radionuclide colloids would likewise be destabilized. This screening technique is easier and faster than the ion exchange dF method reported in the EPRI study (3). Once the polymer(s) and dosage were determined in the millipore-filter screening tests, then the sample water was processed through laboratory-scale columns of ion exchange materials loaded similar to the loading in the vendor process system used to treat liquid waste. Influent and effluent gamma spectroscopy measurements were made to measure the dFs across the media with and without the addition of polymer.

LABORATORY RESULTS

The principal effect being sought in the application of polymers to radwaste processing is improved radionuclide dFs. However, the polymer screening is done on a filtration basis with improved filterability as the indicating parameter for the effectiveness of the polymer addition. After the effectiveness is demonstrated on a filtration basis, confirmation of the dF improvement is conducted on scaled ion exchange and carbon columns representing the radwaste processing configuration currently being provided by the demineralizer vendor.

The polymer screening tests were conducted at 4.0 gpm/ft². Because of the concern with body feed fines passing through the filter screens, the testing was conducted using a DE-Hyflo precoat applied to the screen. A body feed rate of 30 ppm DE-SSC (a Johns Manville Corporation Product) was used for the initial runs. The delta pressure was recorded as a function of time and effluent samples collected for turbidity measurements.

Experience at other plants has shown that the filterability of the waste is improved (i.e., slower rise in the delta pressure curve), and lower turbidities are achieved when the polymer is effective in destabilizing the colloidal suspension in the influent.

The first Waste Collection Tank (WCT) sample was water which had been received prior to the refueling outage and was considered typical for liquid radwaste. The turbidity on the untreated sample measured 8 NTUs. A series of different polymers and dosages were tested. Two polymers from the series were identified as effective in the initial rounds of testing. They were Betz 1153 and Betz 1192. The former polymer is a moderate molecular weight and moderate charge density polymer. The latter is a low molecular weight, high charge density that would be effective for moderate to high surface charges on the colloidal material.

Fig. 3 presents the test results for a no-polymer run and the Betz 1192 polymer runs at different dosages. From the curves, the exhibited dosage range for the effectiveness of the polymer is fairly narrow, 1 to 5 ppm. The optimum dosage from maximum effectiveness is 1 ppm for this par-

ticular waste sample. At 0.5 ppm the polymer is underdosed and at 10 ppm the dosage is on the verge of being in an overdosed condition.

Fig. 4 shows similar results for polymer Betz 1153. The results indicate that an underdosed condition at 2 ppm, a potential overdosed condition at 10 ppm and an optimum dosage at 5 ppm. The ratio of 5 ppm for polymer Betz 1153 and 1 ppm for polymer Betz 1192 is consistent with the ratio of the charge densities and correspondingly the polymer demand.

The delta pressure curves for both polymers, even at the optimum dosage, are relatively steep and are attributed in part to the fine grade of DE-SSC used as body feed material.

To measure the effectiveness of the polymer addition in improving processing dFs, three columns were set up in the laboratory to simulate the vendor waste processing system. The front column was loaded with vendor charcoal media D-310. The second column was loaded with layers of vendor resin media, D-210 and D-70. The third column was loaded with mixed-bed ion exchange resin. The first test run of waste collection tank sample water was made with no polymer addition or filtration to establish a base level performance for the system. Run number 2 was made with 1 ppm Betz 1192 and no filtration. Run number 3 was made with 1 ppm Betz 1192 and prefiltration. Effluent samples were collected after each column for gamma spectroscopy measurements to determine the dFs across each of the columns. Because the front column contained new charcoal which is known to exhibit high removal efficiencies at low throughput capacities, for the cobalt nuclides, the effluents for the remaining columns were below Minimum Detectable Activities (MDA) for all nuclides. This precluded any evaluation of the effectiveness of the polymer.

To avoid the reoccurrence of this problem, the front column of charcoal was bypassed for the next two runs. Run number 4 was made with no polymer addition and run number 5 was made with the addition of 1 ppm Betz 1192. Effluent samples were collected after the mixed-bed column in each run to measure the dFs across the system. The results of all five runs are shown in Table II.

An inspection of the results from runs 4 and 5 indicate that the use of the polymer Betz 1192 increases the dFs for Co-58 and Co-60 by factors of 2 and 5.6, respectively. The polymer reduced the total activity in the system effluent from 6.4 E-7 uCi/ml to 1.50 E-7 uCi/ml. This would indicate a relatively large fraction of the cobalts was ionic rather than colloidal and, therefore, amenable to removal by ion exchange.

The improvements in the dFs listed in Table II are quite large for the use of the polymer. This is particularly true for the nuclides relatively large fraction of colloidal

TABLE II
IP-2 Waste Collection Tank Test Results
(8 NTU Sample)

NUCLIDE	INFLUENT CONC.	COLUMN 1		COLUMN 2		COLUMN 3		SYSTEM dF
		EFFLUENT	dF	EFFLUENT	dF	EFFLUENT	dF	
RUN 1		NO POLYMER ADDITION - NO FILTRATION						
CO-58	6.40E-06	1.10E-06	5.8	<3.7E-8	>173	<2.3E-8	--	>278
CO-60	1.50E-05	4.50E-06	3.3	<4.4E-8	>340	<4.4E-8	--	>340
CS-134	4.60E-06	1.60E-05	0	<2.5E-8	>184	<1.6E-8	--	>288
CS-137	1.10E-06	9.80E-06	0	<4.2E-8	>26	<3.0E-8	--	>37
SB-125	1.80E-05	1.76E-05	0	1.70E-05	0	<4.7E-8	>362	<362
RUN 2		1 PPM BETZ 1192 -- NO FILTRATION						
CO-58	6.40E-06	3.50E-06	1.8	<3.0E-8	>213	<2.8E-8	--	>228
CO-60	1.50E-05	5.00E-06	3.0	<4.4E-8	>341	<3.7E-8	--	>405
CS-134	4.60E-06	1.60E-05	0	<2.2E-8	>190	<1.6E-8	--	>288
CS-137	1.10E-06	1.00E-04	0	<3.9E-8	>28	<2.6E-8	--	>42
SB-125	1.80E-05	1.70E-05	0	1.70E-05	0	<3.0E-8	>573	>573
RUN 3		1 PPM BETZ 1192 -- PREFILTRATION W/HYFLO						
CO-58	6.40E-06	1.90E-05	0	<2.6E-8	>246	<2.5E-8	--	>256
CO-60	1.50E-05	2.70E-05	0	<4.6E-8	>326	<3.8E-8	--	>395
CS-134	4.60E-06	1.90E-05	0	<2.6E-8	>177	<1.4E-8	--	>329
CS-137	1.10E-06	1.10E-04	0	<3.5E-8	>31	<2.8E-8	--	>39
SB-125	1.80E-05	1.80E-05	0	1.80E-05	0	<3.8E-8	>474	>474
RUN 4		NO POLYMER -- NO FILTRATION		COLUMN 1		D-210/D-70		
				COLUMN 2		MIXED-BED		
CO-58	6.40E-06			1.20E-07		53.3		
CO-60	1.50E-05			5.20E-07		28.8		
CS-134	4.60E-06			<3.1E-8		>148		
CS-137	1.10E-06			<4.7E-8		>23		
SB-125	1.80E-05			6.00E-06		3.0		
TOTAL	1.80E-04			TOTAL 6.40E-07				
RUN 5		1 PPM BETZ 1192 -- NO FILTRATION		2 COLUMNS AS ABOVE				
CO-58	6.40E-06			6.00E-08		106.7		
CO-60	1.50E-05			9.30E-08		161.3		
CS-134	4.60E-06			<1.84E-8		>250		
CS-137	1.10E-06			<3.5E-8		>31		
SB-125	1.80E-05			<5.5E-8		>327		
TOTAL	1.80E-04			TOTAL 1.50E-07		1200		

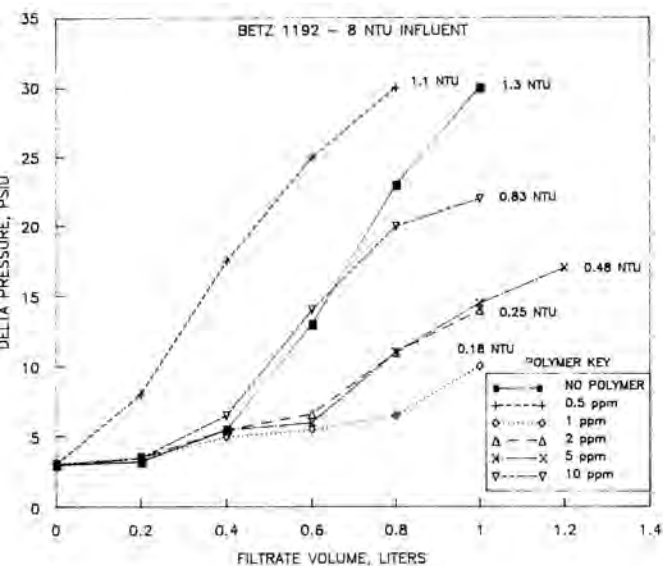


Fig. 3. IP-2 Radwaste Polymer Test Results 30 PPM DE-SSC BF and 4 GPM/Sq. Ft.

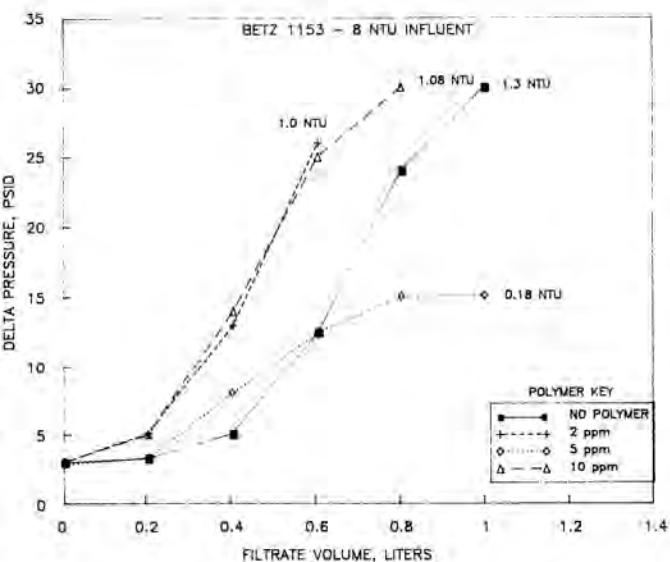


Fig. 4. IP-2 Radwaste Polymer Test Results 30 PPM DE-SSC and 4 GPM/SQ Ft.

species for these nuclides. It is interesting that nuclides such as the two cesiums, which are likely to be soluble, exhibited improved dFs with the use of the polymer. This is likely due to the absorption of the soluble nuclide onto the surfaces of the colloidal particulates. Overall, the Betz 1192 polymer improved the system dF by a factor of 4.3 for 8 NTU water, mostly due to the improvement in the removal of colloidal Co-60.

The methodology listed above was repeated for samples with measured turbidities of 6 and 12 NTU, respectively. The 12 NTU sample contained a large fraction of reactor coolant from the 1989 refueling outage. The results on the 12 NTU water were even more dramatic than the 8 NTU test with an overall system dF of 309 for the polymer addition case compared to the no polymer addition case. Here again, the improvement was mostly due to the removal of colloidal Co-60.

In summary, for the three waste collection tank samples of 6, 8, and 12 NTU obtained during the testing

Turbidity (NTUs)	Polymer Dosage (PPM)	
	Betz 1153	Betz 1192
1-5	5	1
6-10	10	2
10-15	15	5
20	20	10

period, the optimum dosages as a function of turbidity are listed below:

FULL SCALE FIELD TESTING

Con Edison radwaste personnel constructed a full scale polymer body feed skid per Fig. 5. Due to plant concerns regarding risks associated with inadvertently overdosing a 75,000 gallon waste collection tanks, the decision was made to body feed the polymer into the liquid waste transfer line between the waste feed pumps and 150 feet upstream of the waste processing skid. One slight disadvantage of this setup is that the shear and mixing of the waste feed pump impeller is not used to our advantage.

Each waste collection tank was treated as a unique batch of waste. The tank is sampled for conductivity, turbidity, pH, and activity. Based on the turbidity measurement, an appropriate amount of polymer is batched up to maintain a waste stream polymer concentration of 5 to 20 ppm Betz 1153. Essentially all of the testing conducted since April 1989 to present has centered on the use of the Betz 1153 polymer in conjunction with our vendor ion exchange skid. No other body feed material such as diatomaceous earth has been tested on a full scale basis.

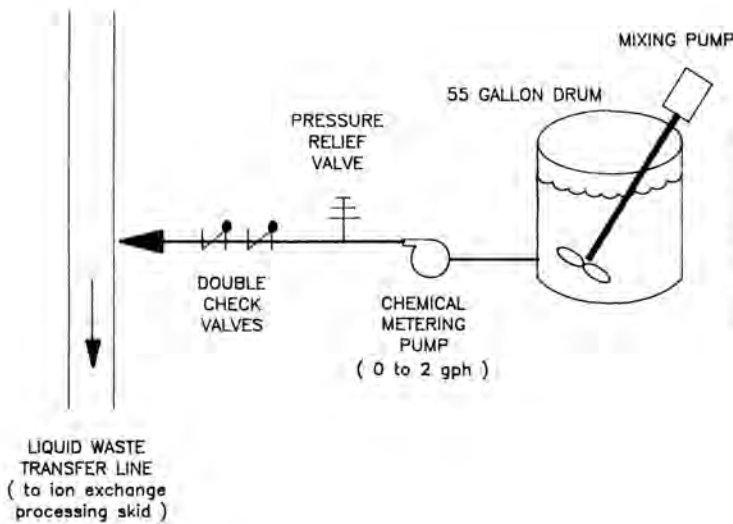


Fig. 5. Indian Point Station #2 Polymer Addition Skid.

Overall, the polymer has performed well. It has allowed us to lower our station effluent limit by a factor of ten from 5×10^{-4} uCi/cc to 5×10^{-5} uCi/cc, while not increasing wet waste resin volumes beyond 600 ft³/yr. This increase is significant when weighted against the ten-fold reduction in activity released to the environment.

Some problems have been encountered with inconsistent performance of the polymer that we believe are related to overdosing. On a few occasions the polymer has provided little or no improvement in system dF. For many other cases, water containing no detectable activity was produced. We have been able to easily adjust for these changing conditions by adjusting the chemical feed pump metering rate or by adjusting our normal processing flow rate of 15 gpm up to 20-25 gpm and monitoring the system dF. To verify system performance, we normally start our system without polymer feed, obtain baseline dF data, and then initiate polymer addition. Fig. 6 illustrates the dramatic effect Betz 1153 had on 10 NTU influent water generated during the Spring 1989 outage. Fig. 7 shows a similar high dF in June, 1989. Fig. 8 shows that polymer dF's can be maintained with 15 NTU influent during normal power operations.

FUTURE PLANS

Additional work remains to optimize our waste pre-treatment program. These efforts include:

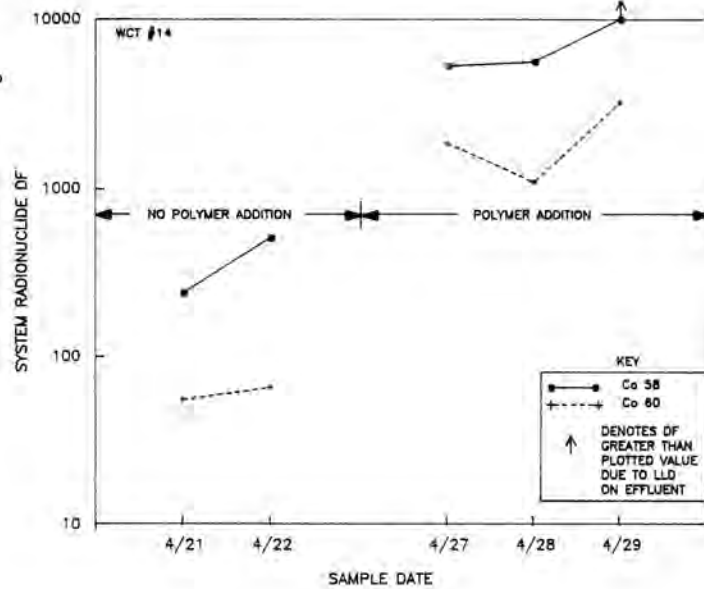


Fig. 6. IP-2 Radwaste Polymer Test Results Betz 1153 Polymer - 10 NTU Influent.

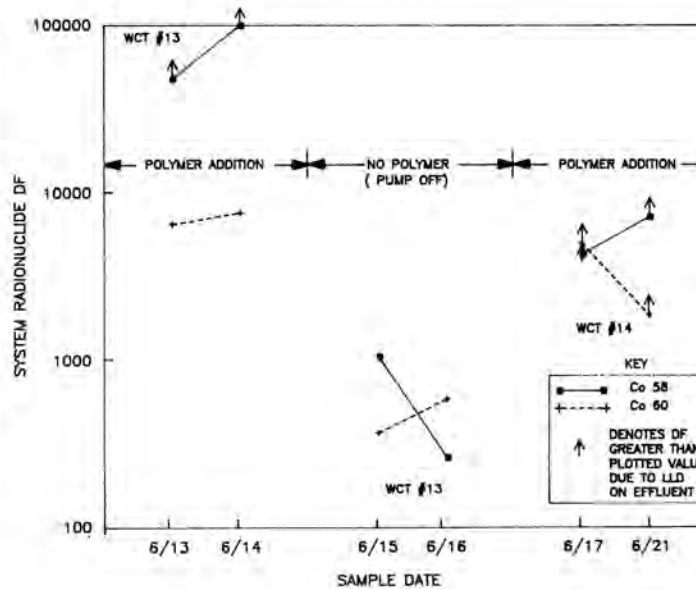


Fig. 7. IP-2 Radwaste Polymer Test Results Betz 1153 Polymer - 12 NTU Influent.

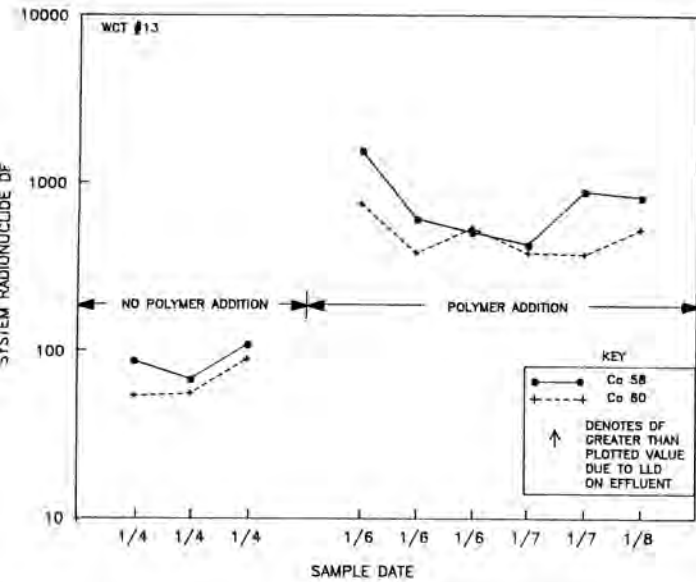


Fig. 8. IP-2 Radwaste Polymer Test Results Betz 1153
Polymer - 15 NTU Influent.

- Alternate polymer testing (i.e., Betz 1192) including the evaluation of use of body feed materials in conjunction with polymers.
- Confirmation of optimal polymer doses over a wider range of turbidity, conductivity, and activity levels.
- Construction of a permanent pre-treatment skid.

REFERENCES

1. W.A. HOMYK, D.J. MAFFEI AND M. KIRSHE, "Optimization of PWR Waste Water Treatment: A Case Study - Consolidated Edison Indian Point II" Waste Management "88", Tucson, AZ. Volume 1, p. 477.
2. J.N. VANCE, "Filtration Improvement Study at Three Mile Island Unit 2," EPRI Report NP-5367, October, 1987.
3. R.M. PROPST et al, "Pretreatment and Selective Materials for Improved Processing of PWR Liquid Radioactive Wastes," EPRI Report NP-5786, July, 1988.
4. J.N. VANCE, "BWR Radwaste Precoat Filter Optimization" EPRI Report NP-5483, April, 1988.