Evaluation of High Cross Linked Cation Gel Resins in an MPA Environment at Byron and Braidwood

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Abstract

The use of 3-methoxypropylamine (MPA) has been instrumental in reducing corrosion product transport to steam generators at the Braidwood and Byron units for over 8 years. During this time the blowdown demineralizers have been operated past the amine break. This operation allows for low level leakage of sodium off of the blowdown demineralizer resin, which increases the sodium to chloride ratio in the steam generator chemistry.

Exelon has many years of operating experience using 20% cross linked macroporous cation resins in the blowdown demineralizers. MPA-to-sodium selectivity coefficients for this resin have been calculated and used to predict the effects of operation past the amine break on steam generator chemistry. More recently, further optimization of the MPA program has been realized through the use of newly developed high cross linked cation gel resins. These resins have a much higher capacity than the macroporous resins. The sodium leakage when operated past the amine break for the new high cross linked cation gel resins will be evaluated in this paper. A comparison of this performance will be made with the experience of the macroporous resins previously used.

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I) INTRODUCTION

The use of high cross linked cation resins have been employed at Exelon since 1995. This choice of resin was part of an overall optimization of the secondary chemistry program which allowed the blowdown demineralizers to be operated past the amine break for a significant period of time.[1] This was a source of great cost savings. The limiting factor in blowdown resin operation is the amount of sodium leakage experienced. With the reduction of sodium source terms in all of the units, the amount of allowable sodium leakage off of the blowdown resins has become a higher contributing factor to the overall steam generator sodium concentration.. Further reductions in blowdown flowrates and the implementation of a strict sodium blowdown concentration goal have impacted on the cost savings of the blowdown resins. Performance issues with the resins are seen in real time in the steam generator chemistry measurements.

The Braidwood and Byron Units are 4 loop Westinghouse design 1200 MW PWRs. Byron is a two unit plant that is located near Rockford Illinois. Braidwood is a two unit plant that is located about 100 miles south of Chicago Illinois. The Unit 1's at both sites have replacement B&W steam generators. The Unit 2's at both sites have Westinghouse Model D5 steam generators. Partial flow condensate polishers are typically used on start ups or during circulating water leaks. The secondary system clean up is attained through the use of blowdown demineralizers. This system has two demineralizers in parallel that contain 3.4 m^3 (119 ft^3) of resin each. Blowdown flow was originally maintained between 300 and 360 gpm with both beds in service. However recently, all four units have reduced the blowdown flowrates to less than 250 gpm through a single blowdown bed with the parallel bed in standby.

The secondary chemistry at all four units uses 3-methoxypropylamine, MPA, as the pH agent with hydrazine for oxygen scavenging. Ammonia is present due to the breakdown of the hydrazine. Typical steam generator blowdown concentrations for MPA and ammonia are 12 ppm and 0.3 ppm respectively. Hydrazine is maintained around 100 ppb in the feedwater.

II) DATA

The following blowdown resins have been used at Byron and Braidwood:

- RWM 270
- Amberlite IRN 99
- Amberlite IRN-170
- Dowex 545C
- Dowex 545C & SBR

Where,

- RW270 is 4:1 by equivalence mixture of Ambersep 200 (20% crosslinked macroporous cation) to a 10% crosslinked gel anion
- IRN 170 is 1:1 by equivalence mixed bed of IRN 99 (16% crosslinked gel cation) and IRN 78 (10% crosslinked gel anion)
- Dowex 545C & SBR are mixed 1:1 by equivalence using 545C (14% crosslinked gel cation) and SBR (10% crosslinked gel anion).

The blowdown beds were loaded with one of the following ratios of these products:

Table I Resin Amounts Used in Exelon Blowdown Demineralizers

	IRN 99	Dowex 545C	RWM 270	Amberlite IRN-170	Dowex 545C & SBR			
Location	Cation Resin, m^3 (ft^3)	Cation Resin m^3 (ft^3)	Mix bed m^3 (ft^3)	Mix bed m^3 (ft^3)	Mix bed m^3 (ft^3)	Total Volume Resin, m^3 (ft^3)	C:A Eq Ratio	Bed Depth, m (ft)
Byron Brwd			3.4 (119)			3.4 (119)	4.0	1.3 (4.21)
Byron	1.4 (49)			2 (70)		3.4 (119)	3.2	1.3 (4.21)
Byron		1.4 (50)			2 (70)	3.4 (120)	3.3	1.3 (4.25)
Brwd	1.4 (49)			2 (70)		3.4 (119)	3.2	1.3 (4.21)

The RWM 270 mixture was used from 1995 through the end of 2001 at Braidwood and through the end of 2003 at Byron. From July 2002 until present, Braidwood has used IRN 99/IRN 170 as shown above.[2] Since February 2004, Byron has used IRN 99/IRN78 and Dowex 545C/SBR.[3]

A set of 10 different blowdown demineralizer runs were analyzed from the Byron data. Individual demineralizer runs from Braidwood were not distinguishable from the data sets since Braidwood frequently aligned the blowdown beds without notation in the data sets. The Braidwood data are used to show the overall effect of two different resin types. However, the Byron data sets are used in actual calculations of performance parameters.

A generalization from the Byron data sets of the sodium leakage curves is given in Figure 1. An upper and lower bound are shown in the curve to typify the data ranges as a function of loading. These curves show the three stages of leakage prior to amine break, during amine break and following amine break. Prior to amine break, no amine is interacting with the trace amounts of sodium being held by the resin at the bottom of the bed. The only competing cation for the resin in the sodium form is the hydrogen ion from the dissociation of water. At a pH of 7, this equates to 1 E-7 equivalents per liter or 0.1 ppb hydrogen ion. Sodium leakage prior to amine break is low because of the selectivity of sodium over hydrogen on the resin and the low concentration of hydrogen ion interacting with that resin. Once the amine begins to break through the bed, the equilibrium between sodium and amine changes the leakage characteristics. Amine ions of higher concentrations as compared with the hydrogen ions begin to elute the sodium off of the resin. The beds take about 10 days to become aminated. During the amination process the equilibrium sodium leakage changes. Once the bed if fully aminated, the leakage becomes more linear with time. Equilibrium leakage at the bottom of the resin bed is the dominant effect on the performance of these resins. Therefore, the purchasing specification for the amount of sodium on the resins is critical to the performance of these resins. The current Exelon purchasing specification for sodium on blowdown cation resins is 50 mg/kg (dry weight).

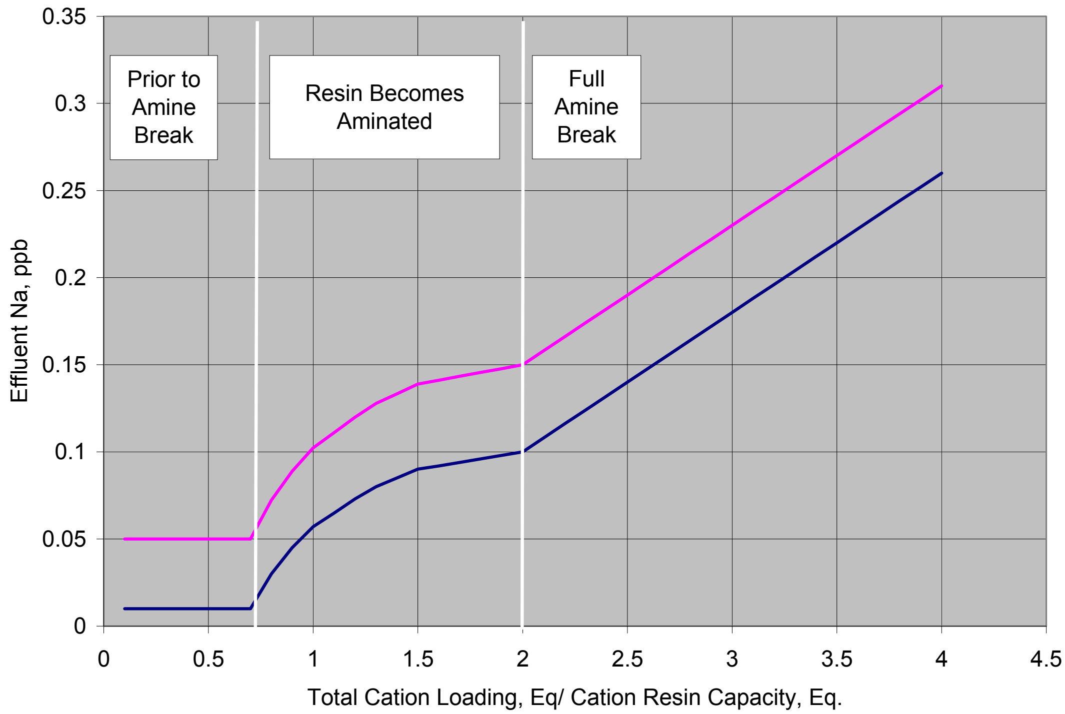


Figure 1 Example of Sodium Leakage With Amine Break RWM 270

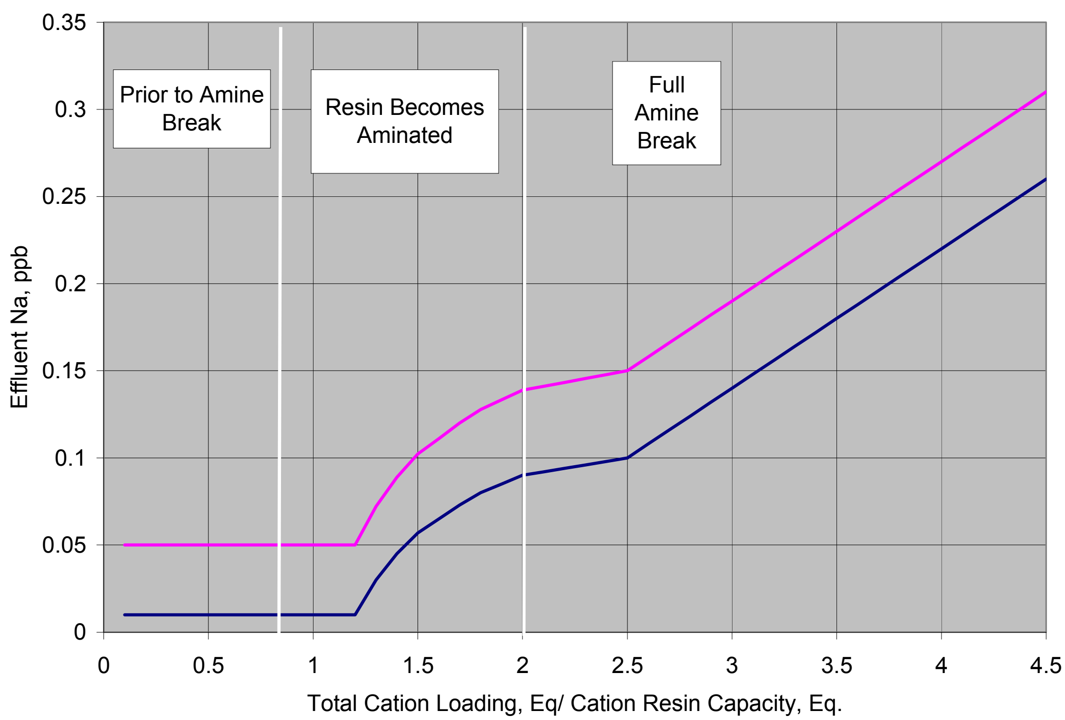


Figure 2 Example of Sodium Leakage With Amine Break IRN 99/545C

III) BRAIDWOOD DATA

In 2002 Braidwood steam generator chemistry was experiencing a source term of sulfates (ionic) which was traced back to the blowdown resins. Sample results from ion chromatographs showed that at times, 1.5 ppb to 2 ppb of sulfates were measured at the effluent of the demineralizers.[2] On January 9, 2003, 3 months prior to the unit 1 cycle 10 refueling outage, the first high cross linked gel cation resins were utilized in the blowdown demineralizers. The bed was loaded with 1.4 m3 (49 ft^3) of IRN-170 at the bottom of the bed and 2 m^3 (70 ft^3) of IRN 99 on the top of the bed. No detectable sulfate was measured off of the bed during the run. Also, the steam generator sodium concentrations were notably lower as compared with the previous measurements during the cycle (See Figures 3 and 4.[4,5] A similar trend was seen in the Braidwood Unit 2 steam generator sodium concentrations when the high cross linked resins were applied at the end of cycle 10 and in cycle 11(Figures 5 and 6).**[6,8]** However, the steam generator sodium concentrations alone can be misleading as performance indicators. Other circulating water related events were impacting the blowdown concentrations during cycles 10 and 11.

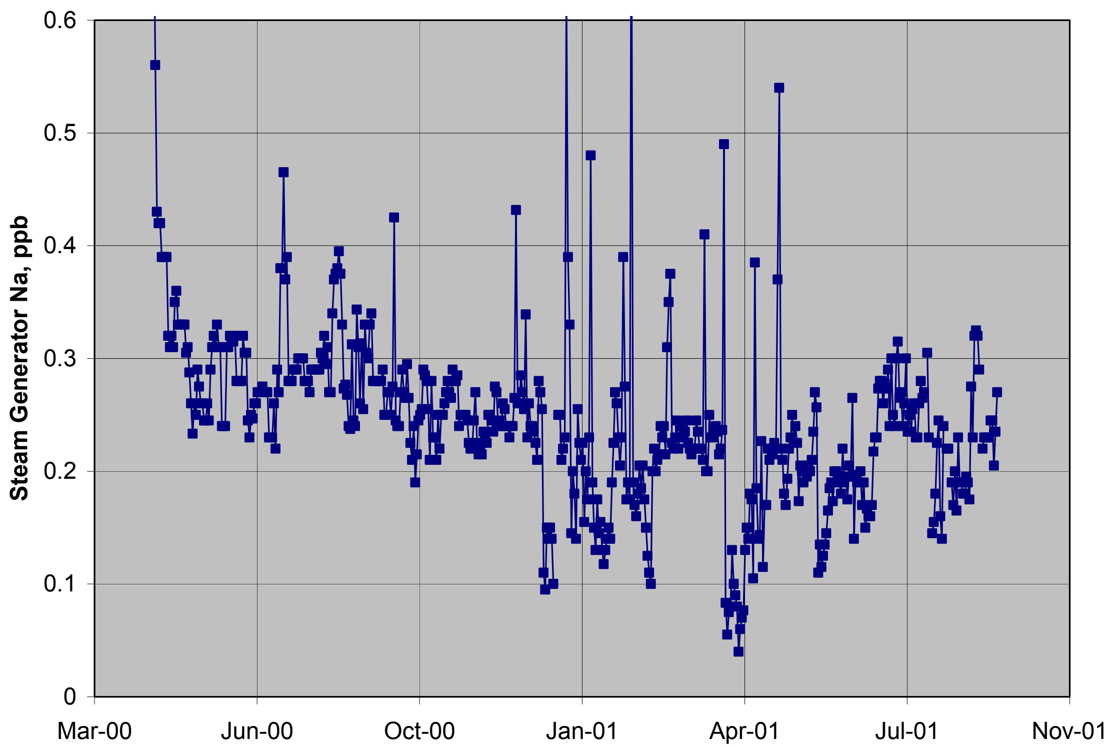


Figure 3 Braidwood Unit 1 Steam Generator Sodium - Cycle 10

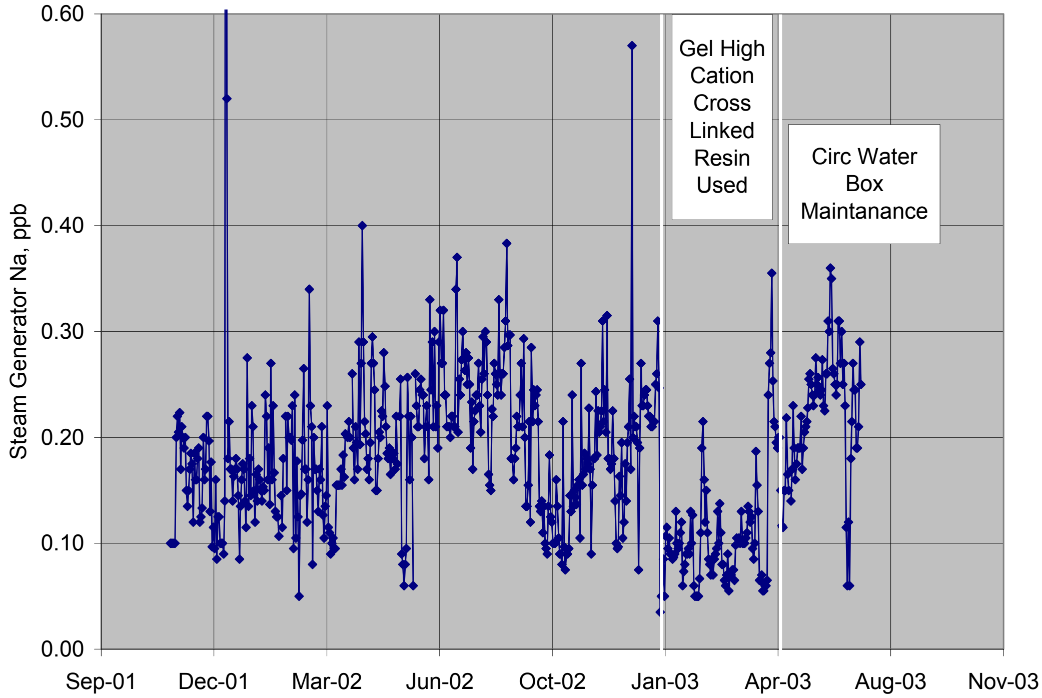


Figure 4 Braidwood Unit 1 Steam Generator Sodium - Cycle 11

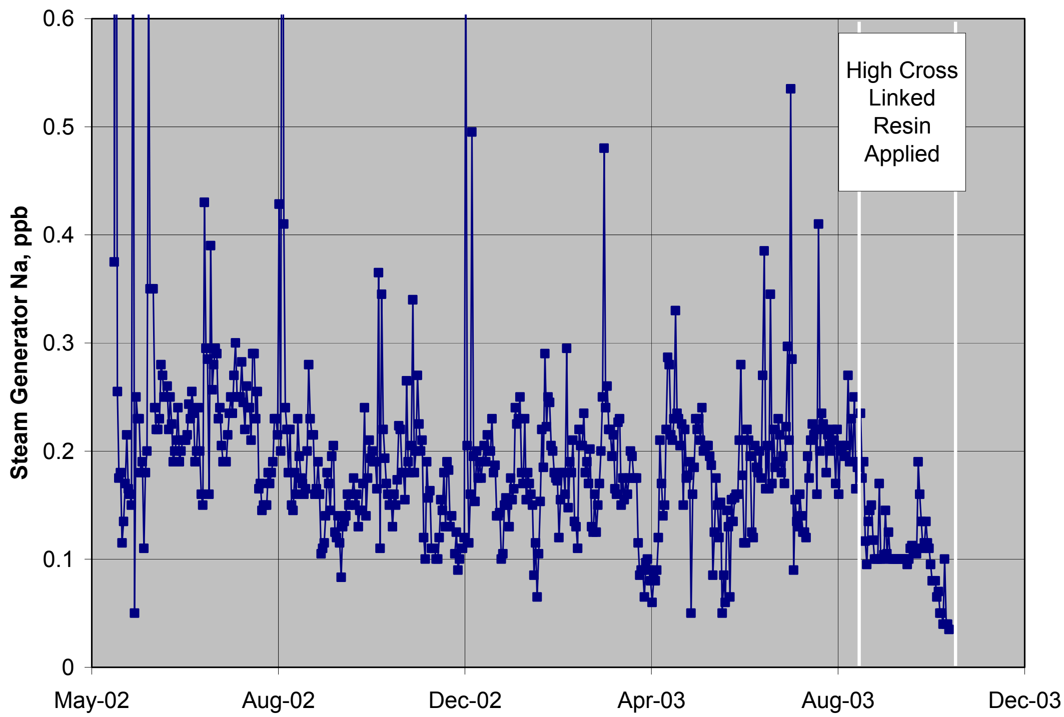


Figure 5 Braidwood Unit 2 Steam Generator Sodium – Cycle 10

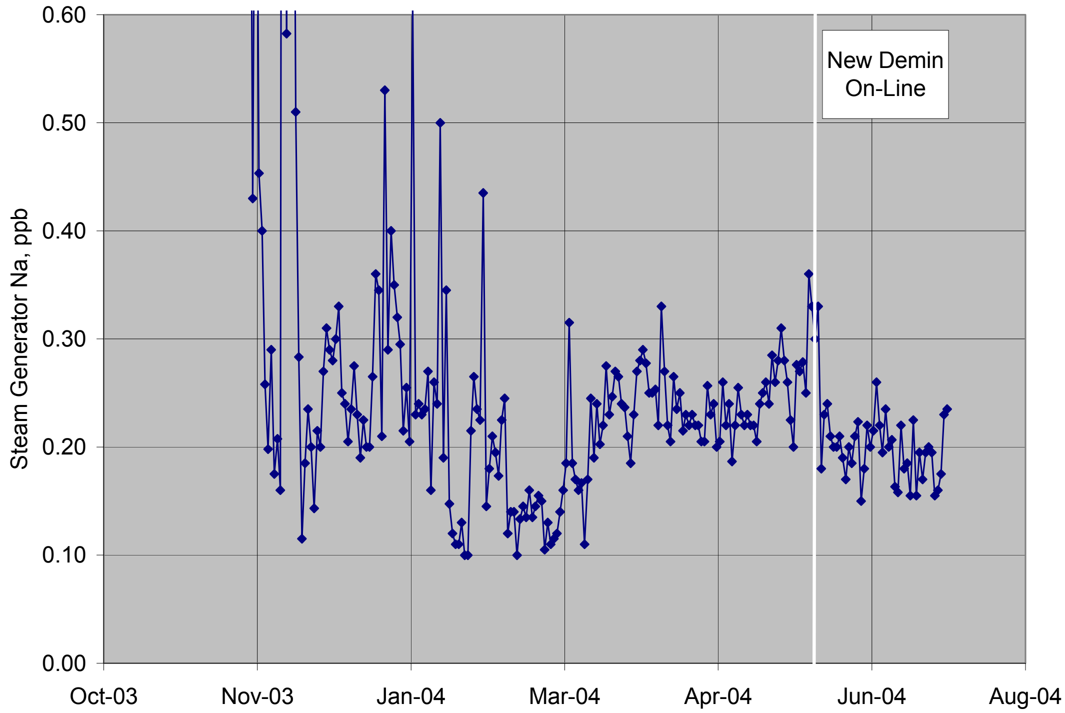


Figure 6 Braidwood Unit 2 Steam Generator Sodium – Cycle 11

IV) BYRON DATA

A more detailed evaluation of the resin performance can be made from the Byron data because of the addition of in-line sodium analyzers on the blowdown demineralizer effluent. From this additional data, the actual sodium leakage curves, and removal efficiencies for sodium on the resin can be assessed as a function of cation loading and amine break. This methodology normalizes effects such as changes in blowdown flowrates and variations in amine concentrations.

The following figures show the performance comparison charts of the Rohm and Haas DVB 20% crosslinked macroporous, the Rohm and Haas IRN 99 and Dow 545C cation resins.

The effluent sodium concentrations follow similar leakage patterns off of all of the resins. Amine break typically occurs at about 0.7 Total Cation Loading per Cation Capacity for all of the resin types. For the macroporous resins, the effluent sodium concentrations before amine break ranged from < 0.03 ppb to 0.17 ppb. During amine break, the effluent concentrations ranged from 0.05 ppb to 0.17 ppb. After amine break, the effluent concentrations were > 0.07 ppb.

The amount of high cross linked gel resin data reviewed was limited; and so, the following ranges are preliminary. For the high cross linked gel resins, the effluent sodium concentrations before amine break ranged from < 0.03 ppb to 0.05 ppb. During amine break, the effluent concentrations ranged from 0.05 ppb to 0.20 ppb. After amine break, the effluent concentrations were > 0.10 ppb. A notable consistent feature in the gel resin is the performance prior to amine break. The macroporous resin experience was more varied in this time frame. However, the effluent sodium concentrations during and after amine break were reasonably matched and in many cases better with the macroporous resin than with the gel.

A calculated removal efficiency of sodium across the bed was used to measure the performance of the sodium removal term. The sodium leakage off of the resin was much more of a function of equilibrium leakage based on the amount of sodium in the resin when received as opposed to the kinetic leakage caused by sodium loading during operation. For the RWM 270 resin, the results were very scattered over all regions of the operating ranges. The high cross linked gel resin showed consistently better performance prior to amine break and a consistent loss of performance during and after amine break.

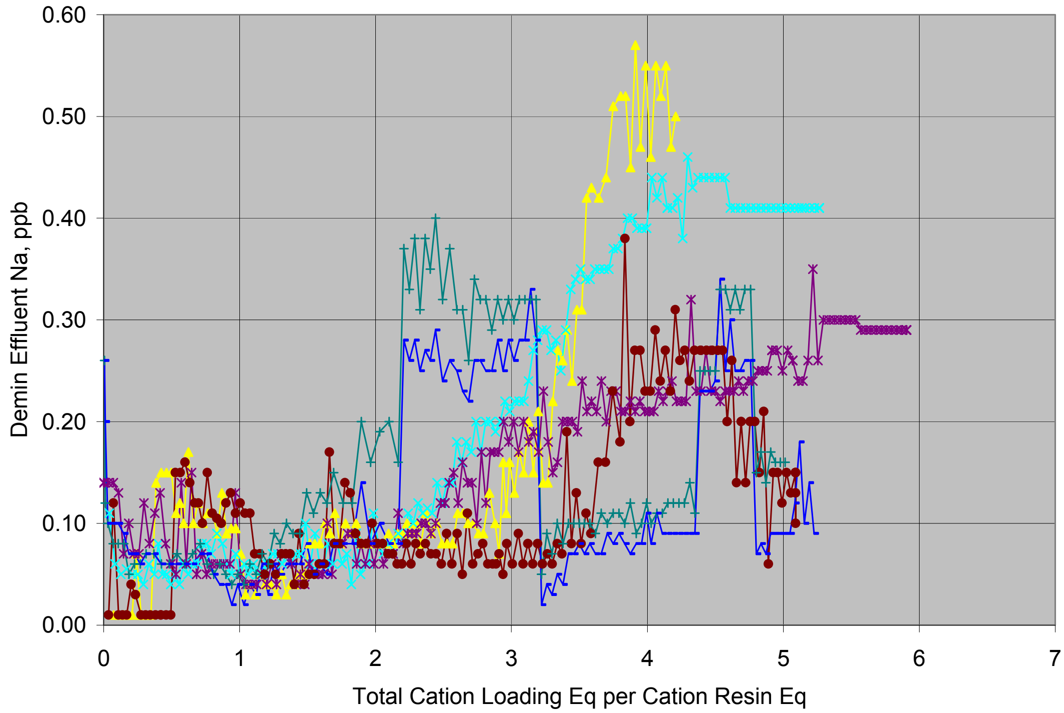


Figure 7 Effluent Sodium vs. Total Loading per Bed Equivalence for RWM 270

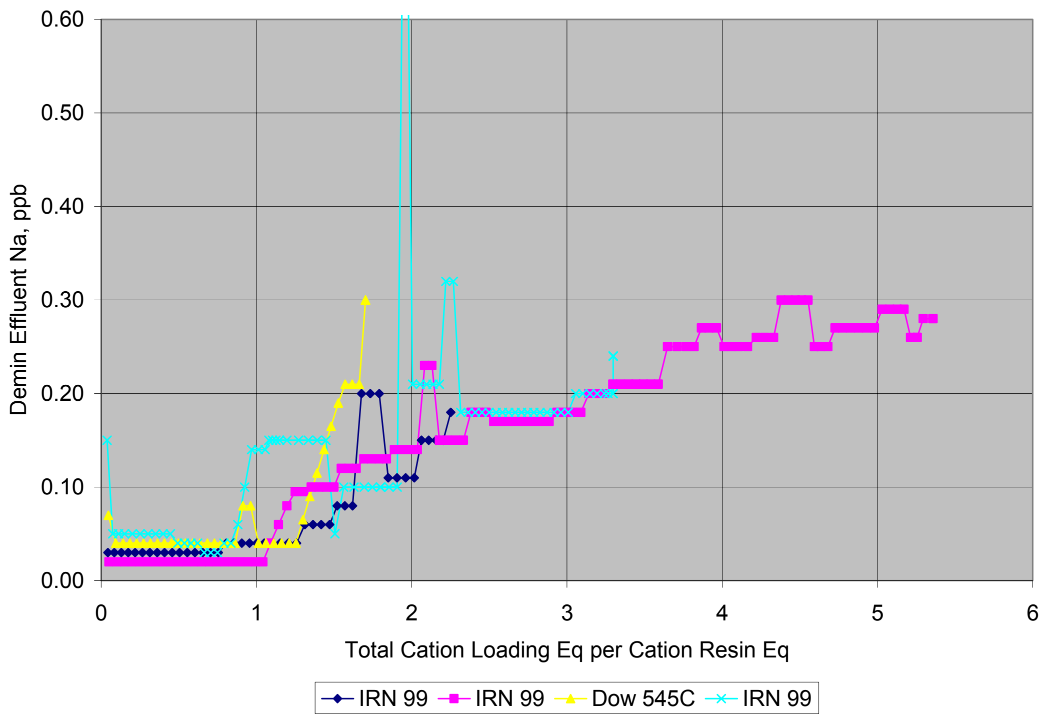


Figure 8 Effluent Sodium vs. Total Loading per Bed Equivalence for IRN 99 and Dow 545C

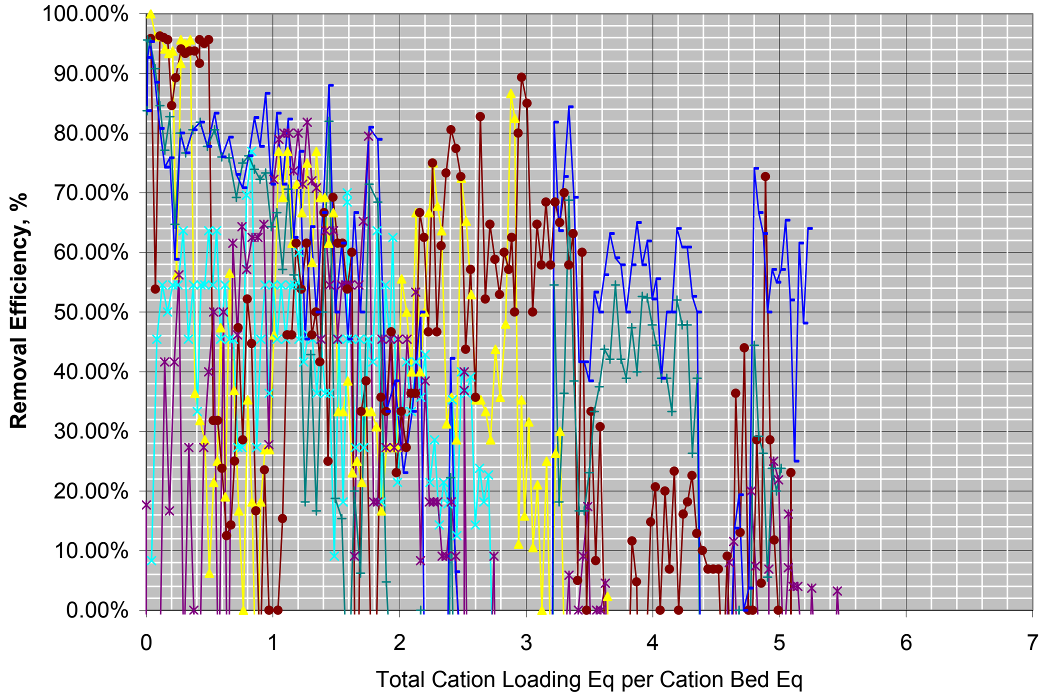


Figure 9 Removal Efficiency of Na vs. Total Loading per Bed Equivalence for RWM 270

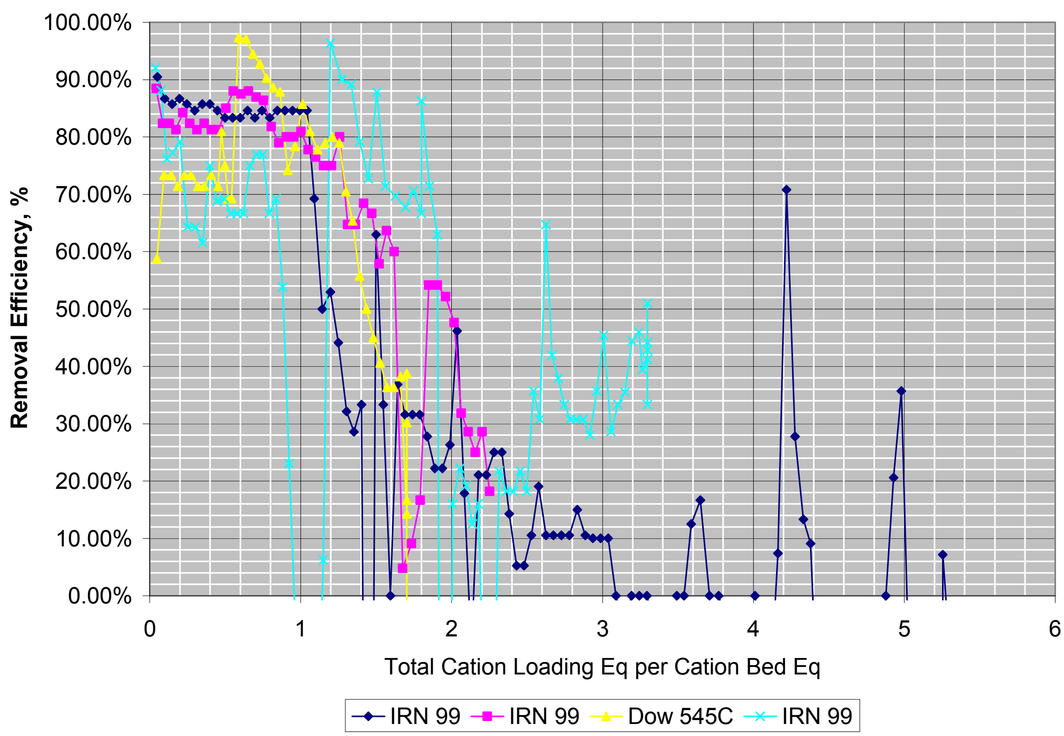


Figure 10 Removal Efficiency of Na vs. Total Loading per Bed Equivalence for IRN 99 and 545C

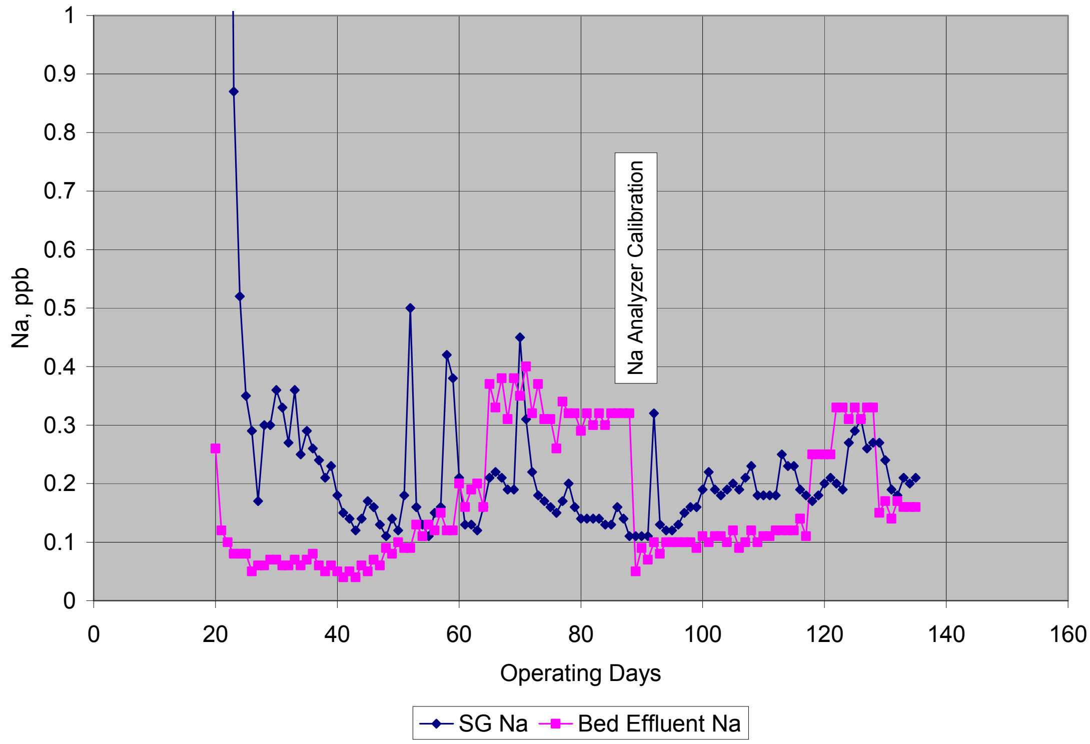
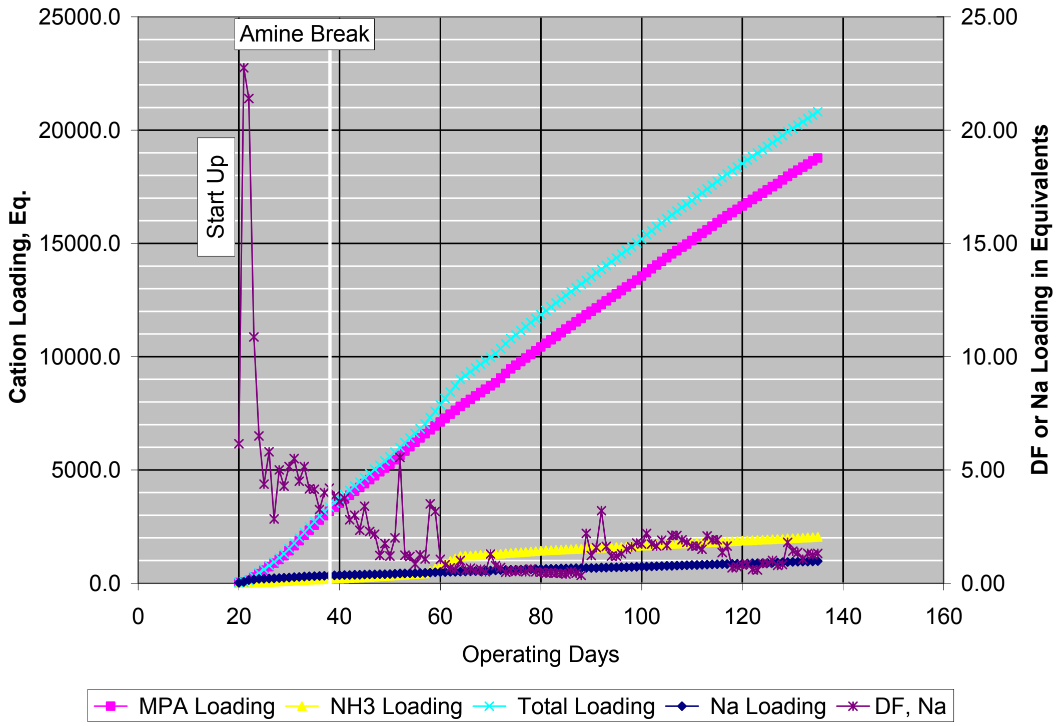


Figure 11 Byron 1A Blowdown Demineralizer March 2002



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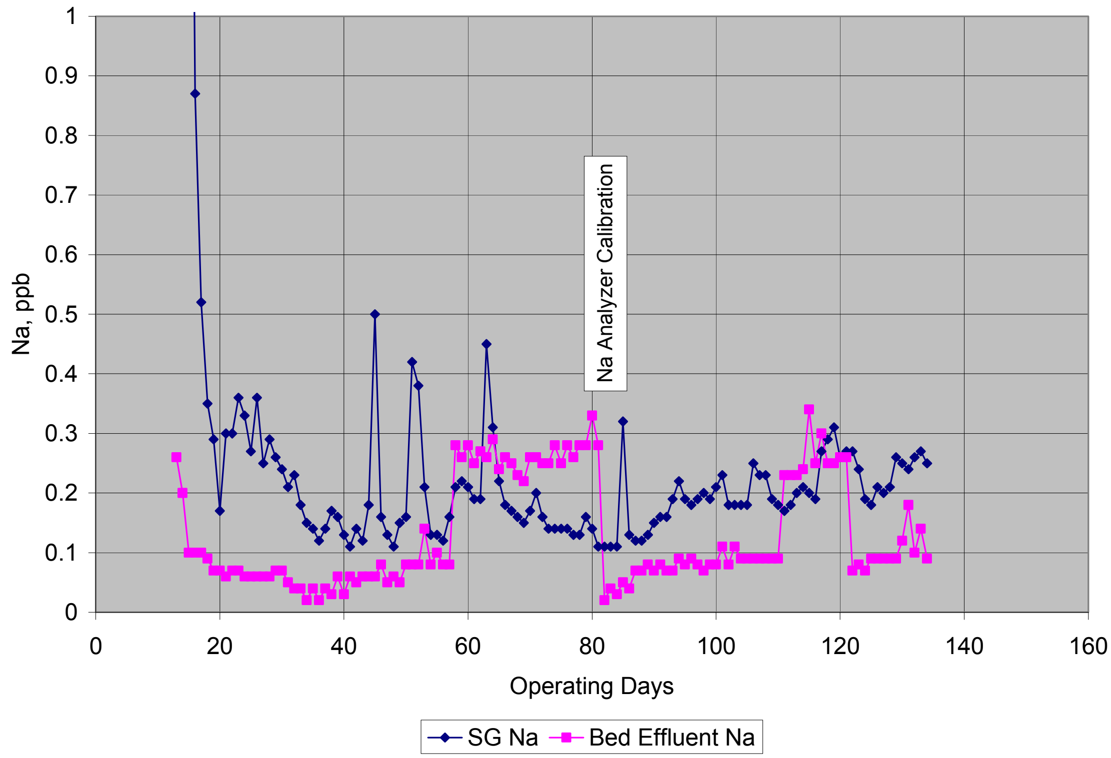
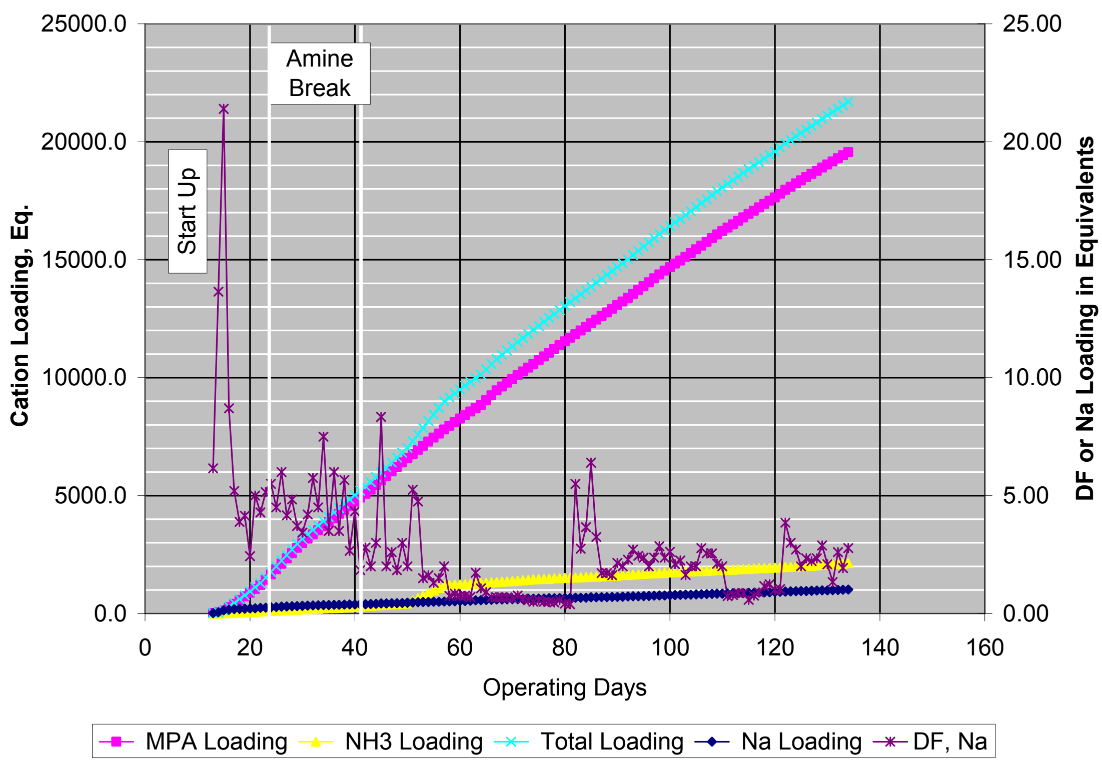


Figure 13 Byron 1B Blowdown Demineralizer March 2002



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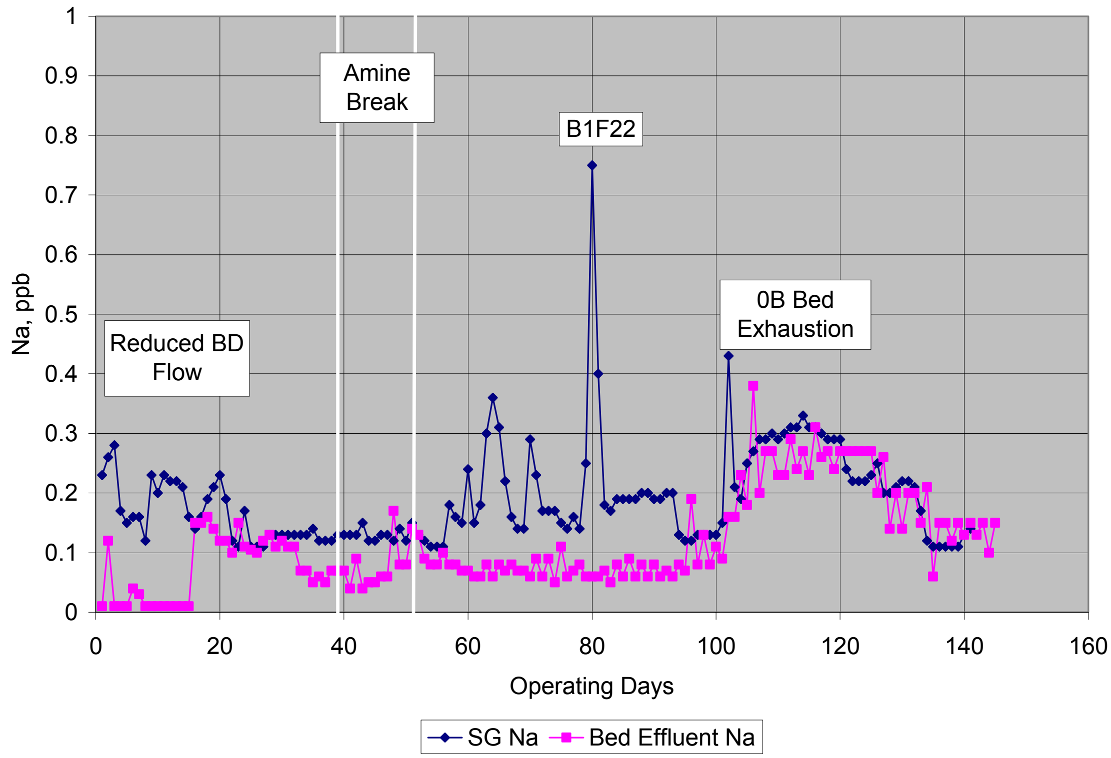
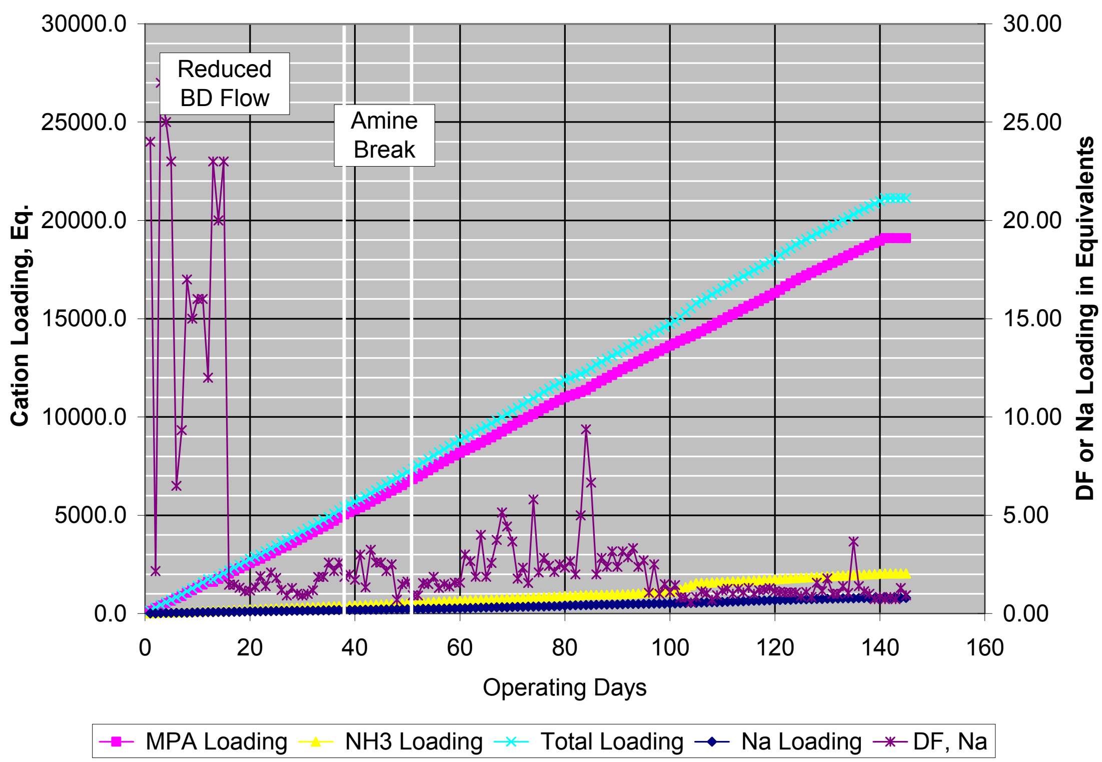


Figure 15 Byron 1A Blowdown Demineralizer July 2002



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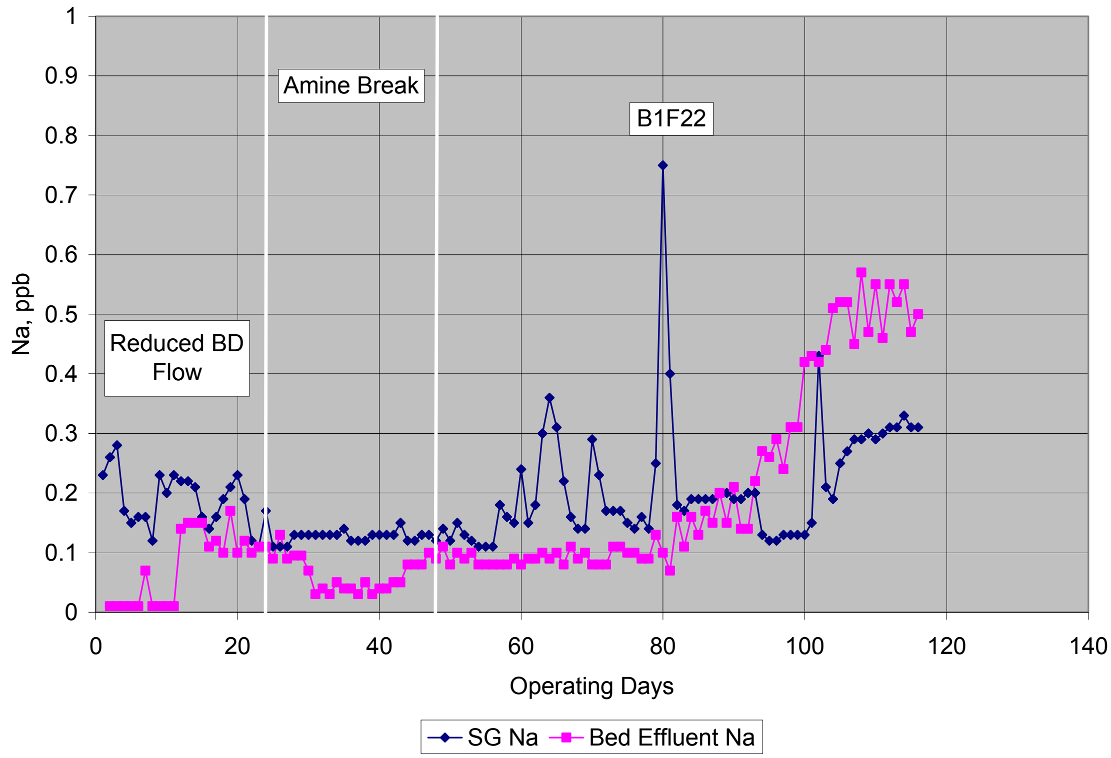

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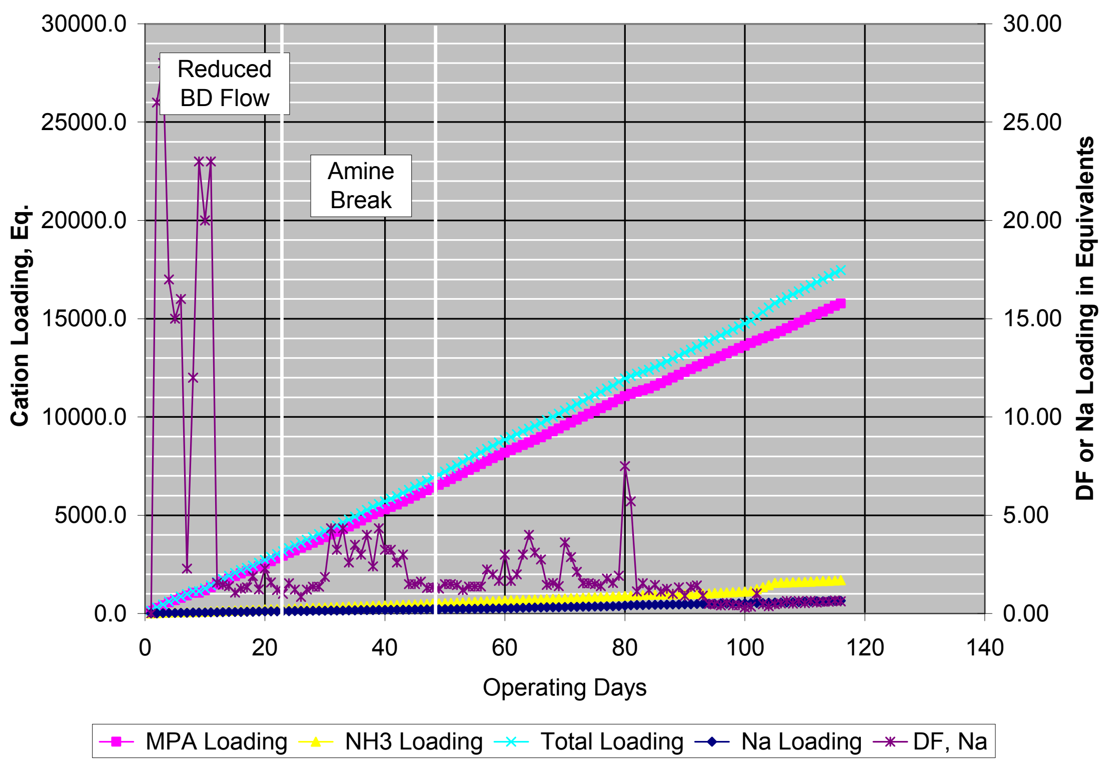

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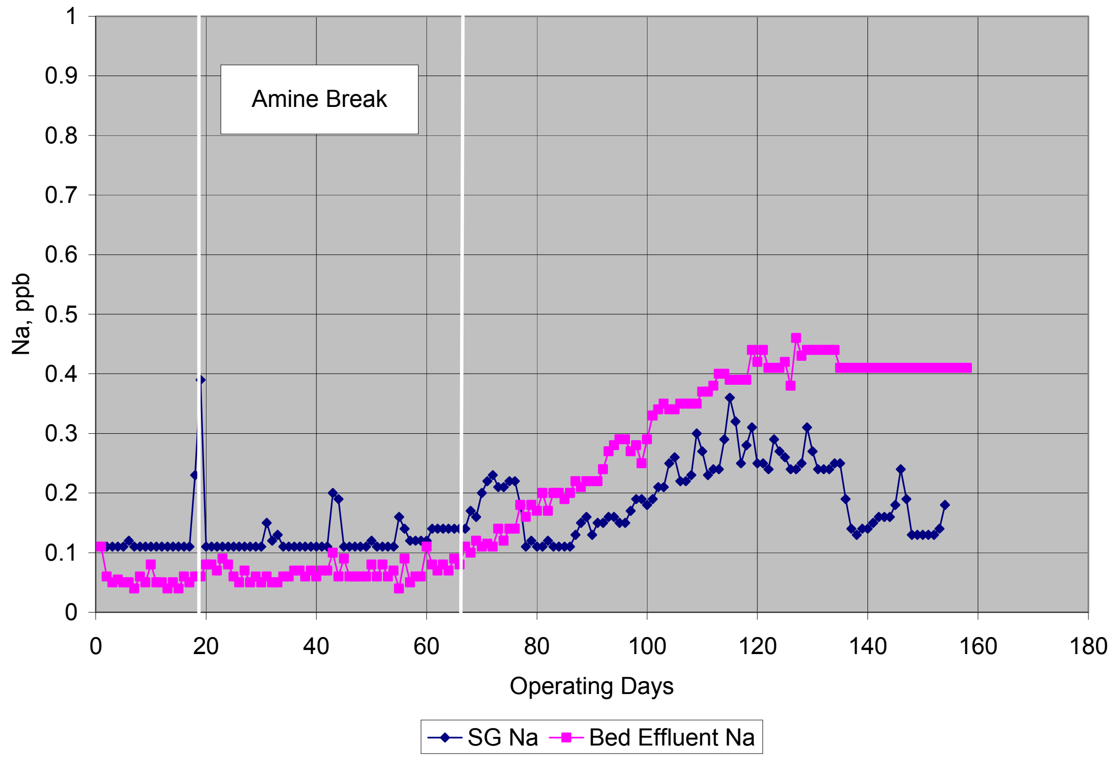
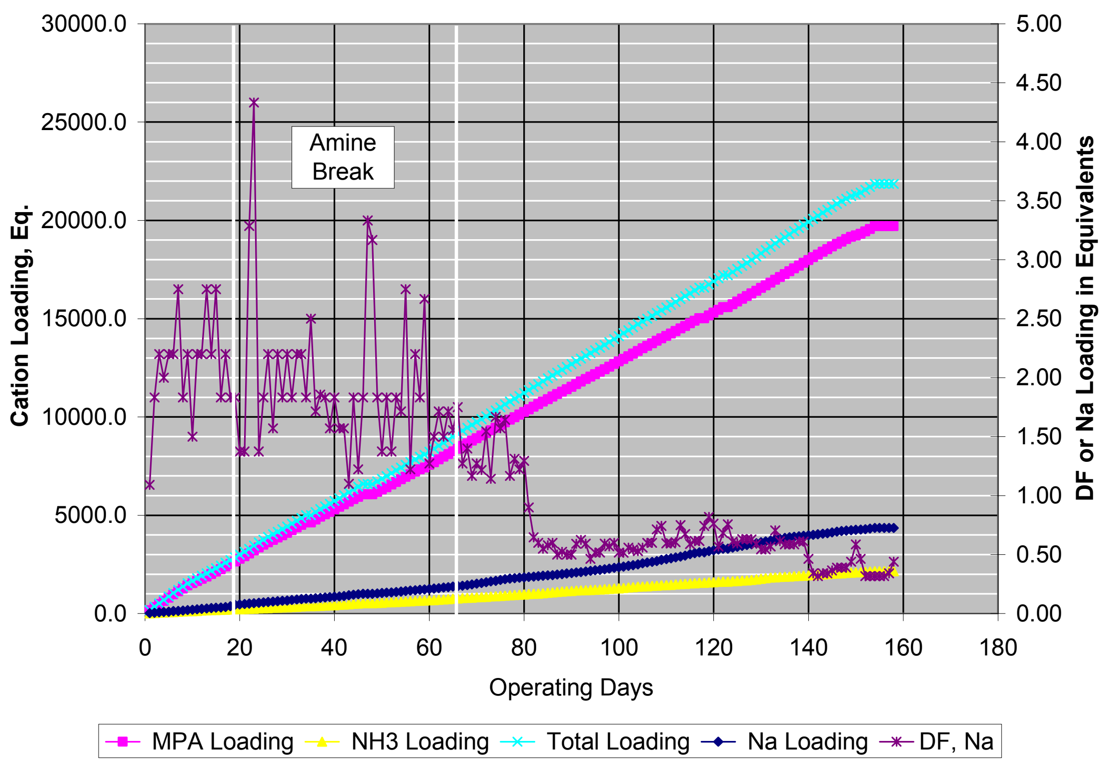


Figure 19 Byron 1A Blowdown Demineralizer November 2002



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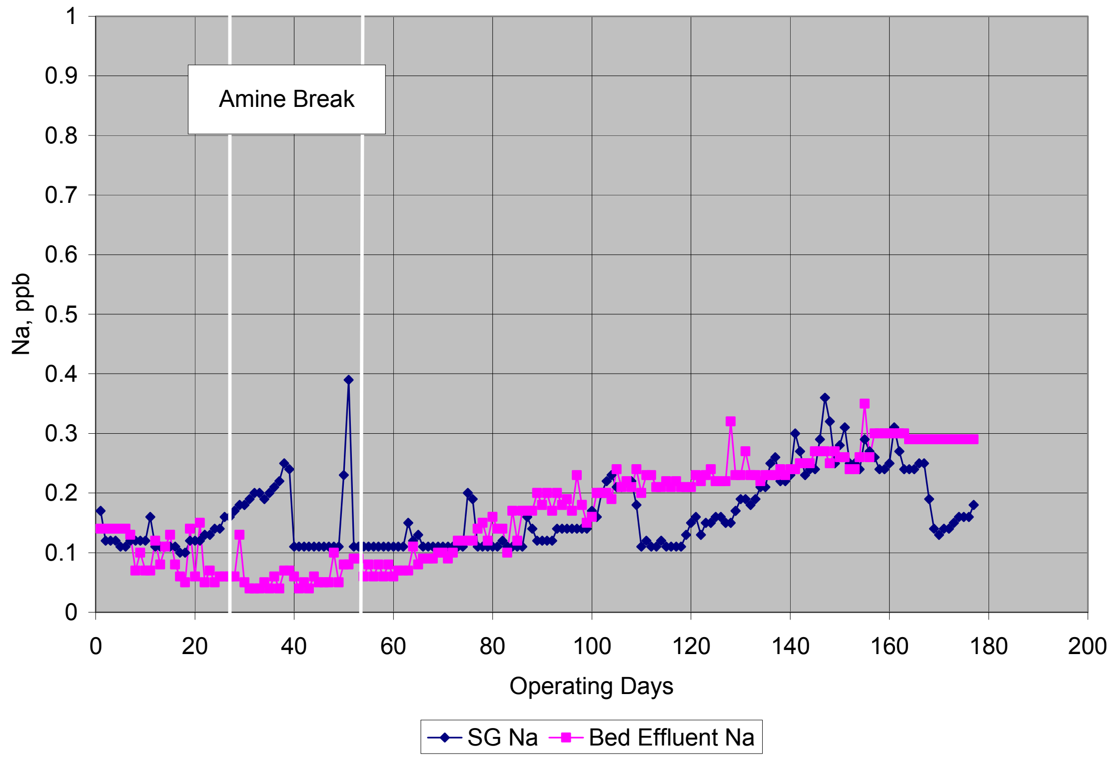

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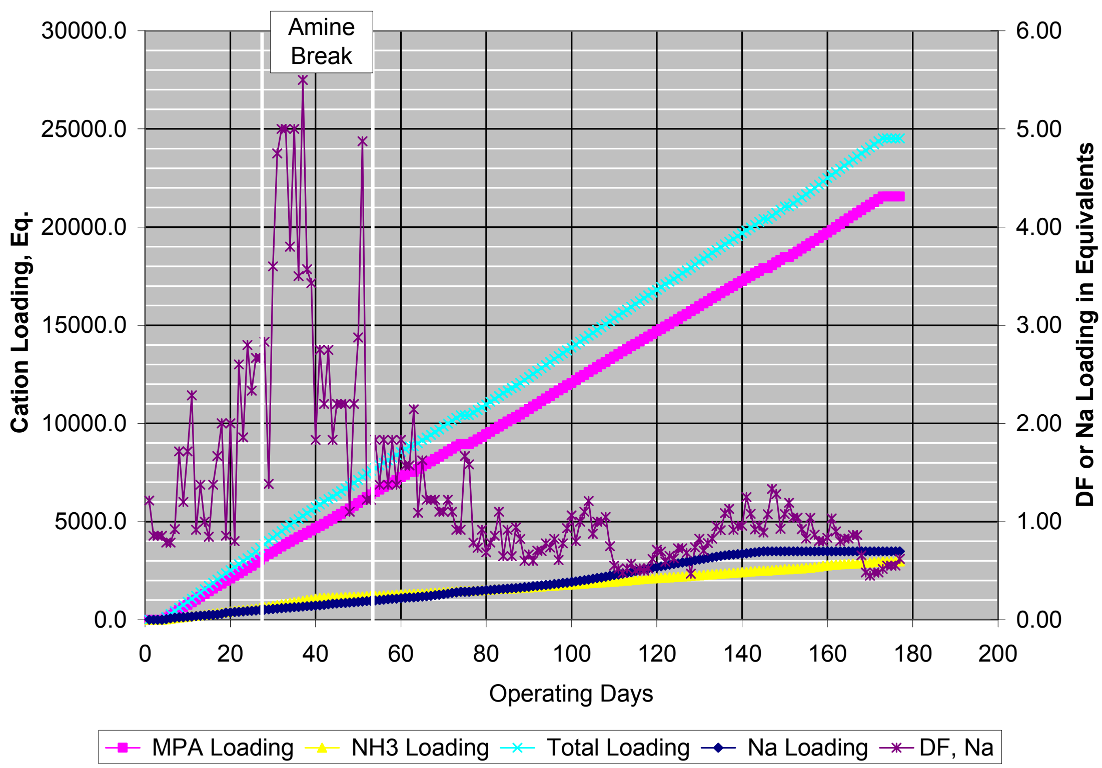

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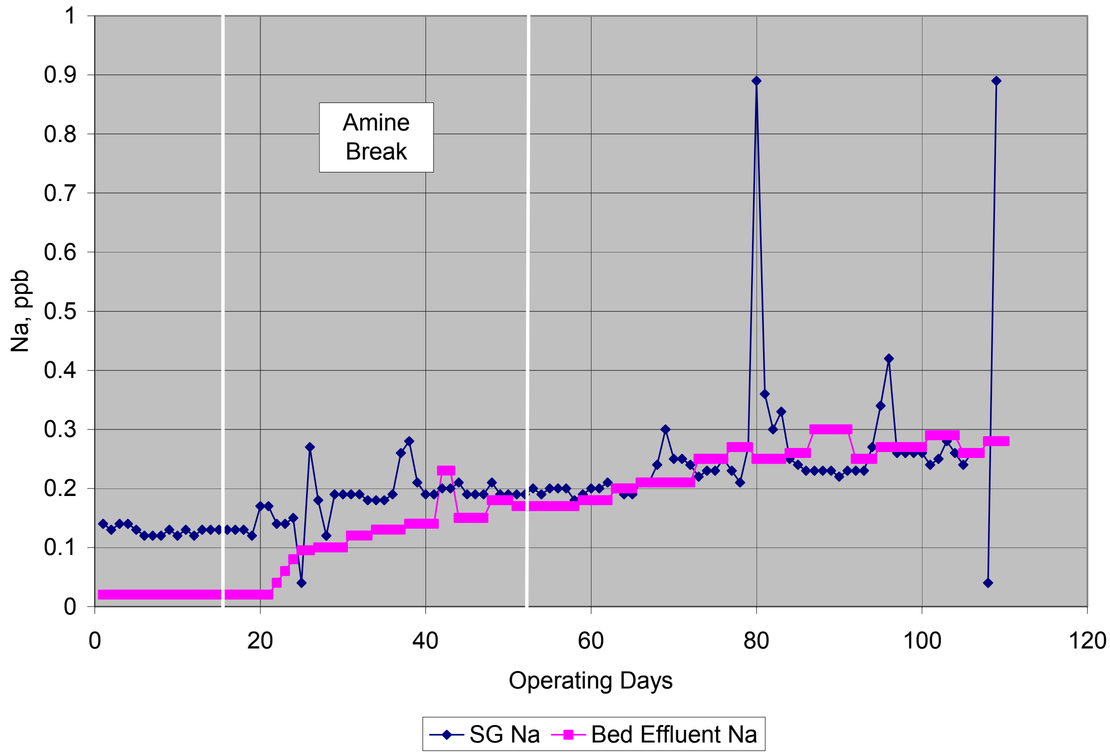


Figure 23 Byron 1A Blowdown Demineralizer December 2003

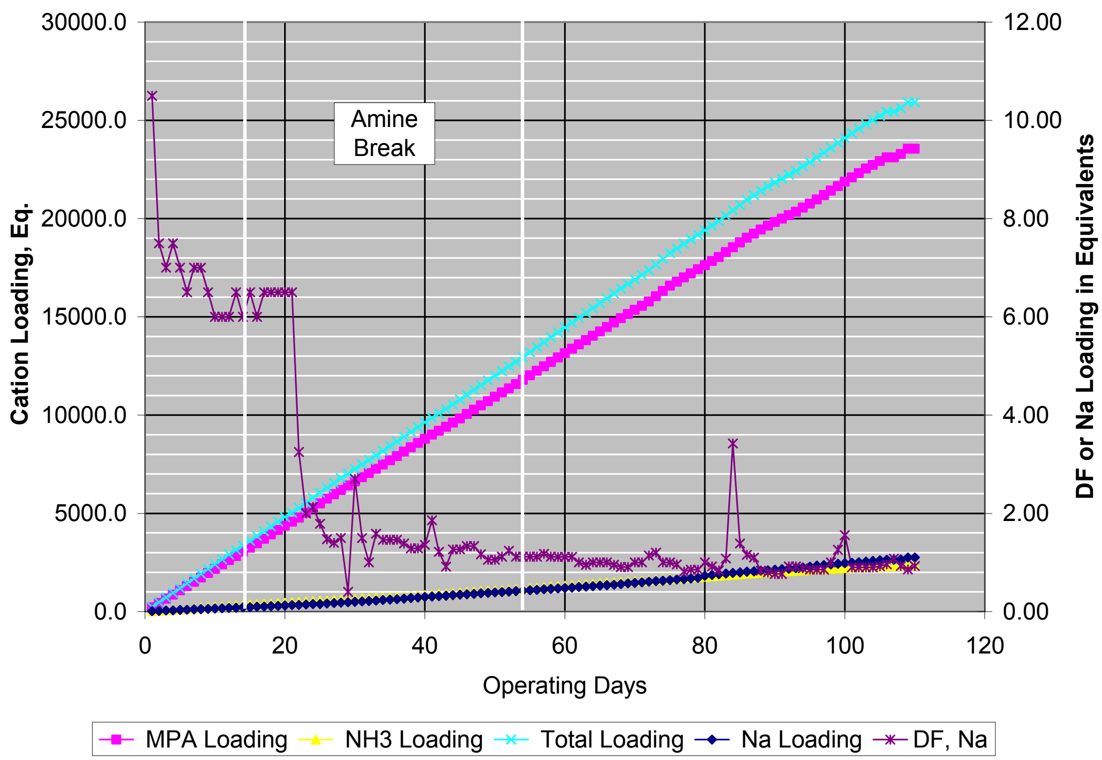


Figure 24 Byron 1A Blowdown Demineralizer December 2003

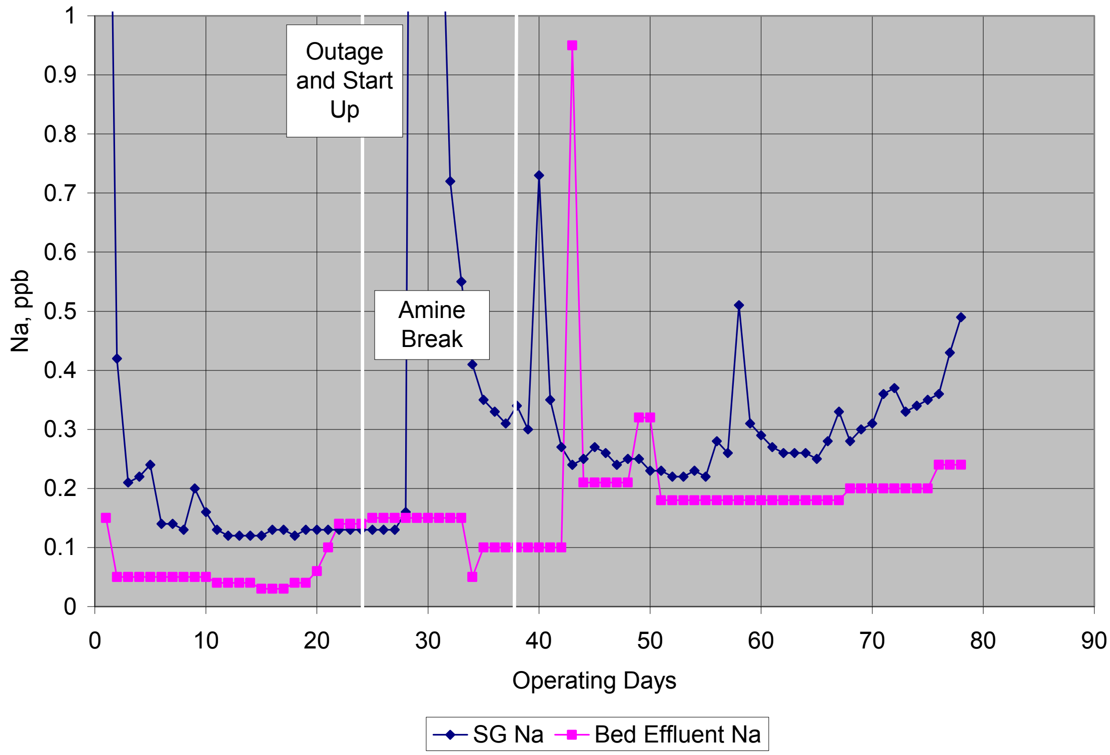
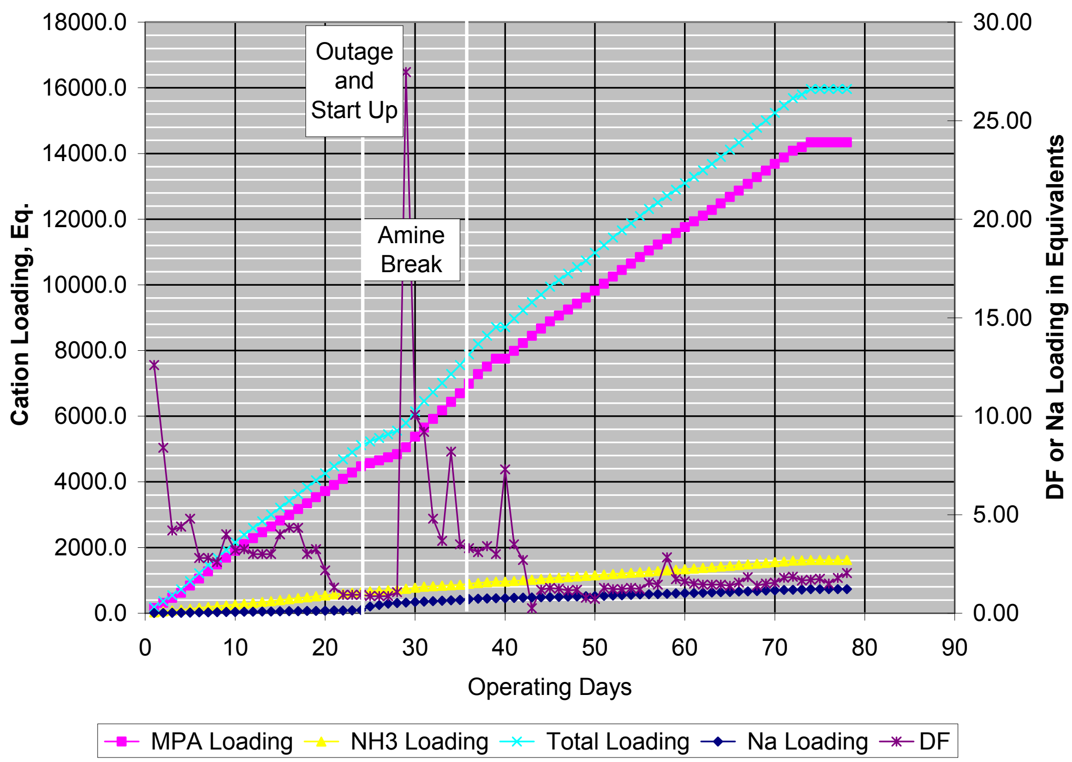


Figure 25 Byron 2C Blowdown Demineralizer December 2003



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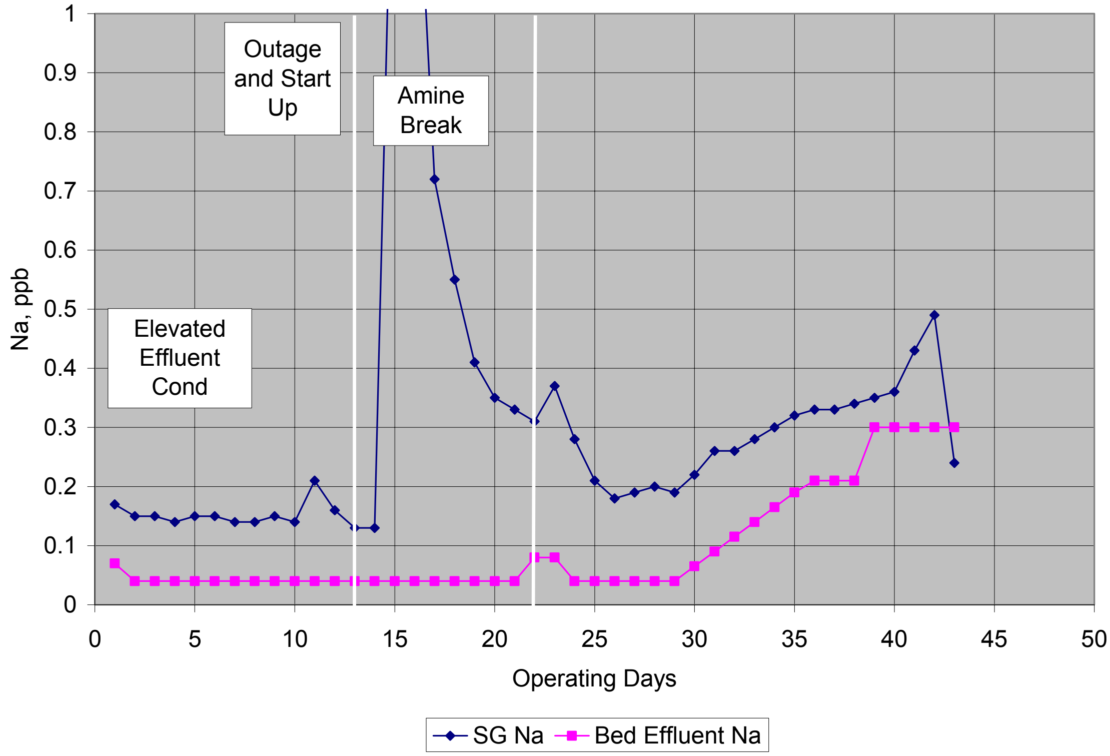

Figure 27 Byron 2D Blowdown Demineralizer March 2004

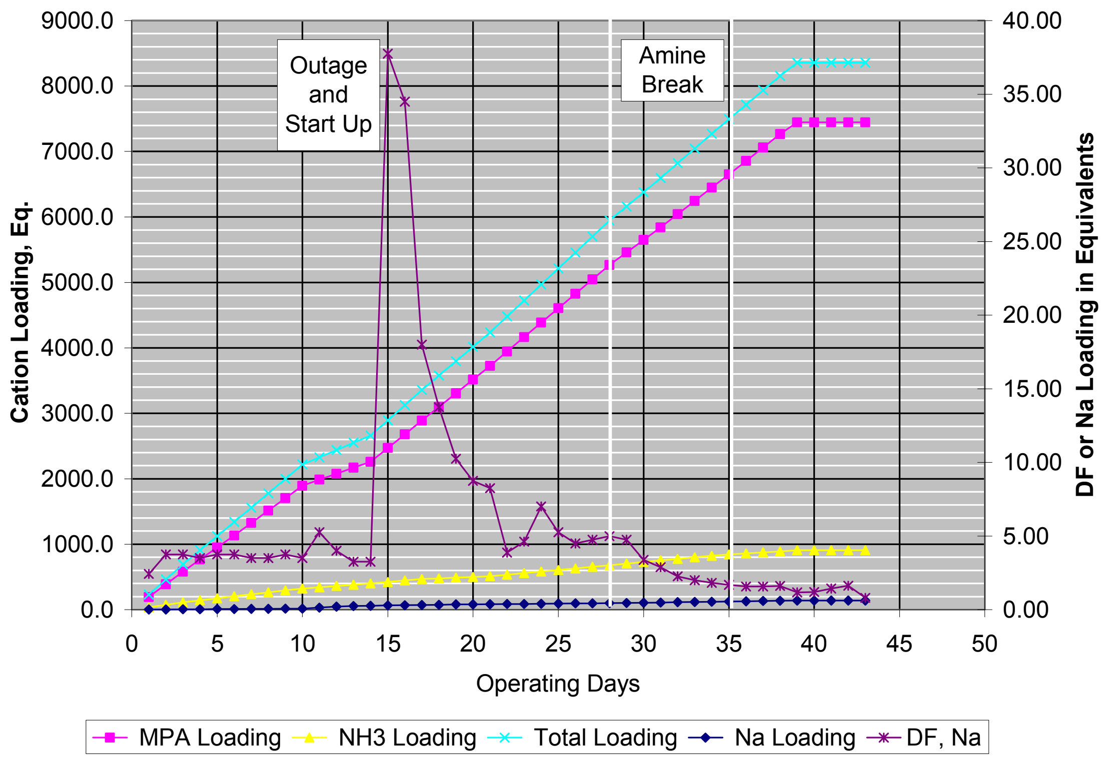

Figure 28 Byron 2D Blowdown Demineralizer March 2004

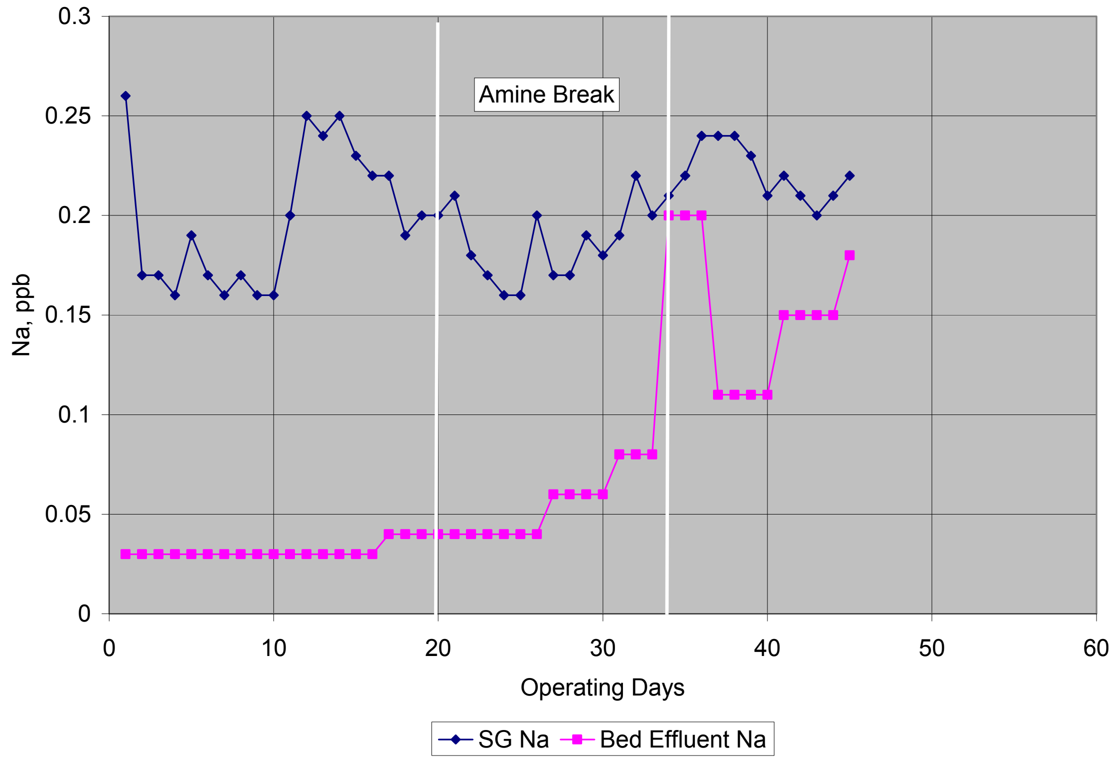

Figure 29 Byron 1B Blowdown Demineralizer May 2004

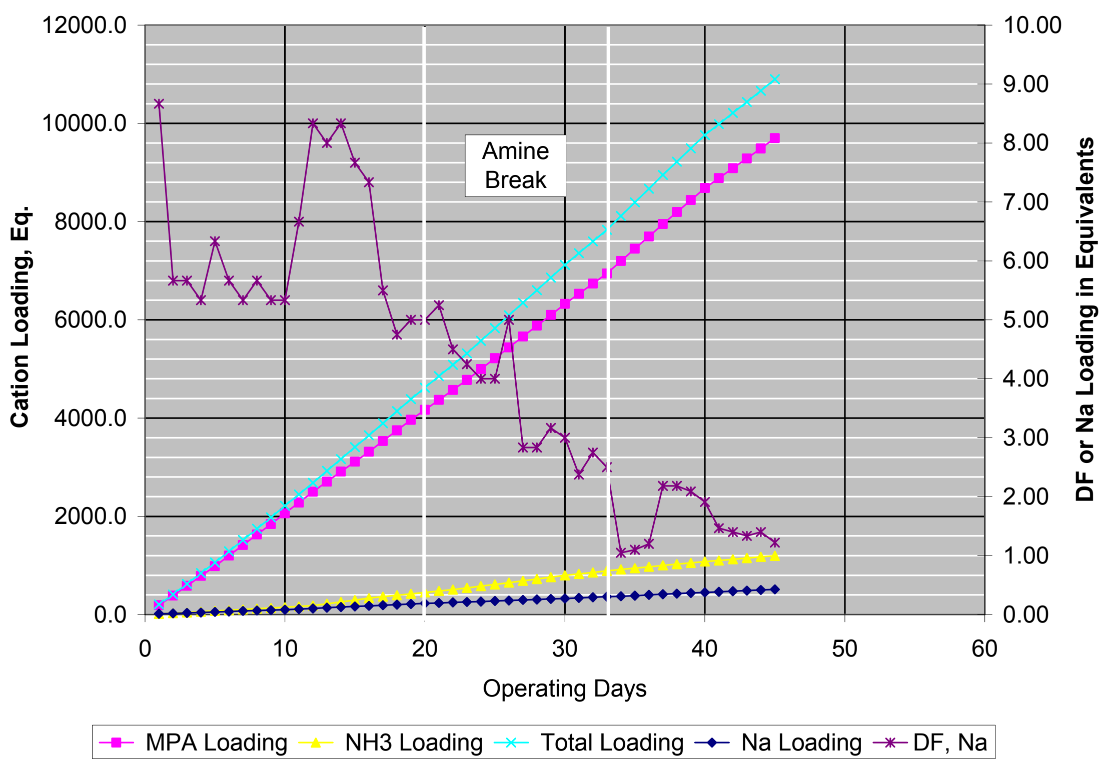

Figure 30 Byron 1B Blowdown Demineralizer May 2004

V) ECONOMIC EVALUATION

The costs of resins, labor to replace the resins, and the disposal of the resins were considered in this evaluation. Although the original Rohm and Haas 20% crosslinked macroporous resins were discontinued due to sulfate issues, the Dow MSC resin, also 20% macroporous was considered in this evaluation.

The labor required to replace a blowdown demineralizer resin was given by the utility as $2,400 per replacement. The disposal cost for resin is dependent on the radioactivity of the resin. The average cost of $5,000 disposal per bed reflects typical station costs and is used in this evaluation.

For predictive run lengths past the amine break, data from previous work were used to determine the sodium leakage rate as a function of initial sodium contamination on the beds.[1] The current resin purchasing specification is 50 mg/kg of Na as dry weight. Also evaluated is a resin purchasing specification for 10 mg/kg of Na. The sodium leakage amount based on the previous work is summarized in the table below:

Table 2 Prediction of Blowdown Resin Operating Days

Initial Conc of Na on Resin, mg/kg	Demin Effluent Na, ppb	Na Leakage Slope, ppb/day	Predicted Operating Days at 200 gpm flow
50	0.160	8.00E-04	96
32	0.080	5.00E-04	266
10	0.032	5.00E-04	333
5	0.016	5.00E-04	356

The first evaluation was performed using the current ratios of cation to anion resins at the sites and initial sodium loading of 50 mg/kg. The second evaluation increases the cation resin amounts and decreases the anion resins to maintain a total bed volume of 3.4 m^3 (120 ft^3) and establish a 5:1 cation to anion equivalence ratio. ***It is noted that the pricing for the two different high cross linked gel cation resins were markedly different due to contract issues at the utility. It is not reasonable to compare the annual cost of the two high cross linked gel resin programs, but rather to compare the cost of the programs from the same manufacturer***. The results of these calculations are given in the following two tables:

Table 3 Cost Evaluation of Resin Mixtures

Resin Na Spec, mg/kg	Macro Porous Cation	Dow 545C	IRN 99	Dow 550A	Cation to Anion Ratio, Eq/Eq	BD Flow, gpm	Cation Loading, Eq/day	Cation Total Cap, Eq	Total Days for the Run	Annual Cost
50	86	0	0	34	3.9	200	242.9	4152.1	47.5	$ 106,633.77
50	0	72	0	48	3.3	200	242.9	4907.5	53.7	$ 116,224.57
50	0	0	71	49	3.2	200	242.9	4839.4	53.2	$ 156,924.27
10	86	0	0	34	3.9	200	242.9	4152.1	82.0	$ 65,284.68
10	0	72	0	48	3.3	200	242.9	4907.5	88.2	$ 70,138.85
10	0	0	71	49	3.2	200	242.9	4839.4	87.6	$ 94,882.06
Maximized Ratios to 5:1 for Lowest Cost Options										
10	91	0	0	29	4.8	200	242.9	4393.5	83.9	$ 61,939.02
10	0	83	0	37	4.9	200	242.9	5657.3	94.3	$ 66,340.80
10	0	0	83	37	4.9	200	242.9	5657.3	94.3	$ 92,060.31

It is assumed in these calculations that the cost of the cation resins increases by \$ 353/m^3 (\$10/ft^3) to comply with the criteria of reducing the initial sodium loading from 50 mg/kg to 10 mg/kg. Based on these results, the 20% macroporous resin is the lowest cost option. However, the better performance of the high cross linked gel resin prior to the amine break and the incidences of ionic sulfate released by the macroporous resins must be considered. Annual costs are based on 90% unit availability. A substantial cost savings is realized when the sodium loading on the bed is reduced from 50 mg/kg to 10 mg/kg.

Since the anion resin cost is greater than the cation, an increased cation to anion ratio is going to yield a lower annual cost. This ratio was limited by the total amount of anion resin in the beds. Conservatively, the amount of anion resin used with the 20% macroporous resin was assumed to be a reasonable minimum amount (> 1 m^3 or 34 ft^3). Therefore, considering the improved performance seen with the high cross linked gel resin and the minimal difference in annual cost between the macroporous and gel options, the recommended program is high cross linked gel at a 5 to 1 equivalence ratio (yielding 1 m^3 or 37 ft^3 of anion resin) with a purchasing specification of < 10 mg/kg Na on the cation resin.

VI)CONCLUSIONS

1. A reduction in steam generator sodium concentration was observed at Braidwood when high cross linked gel resins (HCLGR) were employed.
2. Measurable (1.5 ppb to 2.0 ppb) ionic sulfates were obtained from blowdown resins with 20% macroporous cation resins (MP).
3. No measurable sulfates were determined from the HCLGR.
4. Preliminary: The HCLGR displayed lower sodium concentrations on the effluent of the resin prior to amine break as compared with the MP resins.
5. Preliminary: Performance during and after amine break were similar in both the HCLGR and MP.
6. Demineralizer effluent sodium concentrations were directly related to the amount of sodium on the purchased resin (purchase specification < 50 mg/kg).

VII) RECOMMENDATIONS

1. Continue to employ and evaluate the performance of the HCLGR in the blowdown systems.
2. Reduce the sodium specification in the resin purchasing to 10 mg/kg from 50 mg/kg.
3. The recommended program for blowdown demineralizers is Dow 545C at a 5 to 1 equivalence ratio with Dowex 550A.

VIII) ACKNOWLEDGEMENTS

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