

Technical Position: Unit 1 Steam Generator Layup Chemistry out of Specification During September 24, 1997 to December 31, 1997.

Synopsis:

This technical position documents the evaluation of the out of specification parameters and the potential effect on steam generator corrosion during the time period from September 24, 1997 to December 31, 1997. During this period, the unit remained in mode 5. Revisions 6 and 7 of procedure 12 THP 6020 CHM.201, Steam Generator, governed the steam generator chemistry specifications for all modes of operation, including layup (Ref 1 and 2), during this period. The chemistry control detailed in the Steam Generator procedure was developed using the guidelines in EPRI TR-102134-R4, PWR Secondary Water Chemistry Guidelines-Revision 4, November 1996 (Ref 3).

Following the unit 1 shutdown which commenced on September 8, the steam generators were not placed immediately into wet layup as the length of the outage was not determined. Layup of the steam generators was subsequently started on September 24.

Initially, only carbohydrazide was used as an oxygen scavenger. The steam generators were drained and refilled between December 6 and 9, 1997, to adjust the pH and oxygen scavengers. With the refill, both hydrazine and carbohydrazide were used as oxygen scavengers. Steam generator 12 was drained and refilled December 18, 1997, due to elevated sulfate concentration. According to the monthly reports, the appropriate amounts of chemicals were added when the steam generators were placed in wet layup in September. Although not completely documented in the monthly reports, from the layup data it appears the appropriate amounts of chemicals were added when the steam generators were drained and refilled in December. During January 1998, the steam generators were prepared for startup. The startup did not occur and the steam generators were returned to layup in February 1998 where they have essentially remained.

Independent reviews of the layup data indicated that some parameters were at times out of specification during the period from September 24, 1997, to December 31, 1997. The parameters that were out of specification included boron, ethanolamine, pH, hydrazine and carbohydrazide. During the period, the unit underwent a heatup to about 180°F to 195°F four times. While available data could not confirm, it is possible that some or all of these heatups were in preparation to enter mode 4 and unit restart. If this were indeed the case, pH, hydrazine and carbohydrazide would be controlled lower than typical layup levels to prepare for operating chemistry control. Contaminants and potential corrosive species, sodium, chloride and sulfate, were maintained within specification and were generally very low during the period.

In order to determine the impact of the out of specification condition on the steam generator integrity, a thorough review of chemistry data for the period was conducted. The data that was evaluated was taken from data sheets 12 THP 6020 ADM.010 Attachment 1, with the exception of condensate storage tank dissolved oxygen data that was taken from CDMS. The raw data and graphed data are included in this technical position as attachments 1 and 2 respectively.

Discussion:

Boron:✓

Boric acid is an additive used to mitigate outside diameter stress corrosion cracking, ODSCC, of the steam generator tubes during operation. The control parameter for boric acid is boron. During operation, boron concentration in the steam generator is maintained at about 5 to 10 ppm. During startup, 1000 to 2000 ppm boron is used for crevice flushing and about 50 ppm boron is used for the boric acid soak. As the environment conducive to ODSCC is not present during shutdown, boric acid is not needed during layup. If boric acid is present in the layup solution, it can depress the pH. The consequence of elevated boric acid levels during layup is the need to use more amounts of ethanolamine, ETA, which is used to raise the pH of the layup solution. ETA is used during operation and layup to adjust pH. It does not of itself present a corrosion concern for the steam generators. The EPRI guidelines (Ref 3) do not identify a corrosion concern with elevated levels of boric acid during layup. The guidelines identify the consequence of elevated boric acid levels during layup as the need to use more amounts of ETA. The upper limit for boron during layup is 1 ppm.

During the period from September 24, 1997 to December 31, 1997, the boron was above the 1 ppm limit as shown on the attached graph. When pH was raised above 9.8 and the concentrations of hydrazine and carbohydrazide were increased significantly prior to December 15, 1997, the indicated boron concentrations also increased significantly. It is unlikely that these values were accurate. No boric acid had been added, the steam generators had been drained twice since the shutdown and the reported levels were about ten times normal operating levels. It is more likely that the reported values were a result of interference with the analytical method coincident with the high pH and hydrazine levels. Some samples were checked using ICPMS and no boron was detected when the reported boron levels were ranging from about 20 to 70 ppm. Subsequent conversion to the ICPMS method for boron analysis in layup solutions in January 1998, resulted in the reported boron levels being less than 1 ppm. The possible interference may have also contributed to the reported boron levels being above 1 ppm during the previous part of the layup.

Regardless of whether the values were accurate, having boron greater than 1 ppm during this period did not result in an increase in steam generator corrosion.

Ethanolamine (ETA):

ETA is used to raise the pH of the secondary side during operation and layup to minimize corrosion of low alloy or carbon steel. The upper limit of 50 ppm for ETA during layup is based on environmental considerations when draining the steam generators. There is no corrosion concerns with layup relative to the upper limit of ETA. The procedure was revised effective February 6, 1998, to raise the upper ETA limit to 100 ppm. ETA does not present a corrosion concern. The EPRI guidelines (Ref 3) do not set limits for the pH additive during layup, rather

the level of pH additive is determined by the desired pH level. A corrosion concern with high levels of the pH additive is not identified.

During the period under review, ETA was above the 50 ppm limit in steam generators 11 and 12 for essentially the entire period. For steam generators 13 and 14, ETA was above the 50 ppm limit for a short period in mid November and from December 8 to 31, 1997. The high concentrations during December were used effectively to raise the pH in the steam generators to provide corrosion protection.

An increase in steam generator corrosion would not result from the period when ETA levels were above 50 ppm as ETA is not corrosive to steam generator materials at the levels experienced.

Nitrogen Overpressure:

Use of nitrogen overpressure during layup is recommended but not required by procedure 12 THP 6020 CHM.205 Rev 1, Steam Generator Wet Lay-up (Ref 4), and the EPRI guidelines (Ref 3). The purpose is to minimize air ingress above the water level during layup. The use of nitrogen overpressure is dependent on the mode the unit is in, the length of the outage and the maintenance scheduled to be performed on the steam generators, feedwater and steam piping, turbine and condensers. The personnel safety hazard is a primary concern when determining if nitrogen will be used. Nitrogen overpressure is typically used for extended outages in modes 5 and 6 when, as described above, plant conditions permit. It is not atypical that a nitrogen overpressure was not maintained during the entire layup period.

Prior to placing the steam generators in initial layup in September, they were drained with a nitrogen overpressure. This prevented air ingress. After adding layup chemicals and filling the steam generators, they were sparged with nitrogen. The sparging along with draining under nitrogen ensure an oxygen free environment in the steam generators during layup. Sparging was done repeatedly during the period under review. Steam generators 11 and 14 were sparged at the end of October. Steam generators 12, 13 and 14 were sparged between November 10 and 13. All steam generators were sparged before and after the drains and refills in December and at the end of December.

Nitrogen use during the period was acceptable. It provided an oxygen free environment and corrosion protection.

pH and Oxygen Scavenger (Carbohydrazide and/or Hydrazine):

These parameters are being addressed together as their function of corrosion protection during layup is interrelated. Carbohydrazide and hydrazine can be used together or individually.

Unlike under operating conditions, pH is a control parameter for layup. Elevated pH in conjunction with an oxygen scavenger is used to provide corrosion protection of the low alloy or carbon steel components of the steam generators. These components include the tubesheet, tube support plates, wrapper, shell, and the feed ring. To prevent localized attack, such as pitting, of the alloy 600 steam generator tubes during layup, reducing conditions should be maintained or the pH should be greater than 8.5. Also, chloride and sulfate concentrations should be kept below 1 ppm (Ref 3 and 7).

In an oxygenated environment, elevated pH in conjunction with an oxygen scavenger aids in the formation of a stable iron oxide film on carbon steel components. This film helps to minimize corrosion by acting as a barrier to diffusion. In the absence of oxygen, there is no significant corrosion of steel in neutral or near neutral water at ambient conditions (Ref 5, 6). In the absence of oxygen and minimum levels of other corroding species such as chloride and sulfate, it is expected that the result would be the same at the layup temperatures of 140°F to 195°F.

Most of the test data contained in reference 6 were obtained using cleaned carbon steel specimens with no existing protective layer. The carbon steel surfaces in the steam generators enter an outage with a protective oxide layer as a result of the reducing, high pH environment present during operation. Therefore, the test conditions used in reference 6 are much more severe than the conditions in the steam generators during layup.

Per procedure 12 THP 6020 CHM.201, the lower limit for layup pH is 9.2 when using carbohydrazide as the oxygen scavenger and 9.8 when using hydrazine. Carbohydrazide is very reactive and tends to react quickly, significantly faster than hydrazine, to scavenge oxygen and passivate the metal surfaces in the steam generator. A result of this reaction is the generation of carbon dioxide. This acts to depress the pH, which is the reason for the lower pH limit when using carbohydrazide. The lower limit given in the procedure for carbohydrazide and hydrazine is 10 ppm and 75 ppm respectively. The EPRI guidelines recommend a minimum pH of 9.8 and minimum hydrazine concentration of 75 ppm to provide corrosion protection during layup. The guidelines do not specifically address carbohydrazide but allow alternatives to hydrazine.

The high minimum levels for pH and hydrazine are intended to provide protection under aerated conditions and to provide protection in the event of air ingress. As discussed in references 5, 6 and 7, pH and hydrazine levels need not be as high if the environment is deaerated and without significant levels of other contaminants. It is conservative and good practice to maintain the elevated levels in the event of air ingress. However, in a deaerated environment, corrosion protection exists without these high levels.

From the start of layup to the drain and refill on December 6 to 9, 1997, carbohydrazide was used as the oxygen scavenger. Carbohydrazide was below the lower limit for this period. A sufficient amount of carbohydrazide was added when the steam generators were initially placed in wet layup to achieve a level near the upper limit of 40 ppm. However, the carbohydrazide reacted quickly to passivate the internal metal surfaces of the steam generators and a significant level was not maintained in the steam generators. During this time, the pH in two of the steam generators, 12 and 14, was maintained above 9.2. The pH in steam generator 11 was above 9.2

except for two weeks preceding the drain and refill when the pH was at about 9.0. The pH in steam generator 13 was above 9.2 except for one week preceding the drain and refill when the pH was 9.1.

Following the drain and refill, hydrazine and carbohydrazide were used. Hydrazine and carbohydrazide were above the lower limits for steam generator 11. Hydrazine was above the lower limit for steam generator 12. Carbohydrazide was below the lower limit part of the time, ranging from 5.3 to 20.8 ppm. For steam generator 13, hydrazine was below the lower limit part of the time, ranging from 47 to 194 ppm. Carbohydrazide was below the lower limit, ranging from 5.4 to 8.1 ppm. For steam generator 14, hydrazine was below the lower limit part of the time, ranging from 55.2 to 162.8 ppm. Carbohydrazide was below the lower limit part of the time, ranging from 8.5 to 13.6 ppm. The hydrazine values reported on December 15 are apparently in error based on hydrazine levels before and after December 15, and the fact that another chemical addition was not made. Following the drain and refill, the pH was maintained at or above 9.8.

During the period under review, dissolved oxygen in the steam generators was 0 ppb. The dissolved oxygen in the fill source, unit 1 condensate storage tank, during the initial and subsequent fills was low. Chloride and sulfate were within limits during the period and generally maintained low. Sulfate did spike up during the second half of December but was maintained within limits.

The environment in the steam generators was deoxygenated. The carbon steel surfaces in the steam generators have an existing protective oxide layer entering the outage. An oxygen scavenger was added with the initial fill that acted to passivate the carbon steel surfaces. Oxygen scavengers, both carbohydrazide and hydrazine, were added during subsequent fills and a significant residual maintained. The pH was elevated and above 9.2 for all or most of the time up to the December 6 to 9 period. Following this it was generally greater than or equal to 9.8. Contaminant levels, such as chloride and sulfate, were low. As a result of these conditions, adequate corrosion protection was provided during the period.

Position:

Considering the environment was deoxygenated, pH was elevated and contaminant levels were low, adequate corrosion protection was provided during the period of September 24 to December 31, 1997. The conditions in the steam generators during the period of September 24 to December 31, 1997 when layup chemistry was out of specification did not present an increased risk of corrosion over that which would have been present had the chemistry been maintained within specification the entire time.

Perform the following actions:

1. Revise 12 THP 6020 CHM.205, Steam Generator Wet Layup, to include the lower limit for carbohydrazide and hydrazine during layup that had been deleted from 12 THP 6020 CHM.201 in rev 8.

2. To provide optimal corrosion protection in the event of oxygen ingress during layup, increase the minimum pH limit to 9.8 when using carbohydrazide.
3. Perform an internal visual inspection of secondary side of at least one steam generator in the area of the water level during layup. Although the chemistry data indicates that corrosion protection was provided, the inspection is prudent considering the length of the outage.

References:

1. 12 THP 6020 CHM.201, Revision 6, Steam Generator, Effective Date September 11, 1997.
2. 12 THP 6020 CHM.201, Revision 7, Steam Generator, Effective Date October 6, 1997.
3. PWR Secondary Water Chemistry Guidelines-Revision 4, Project 2493, S520 Final Report. Palo Alto, CA.: Electric Power Research Institute, November 1996. TR-102134-R4.
4. 12 THP 6020 CHM.205, Revision 1, Steam Generator Wet Lay-up, Effective Date February 28, 1997.
5. H. H. Uhlig and R. W. Revie. Corrosion And Corrosion Control, Third Edition. New York: J. Wiley & Sons, 1985 pp. 91-99.
6. J. A. Armantano and V. P. Murphy. "Standby Protection of High Pressure Boilers" Proceedings of the 25th Annual Water Conference of the Engineers' Society of Western Pennsylvania, Pittsburgh, PA., September 28-30, 1964, pp. 111-124.
7. Laboratory Program to Examine Effects of Layup Conditions on Pitting of Alloy 600, Research Project S124-1 Final Report. Palo Alto, CA.: Electric Power Research Institute, April 1983. NP-3012.

Prepared by: *Michael J. Kofke* Date: 1/25/99

Approved by: *John H. Kofke* *T. C. C.* Date: 1-27-99

Attachment I

Layup Chemistry Data ADM 010 Sheets SG 11											
Date	pH	Carbo ppm	N ₂ H ₄ ppm	DO ₂ ppb	Sodium ppb	Chloride ppb	Sulfate ppb	Boron ppm	ETA ppm	Ammonia ppm	Comments
9/24/97	9.31		2.2020	ND	0.4			1.70	62.70		Added 4 gal ETA & 10 gal carbo
10/3/97	9.52		0.1180	0	0.6	7.4	29.5		68.40	6.80	
10/7/97	9.27	0.170		0	0.8	2.9	35.8	2.60	59.00		
10/13/97	9.37	0.251		0	2.3	12.9	40.2		59.00		
10/20/97	9.74	0.256		0	1.1	3.2	30.6		60.00	6.30	
10/27/97	9.55	ND		0	3.8	3.6	40.0		60.40	7.40	RCS heat up to 187 10/24-29
10/29/97		ND							64.90	8.80	Sparge for release 10/29 no drain
11/5/97	9.44	0.051		0	1.4	1.6	40.0		63.00		
11/10/97	9.56	0.053		0	1.3	2.3	40.3		60.10		
11/17/97	9.37	0.000		0	1.6	7.6	46.7		65.00	10.00	RCS heat up to 190 11/12-15
11/24/97	9.02	ND		0	1.7	4.2	67.0		64.80	11.60	RCS heat up to 195 11/18-23
12/3/97	9.00	ND	0.0046		2.1	10.7	40.4	0.00	64.60	12.00	
12/6/97			0.0011					4.00			Drain 12/7
12/9/97	9.45			0					58.00	4.50	12/8 refill, add 3.5gal ETA, 15.5gal N ₂ H ₄ , 9gal carbo(assumed)
12/9/97			44.1520								12/9 + 1.4gal ETA, 15.5gal N ₂ H ₄ , 9gal carbo
12/9/97	9.52		18.7000	0					45.20		RCS heat up to 180-190 through 12/31
12/15/97	9.88	30.602	16.7600	0	5.7	17.1	45.7	46.20	68.70	9.30	Hydrazine likely inaccurate does not correspond with other data
12/22/97	9.94			0	2.6	5.9	58.9	72.90	86.70	19.90	
12/28/97	9.98	20.500		ND	1.9	33.0	121.8	47.00	51.20	16.40	
12/29/97			137.0000								
12/30/97							50.0				
12/31/97			137.6000					0.04			Sparge for release 12/31 drain to norm op
ND: value reported as less than detectable. <50ppb for carbonylhydrazide, <5ppb for dissolved oxygen											

Layup Chemistry Data ADM.010 Sheets SG 12											
Date	pH	Carbo ppm	N ₂ H ₄ ppm	DO ₂ ppb	Sodium ppb	Chloride ppb	Sulfate ppb	Boron ppm	ETA ppm	Ammonia ppm	Comments
9/24/97	9.66		3.126	ND	0.3			1.60	55.80		Added 4 gal ETA & 10 gal carbo
10/3/97	9.59		0.0395	0	1.1	23.1	27.2		52.3	6.1	
10/7/97	9.41	19.2		0	0.5	5.4	18.1	2.4	53.6		
10/13/97	9.59	0.549		0	0.6	6.0	23.3		50		
10/20/97	9.64	0.178		0	0.9	2.1	27.0		48	5.3	
10/27/97	9.49	0.26		0	3.5	3.0	30.1		51.1	7.6	RCS heat up to 187 10/24-29
11/5/97	9.39	0.124		0	0.8	2.3	29.0		54		
11/10/97	9.48	0.123		0	1.9	2.0	30.2		62.9		Sparge for release 11/13 no drain
11/17/97	9.47	0		0	1.0	3.1	44.9		57.2	9.5	RCS heat up to 190 11/12-15
11/24/97	9.36	ND		0	1.1	9.4	65.0		60.4	11.7	RCS heat up to 195 11/18-23
12/3/97	9.23	ND	0.0052		6.6	42.8	36.4	0	65.4	13	
12/6/97			0.0064					5.7			Drain 12/6
12/8/97	9.92		269	ND					165	31	12/7 refill, add 3.5gal ETA, 15.5gal N ₂ H ₄ , 9gal carbo(assumed)
12/9/97	9.97		102.4			21.0	142.4		132.1		RCS heat up to 180-190 through 12/31
12/15/97	10.08	20.839	14.472	0	4.0	18.7	926.2	34.5	109.5	27.9	Hydrazine likely inaccurate doesn't correspond with other data
12/20/97	9.88		124.6	0	1.2			46.6		63.4	Drain 12/18 N ₂ H ₄ 130-190ppm in drain sample, refill 12/19
12/22/97	9.93			0	2.7	9.3	61.4	37.2	73.4	16	
12/28/97	9.94	5.3		ND	1.7	9.6	348.0	36	50	23.3	
12/29/97			91.2								
12/30/97							84.0				
12/31/97			95.79			9.0	28.9	29.4			Sparge for release 12/31 drain to norm op
ND: value reported as less than detectable. <50ppb for carbonylhydrazide, <5ppb for dissolved oxygen											

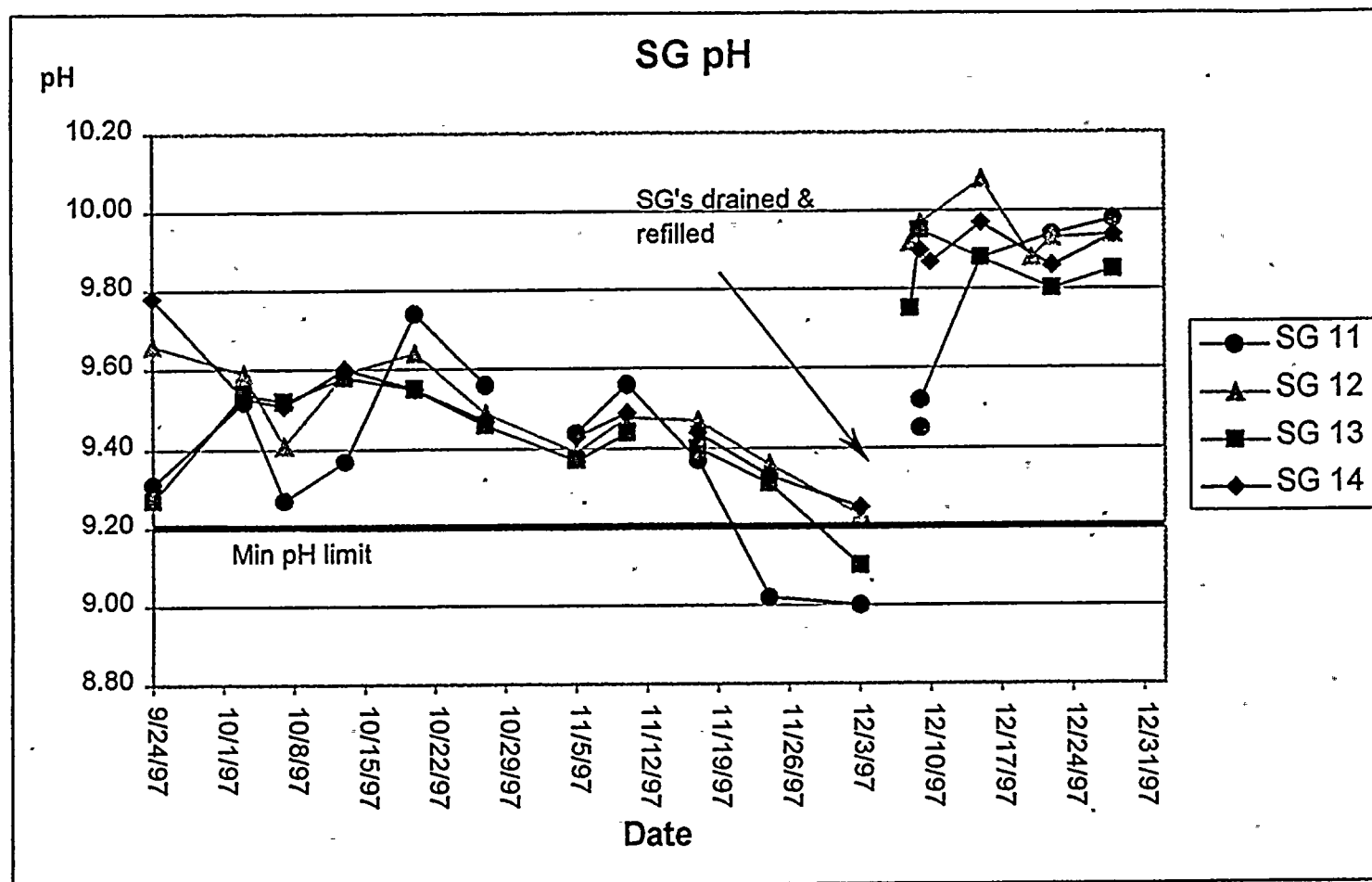
Attachment 1

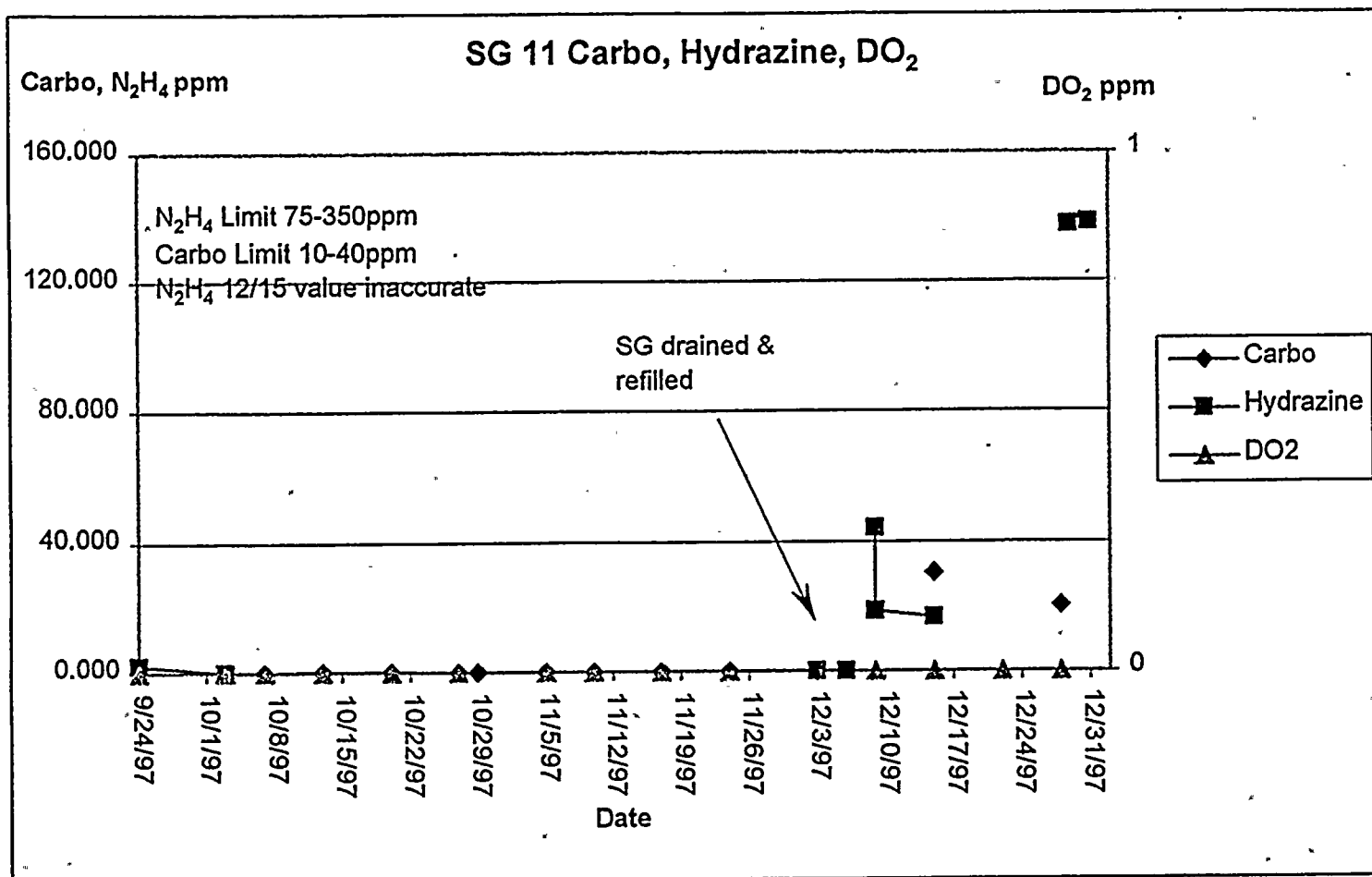
Layup Chemistry Data ADM.010 Sheets SG 13

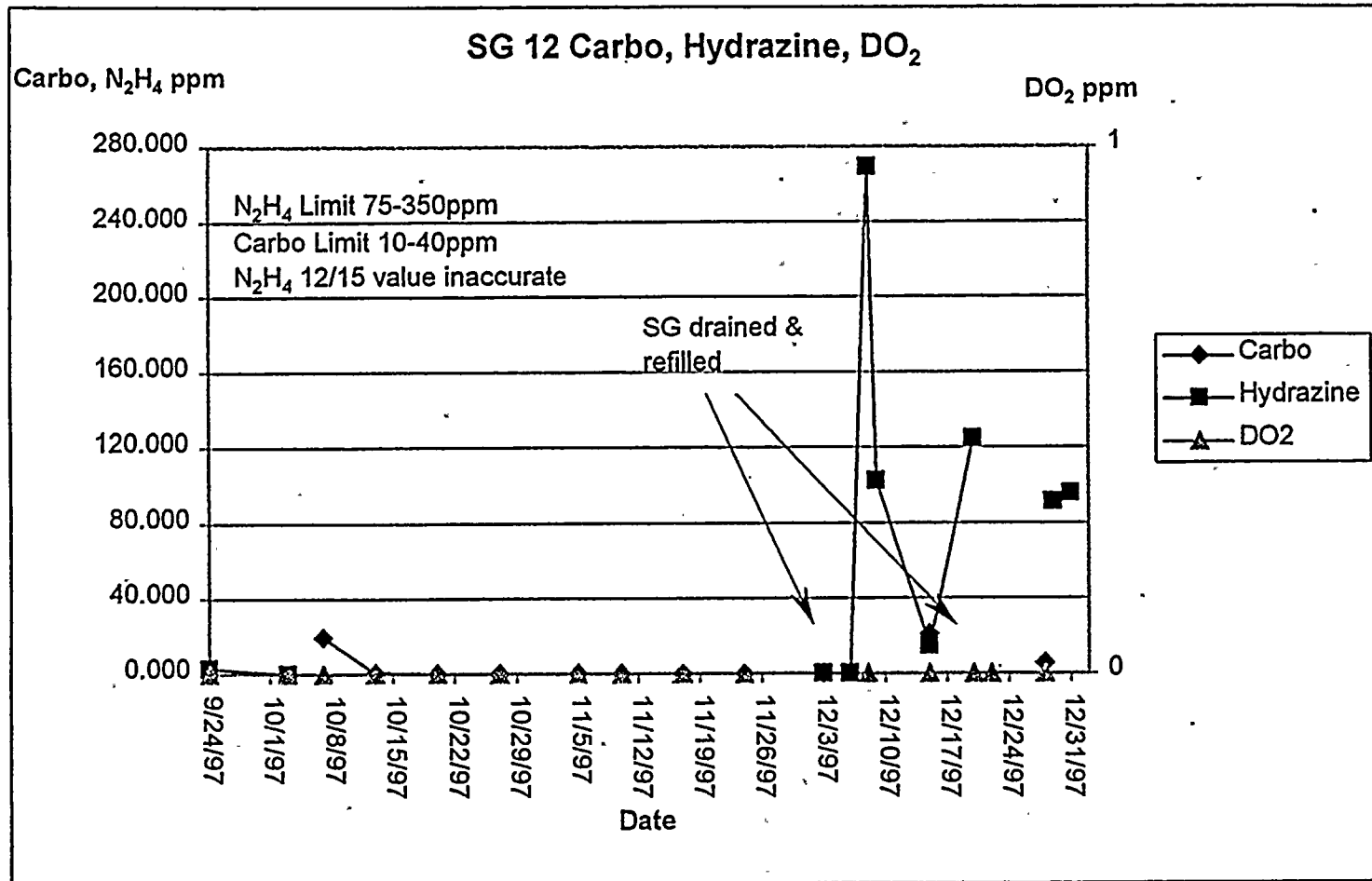
Date	pH	Carbo ppm	N ₂ H ₄ ppm	DO ₂ ppb	Sodium ppb	Chloride ppb	Sulfate ppb	Boron ppm	ETA ppm	Ammonia ppm	Comments
9/24/97	9.27		4.653	ND	0.3			1.80	43.1		Added 4 gal ETA & 10 gal carbo
10/3/97	9.54		0.0085	0	0.6	18.6	25.2		43.9	5.0	
10/7/97	9.52	ND		0	0.5	1.6	18.6	1.7	46.2		
10/13/97	9.58	0.754		0	0.9	4.1	26.0		48.0		
10/20/97	9.55	0.231		0	1.8	1.9	31.9		43.0	4.9	
10/27/97	9.46	ND		0	4.4	2.2	41.2		46.2	6.8	RCS heat up to 187 10/24-29
11/5/97	9.37	0		0	1.6	1.4	44.0		45.0		
11/10/97	9.44	0		0	1.2	1.7	44.5		48.9		
11/11/97			0.0064			2.0	50.0		50.7	4.1	Sparge for release no drain
11/17/97	9.40	0		0	2.0	2.8	61.7		49.8	7.4	RCS heat up to 190 11/12-15
11/24/97	9.31	ND		0	2.2	3.2	77.0		47.1	8.1	RCS heat up to 195 11/18-23
12/3/97	9.10	ND	0.0045		3.5	10.7	46.4	0	48.8	10.2	
12/6/97			0.0043					4.5			Drain 12/6
12/8/97	9.75		194	ND					154.0	26.0	12/7 refill, add 3.5gal EJA, 15.5gal N2H4, 9gal carbo(assumed)
12/9/97	9.95		97.796			18.1	447.0		99.1		RCS heat up to 180-190 through 12/31
12/15/97	9.88	8.1	7.186	0	5.2	16.3	61.0	12.7	94.4	19.9	Hydrazine likely inaccurate doesn't correspond with other data
12/22/97	9.80			0	3.1	7.0	38.1	41.1	77.1	19.2	
12/28/97	9.85	5.4		ND	2.0	18.4	168.3	18	88.4	18.8	
12/29/97			48.6								
12/30/97							79.0				
12/31/97			47					0.02			Sparge for release 12/31 drain to norm op
ND: value reported as less than detectable. <50ppb for carbohydrazide, <5ppb for dissolved oxygen											

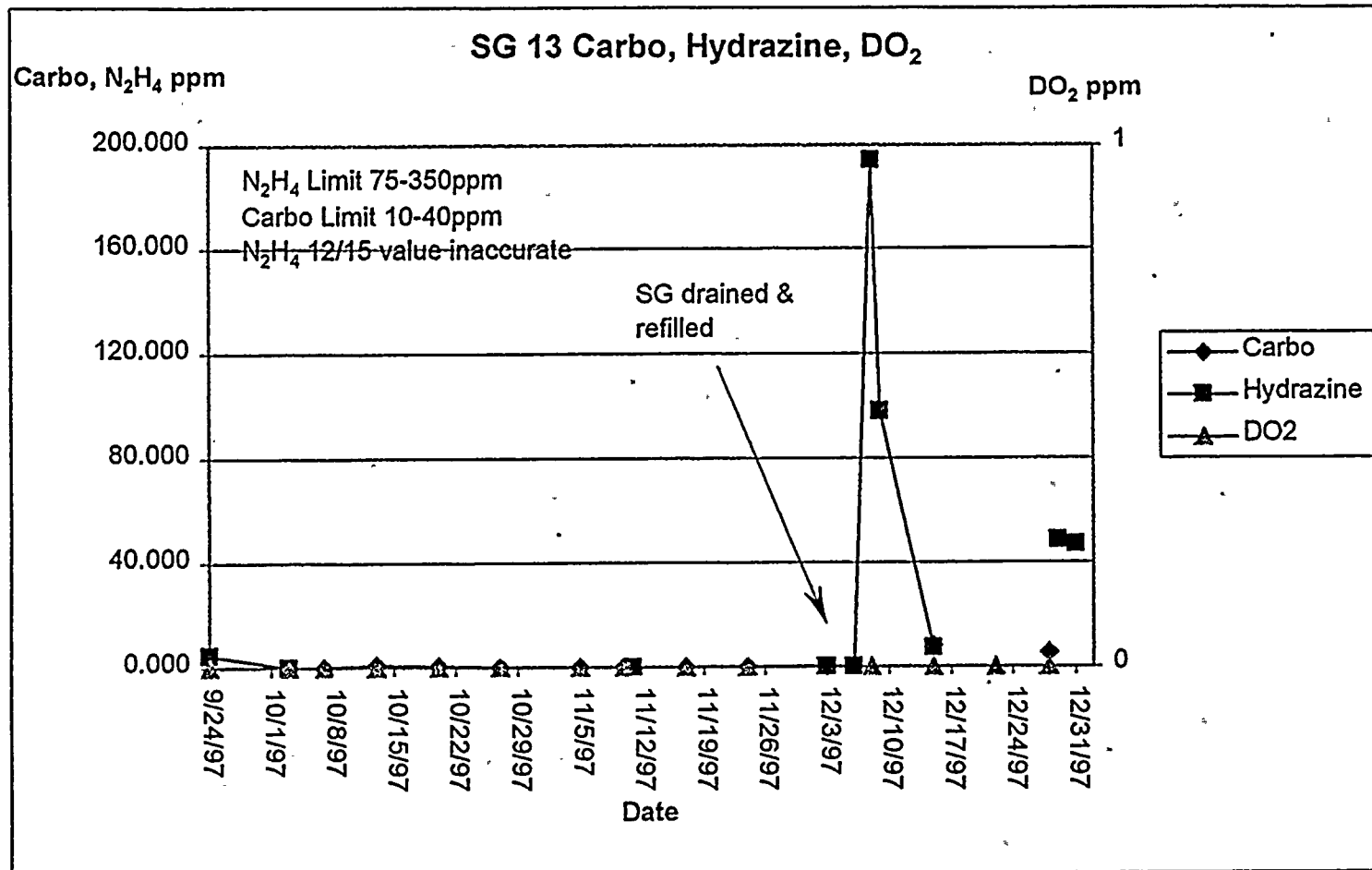
Attachment 1

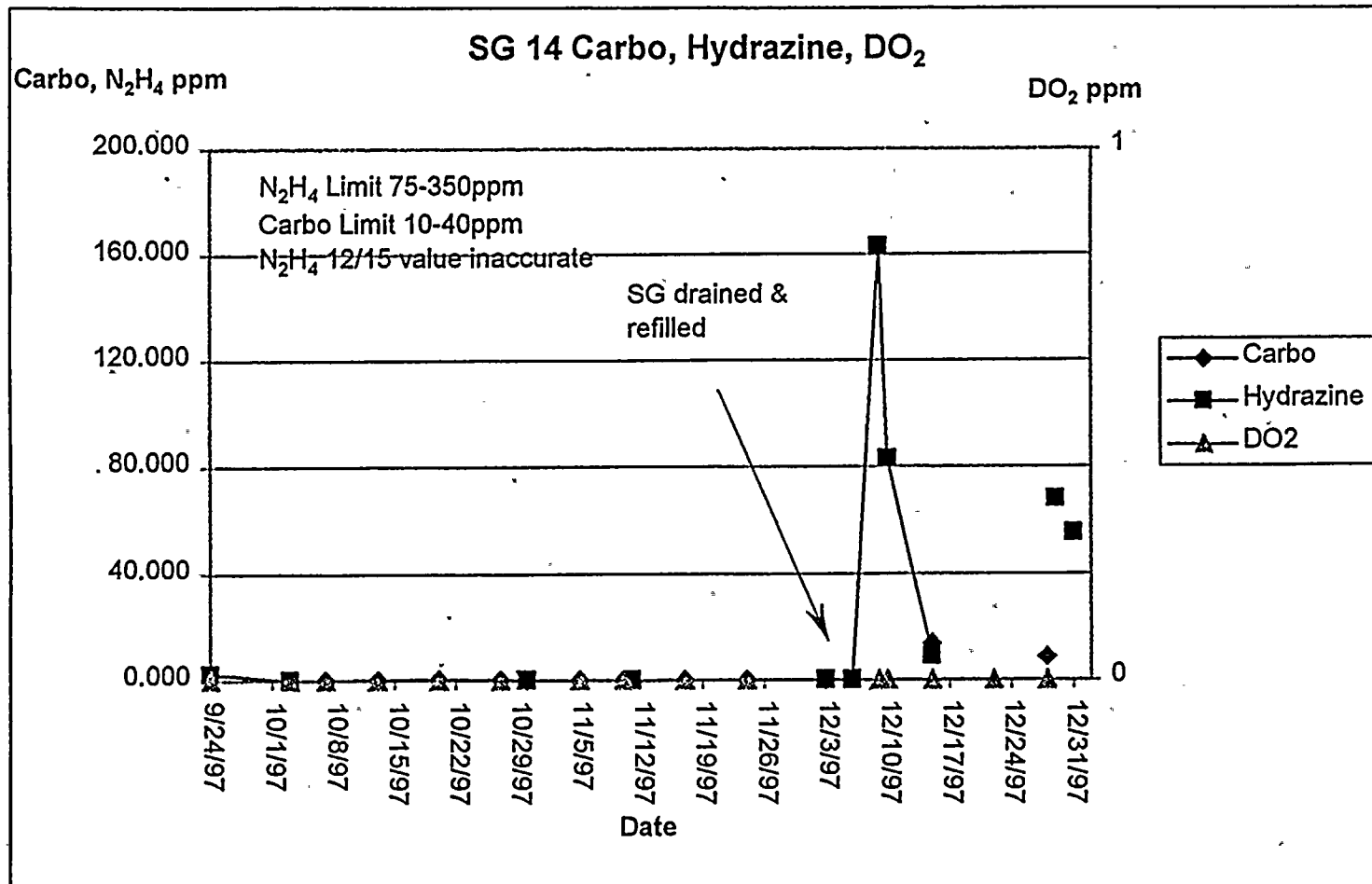
Layup Chemistry Data ADM.010 Sheets SG 14											
Date	pH	Carbo ppm	N ₂ H ₄ ppm	DO ₂ ppb	Sodium ppb	Chloride ppb	Sulfate ppb	Boron ppm	ETA ppm	Ammonia ppm	Comments
9/24/97	9.78		2.460	ND	0.2			1.90	44.4		Added 4 gal ETA & 10 gal carbo
10/3/97	9.53		0.0102	0	0.5	17.9	27.5		43.4	4.8	
10/7/97	9.51	ND		0	0.6	1.3	19.1	1.9	43.0		
10/13/97	9.60	0.182		0	2.4	3.5	25.2		43.0		
10/20/97	9.55	0.297		0	1.1	4.1	56.5		44.0	5.0	
10/27/97	9.47	0.12		0	3.8	3.0	40.6		45.9	6.7	RCS heat up to 187 10/24-29
10/30/97		ND	0.0056						43.6	5.4	Sparge for release 10/30 no drain
11/5/97	9.43	0		0	1.0	2.5	33.0		45.0		
11/10/97	9.49	0.059		0	1.0	2.9	30.8		59.4		Sparge for release no drain
11/11/97			0.0057					2.2	56.6	3.6	
11/17/97	9.44	0		0	1.1	3.3	33.7		51.4	6.1	RCS heat up to 190 11/12-15
11/24/97	9.33	ND		0	1.2	40.0	63.0		49.6	7.9	RCS heat up to 195 11/18-23
12/3/97	9.25	ND	0.0046		1.6	9.3	31.6	0	48.1	8.7	
12/6/97			0.0018					3			12/8 refill, add 3.5gal ETA, 15.5gal N ₂ H ₄ , 9gal carbo(assumed)
12/9/97	9.90		162.83	0					138.0	14.0	RCS heat up to 180-190 through 12/31
12/10/97	9.87		82.8	0					101.3		
12/15/97	9.97	13.6	8.843	0	4.2	17.5	51.3	18.8	109.5	16.7	Hydrazine likely inaccurate doesn't correspond with other data
12/22/97	9.86			0	1.7	7.3	36.7	26.2	82.4	17.7	
12/28/97	9.94	8.5		ND	1.6	15.3	298.0	44	98.8	17.6	
12/29/97			67.9								
12/30/97							54.0				
12/31/97			55.2					0.02			Sparge for release 12/31 drain to norm op
ND: value reported as less than detectable. <50ppb for carbonylhydrazide, <5ppb for dissolved oxygen											

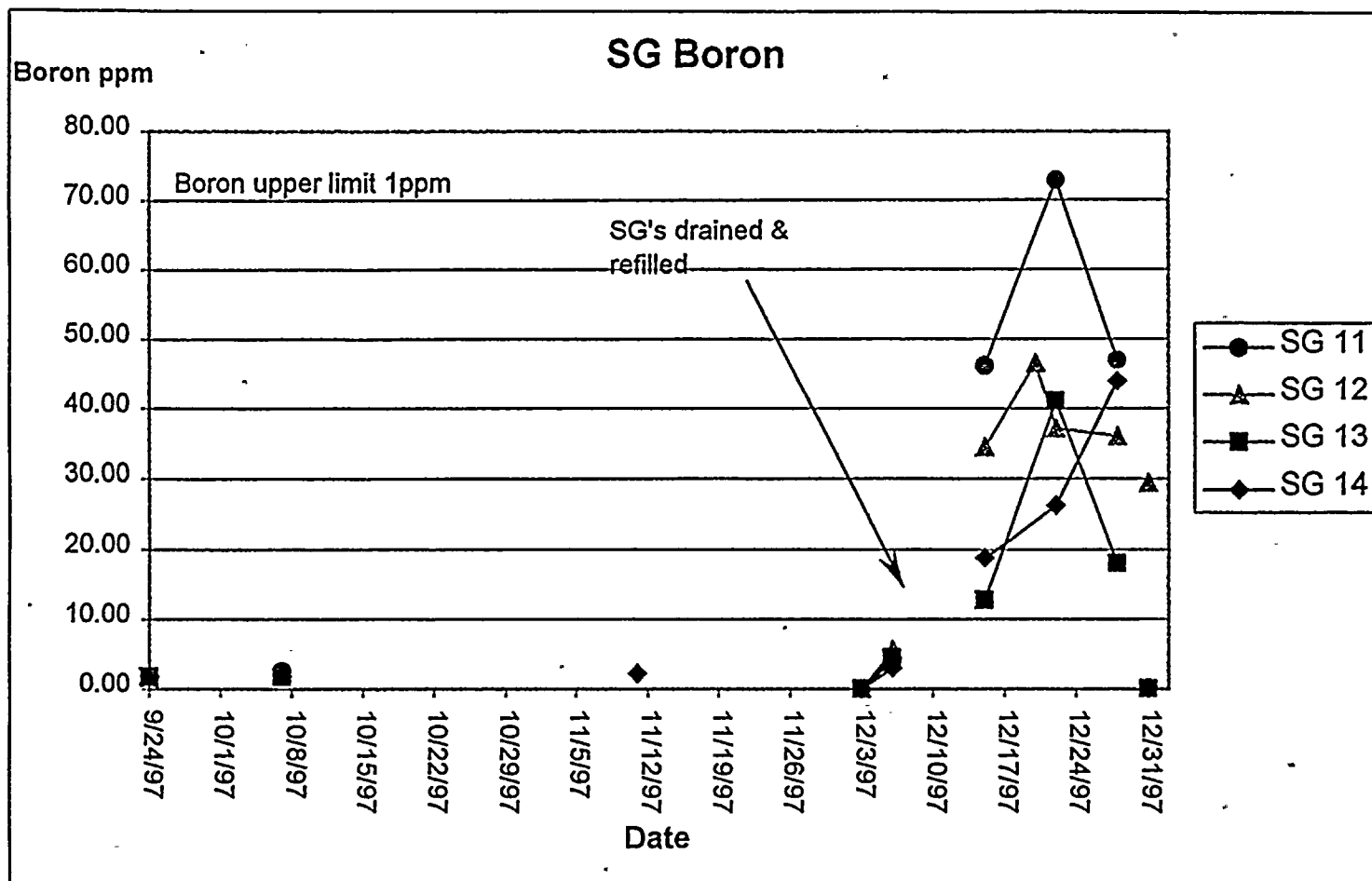


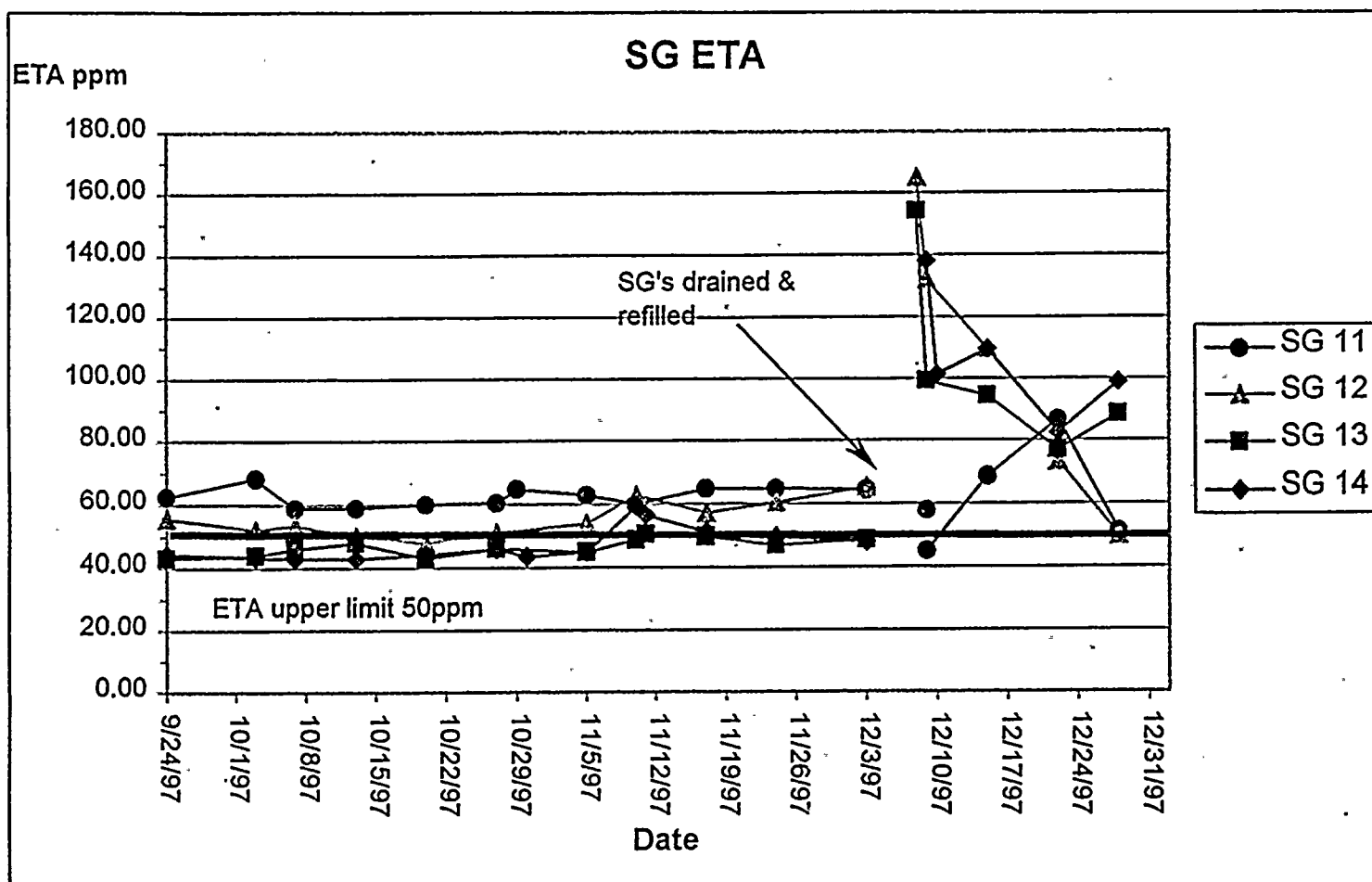


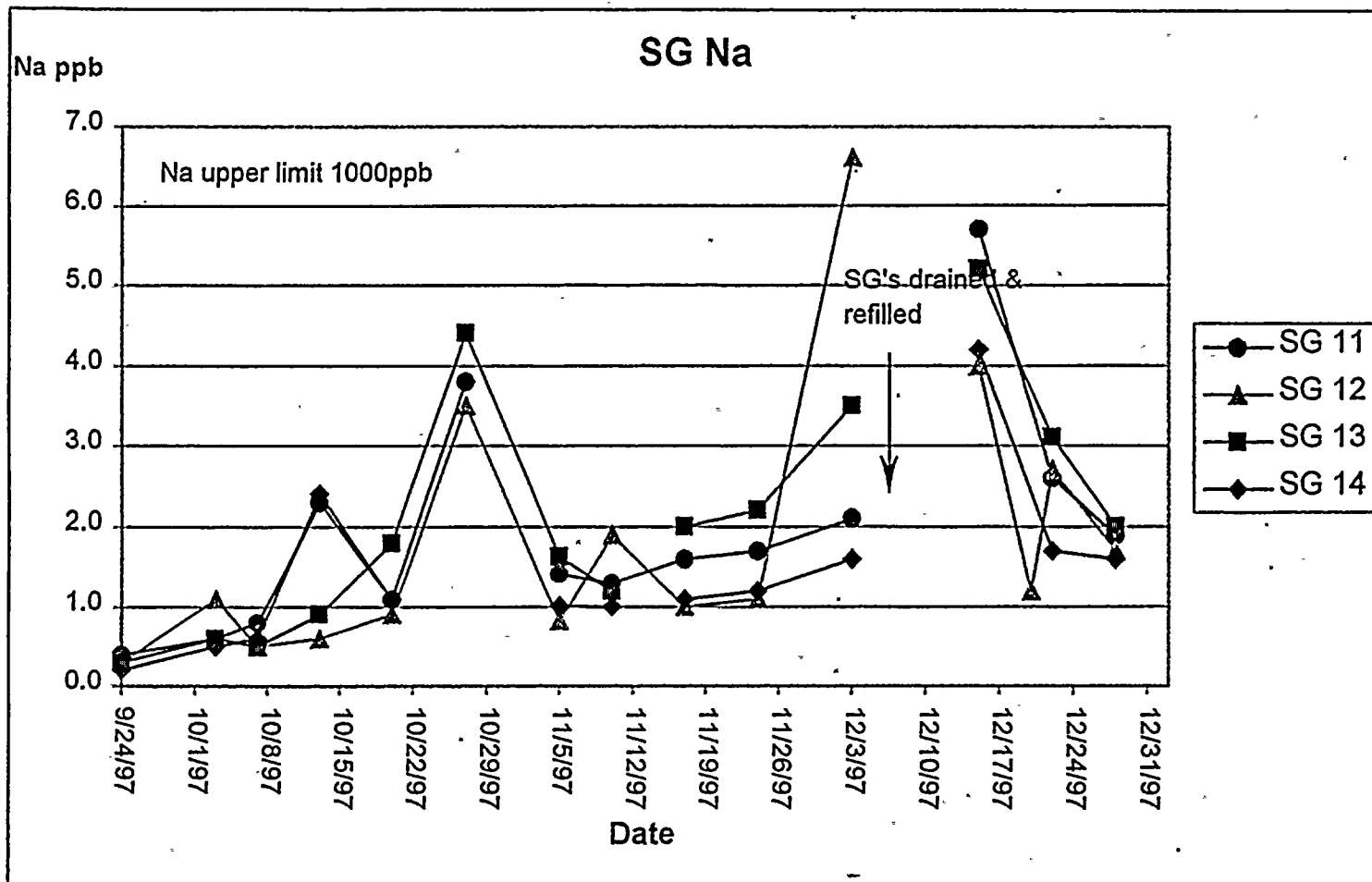


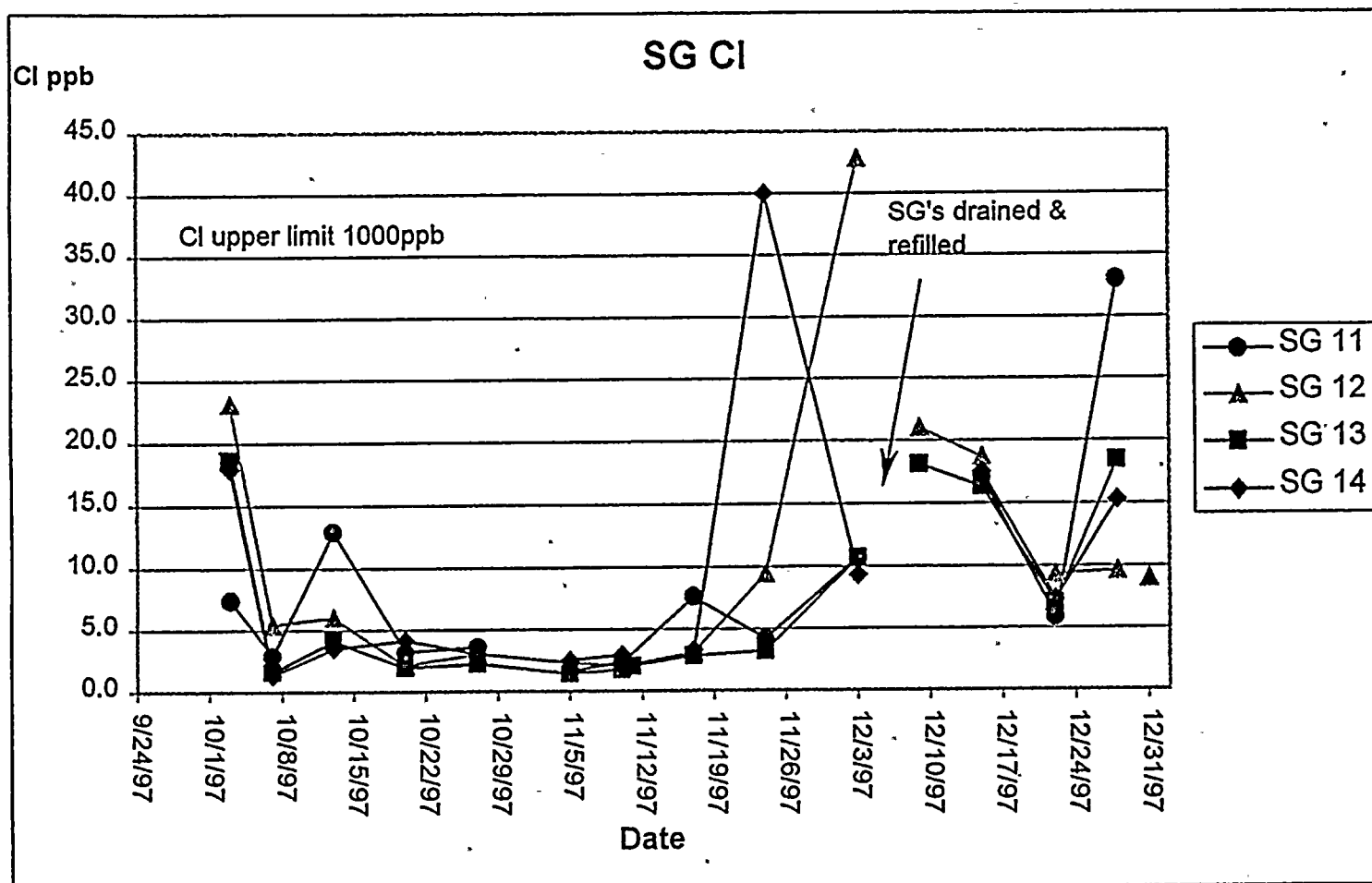


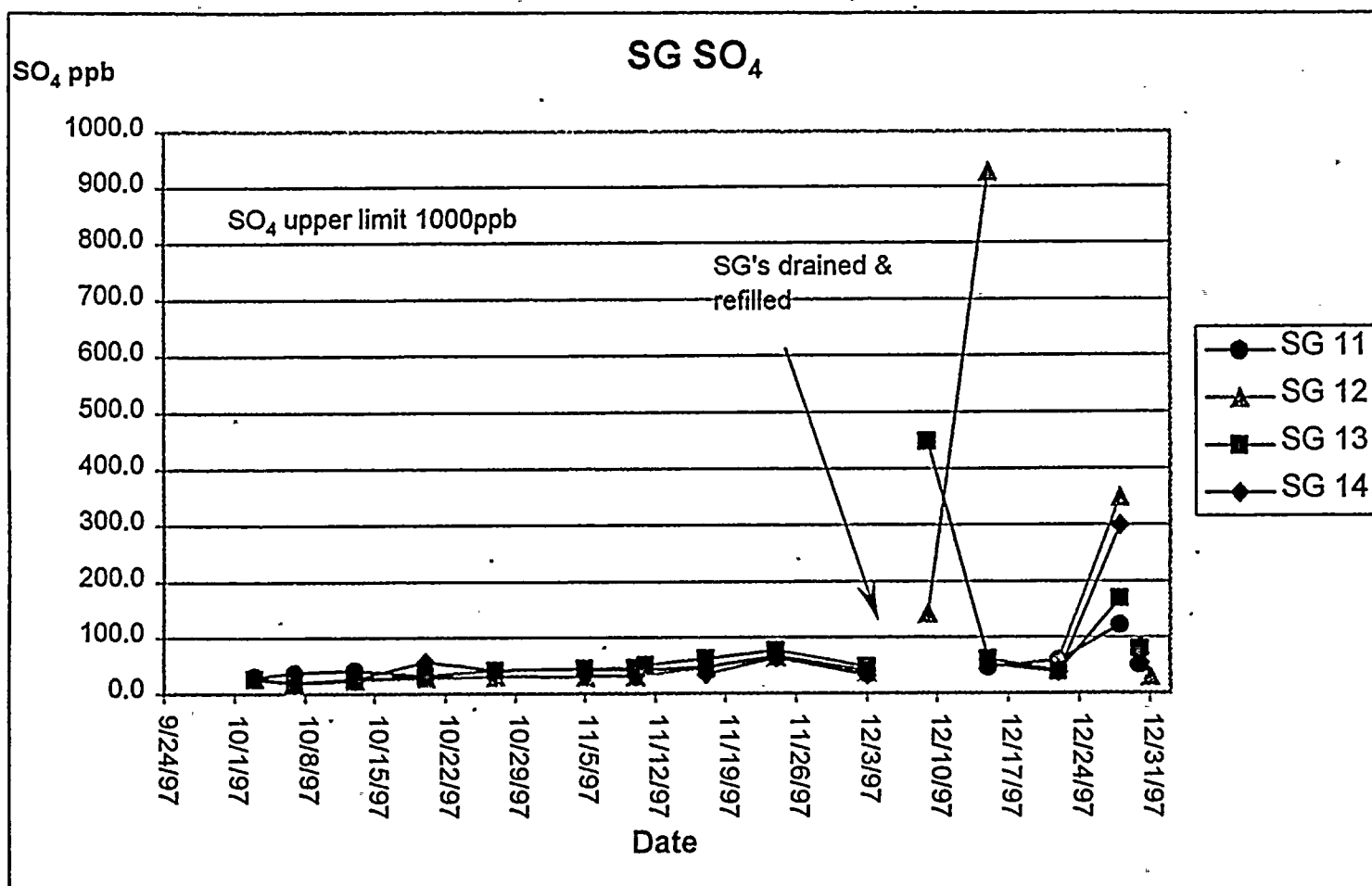


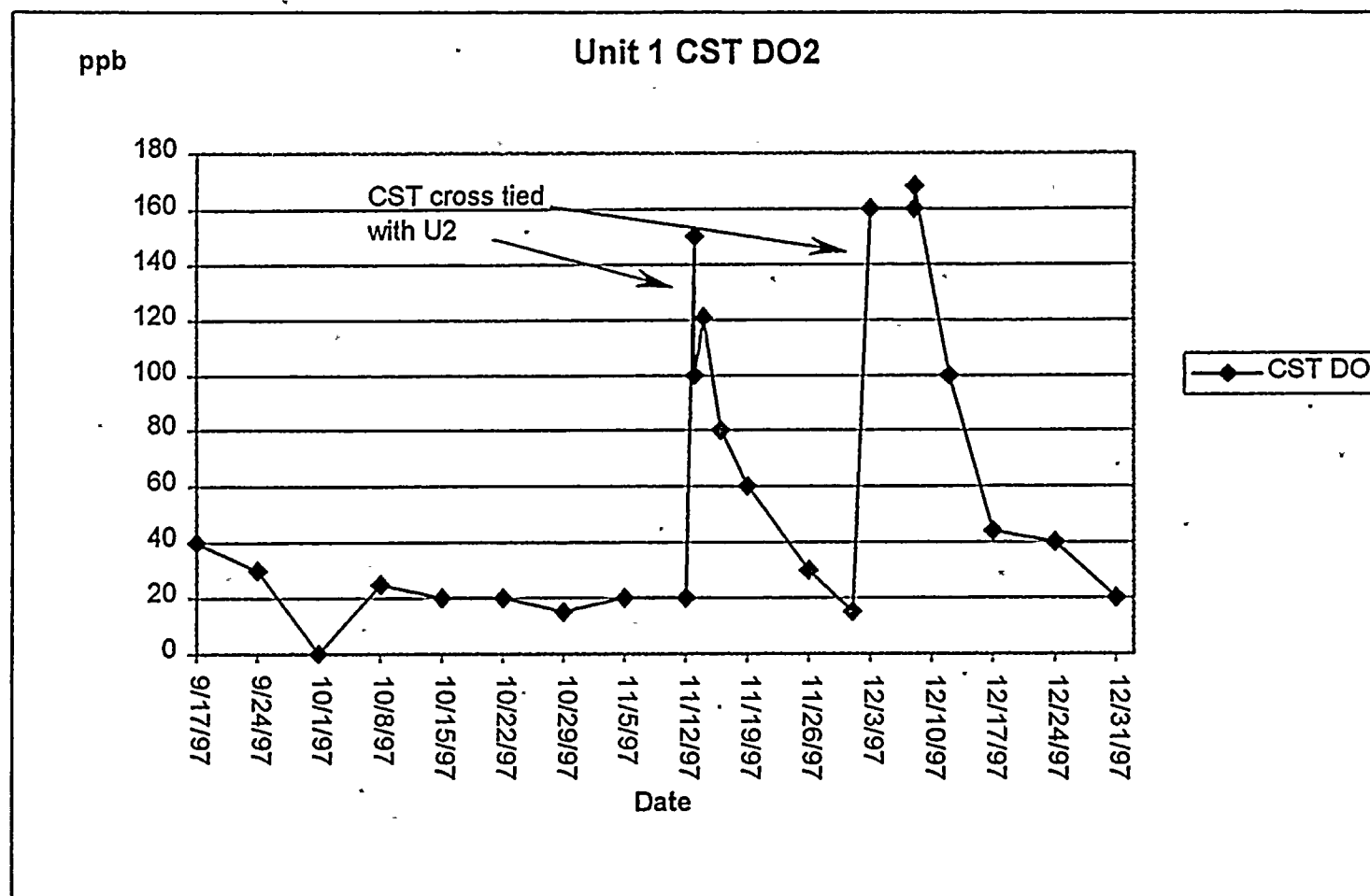












ATTACHMENT 2 TO AEP:NRC:1295B

SUMMARY OF UNIT 1 STEAM GENERATOR LAYUP CHEMISTRY FROM
JANUARY 1, 1999 TO FEBRUARY 18, 1999

ATTACHMENT 2 TO AEP:NRC:1295B

SUMMARY OF UNIT 1 STEAM GENERATOR LAYUP CHEMISTRY FROM
JANUARY 1, 1999 TO FEBRUARY 18, 1999

