

Regional Administrator

Nuclear Regulatory Commission 611 Ryan Plaza Drive, Suite 1000

Attention: Mr. E. H. Johnson

Region IV

Public Service Company of Colloradio

January 31, 1985 Fort St. Vrain Unit No. 1 P-85036

FEB - 1 1985

Docket No. 50-267

SUBJECT: Chloride Source Report

REFERENCES: 1) NRC Letter, R. D. Martin to O. R. Lee, 1/17/85

> 2) PSC Letter, O. R. Lee to E. H. Johnson, 1/28/85 (P-85030)

Dear Mr. Johnson:

Please find attached our report "An Investigation into the Sources of Chloride in the Fort St. Vrain Primary Circuit." As we indicated in our January 15, 1985 meeting, we are also preparing a report regarding our investigations of the effects of chlorides on major components in the primary circuit. This report will be sent to you on or before February 28, 1985.

If you have any questions, please call Mr. M. H. Holmes at (303) 571-8409.

Very truly yours,

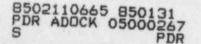
D. W. Warenhour

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Attachment

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AN INVESTIGATION INTO THE SOURCES OF CHLORIDE IN THE FORT ST. VRAIN PRIMARY CIRCUIT

1.0 SUMMARY AND CONCLUSION

The discovery of chloride stress corrosion of a Fort St. Vrain (FSV) CRD cable prompted an investigation into the possible sources of the chloride. The total chlorine (Cl) in the primary corcuit is speculated to be 100 g, not including possible higher amounts in crevice areas. Samples of virtually all materials of construction in the primary circuit were screened for possible release of chloride either by water leaching or by heatup. It was found that almost all materials tested leached chloride, presumably as salt, with PCRV concrete leaching the most. In heatup tests, fuel rods were found to release HCl gas when heated to 1740°F. Subsequent long term heating of the fuel rods caused no further release of HCl. The total amount of HCl released from the core 1 fuel into the primary circuit was about 90 gm. The following is a list of major conclusions of this investigation:

- Chloride on the CRD cable and on the bolt is more concentrated than found on other primary coolant surfaces. This suggests concentration of Cl in crevices or stagnant areas.
- The water ingressed into FSV is not a source of chlorine, except for possible leaching that it causes.
- The fuel releases HCl gas during startup, under dry conditions there is no continuous release, under wet conditions at operating temperature the fuel may release small amounts of HCl.
- Core graphite (H-327) and side reflector graphite (HLM) are not major sources under dry or wet conditions.
- The titanium (Ti) sponge is not a major source of chlorine. It is possibly a minor transient source during initial heatup, which possibly contaminated the CRDs above the shield plug.
- 6. Leaching of concrete and/or thermal insulation is not ruled out, however, leaching would yield chlorine as salt, which is non volatile, and therefore may not readily circulate. Circulation of small amounts of salt particulates entrained in the helium is, of course, possible.
- Multiple sources are quite probable.

2.0 Introduction

Control rod cables and some circulator bolts have experienced stress corrosion cracking accelerated by chloride. The chlorine content of the cable in the cracked region is 138 µg/gm wire. Chlorine on the C2102 bolt was 1 mg. These values equate to 10 and 14 µgm Cl/cm² for wire and bolt respectively. These concentrations of chlorine are higher than that found on the circulator inlet duct about 2 µgm/cm² or on plateout probe diffusion tubes which were about 1 µgm Cl/cm². This suggests that the chloride concentrates on surfaces with cracks or crevices like the cable or the bolts, relative to smooth or well swept surfaces. Extrapolating 1 to 2 µgm Cl/cm² to all metallic surface, 7 x 10⁷ cm² yields a total burden of 50 to 200 gm. The total could be greater due to the possible concentration in crevices or stagnant areas.

Tests were conducted to determine the most likely source or sources of chloride in the reactor. Materials of construction within the PCRV were tested for potential chlorine content or release. These include FSV water, concrete, Ti sponge, fuel, graphite, and ceramic insulation. The release of chlorine can potentially occur from these materials during intitial heatup. and later via hydrolysis reactions during water ingress, or in the case of Kaowool and concrete, by water leaching. Large ingress would cause condensation of water on the relatively cool penetration walls, subsequently causing chlorine containing rain onto the control rod cables. Evaporation of water from the cables would concentrate chlorine thereon. Table 1 lists the important potential sources. Notice that there are two potential species, HCl gas which would be easily transported around the circuit and salt which would be less easily transported. The HCl gas, therefore, may be responsible for Cl contamination on virtually all swept surfaces while leaching of salt would result in high local concentrations, particularly in the bottom plenum or other areas where water would accumulate.

TABLE 1

SOURCES OF CHLORINE IN THE PRIMARY CIRCUIT

Source	Species Released	Transport Mechanism
Fuel rods	HC1	Heatup and hydrolysis of metal chloride
H-327/H-451 graphite	HC1	Heatup and hydrolysis of metal chloride
PGX/HLM graphite	HC1	Heatup and hydrolysis of metal chloride
Ti sponge	нс1	Heatup and hydrolysis of metal chloride
Ceramic insulation (Kaowool, masrock, etc.)	Salt	Water leaching due to condensation on PCRV liner
Concrete	Salt	Water leaching of core support floor
Water	Salt	Direct ingress with water leaks

3.0 EXPERIMENTAL

3.1 Phase I - Screening

The work is in two phases. In phase I all materials were screened by leaching in boiling water to determine which material is a likely source. In addition, the water sources at FSV were tested to determine the chlorine content. Table 2 lists the various water sources at FSV and their chlorine content.

In Table 2, all of the water sources, systems 21, 22, 31, 46, and 47, are low in chlorine, i.e., chlorine is in the ppb range. System 23, however, is water removed from the primary circuit which contains a few ppm to 400 ppm chlorine. In other words, water enters the primary circuit free of chlorine and comes out contaminated with chlorine. Clearly, there is a source of chlorine within the PCRV.

Table 3 lists the screening tests on the potential sources within the PCRV. The results in Table 3 show that the PCRV concrete is by far the largest source of chlorine in the system. How the chlorine in the concrete would get in the primary circuit is not clear, however. Presumably, during shutdown, some water in the support floor concrete could leak into the PCRV through the cracked liner and carry with it salts leached from the concrete. Obviously, this source would be difficult to quantify.

The other sources, all have low ppm levels of chlorine but because they have large total masses, the total chlorine can be significant. For example, the HLM graphite, total weight approximately 7 x 10^5 lbs, could contain almost a kilogram of leachable chlorine, whereas the fuel rods have only up to 230 g leachable. These figures do not tell the whole story, for all of these materials have a residual chlorine content that is not easily leached. The residual chlorine ranges from 10 to 100 ppm in the graphite and kaowool, up to 1000 ppm in the

TABLE 2

ANALYSIS OF WATER SYSTEMS AT FSV(a)

No.	System	ppm Chlorine
21	Circulator bearing water	<0.025
22	Main steam	<0.020 to 0.193
31	Feedwater	<0.020 to 0.090
46	Liner cooling	<0.020 to 0.090
47	Purification system cooling	0.088 to 0.470
23	Drier regeneration	3.8 to 4.0
23	HPS front end knockout pot	3.8 to 400

(a)All data supplied by PSCo Chemistry. The system
23 values may be high because of Cl contamination in the sample
storage drums.

Material	Chlorine (ppm)	Sodium (ppm)	Mass In Reactor (kg)	Total Leachable Chlorine in Reactor (d) (g)
Fuel rods	9		27,000	230
H-327 graphite	<1	1.0	220,000	<220
H-451 graphite	<1	<0.2	21,000	<21
PGX-112 graphite	<1	0.3	50,000	<50
PGX-138 graphite	<1	0.5	50,000	<50
HLM graphite	2.1	0.2	320,000	627
PCRV concrete ^(b)	160	1.8	>10 ⁶ (floor)	>>1,000
Kaowoo1	10 to 44 ^(c)		27,000	270 to 1,200 ^(c)
Masrock	~23		5,000	100
Quartz et silice	9		400	4
Ti sponge (fresh)	44	10	95	4

			TAB	LE :	3		
RESULTS	OF	WATER	LEACHING ^(a)	OF	PRIMARY	CIRCUIT	MATERIALS

(a) Boiling crushed materials 2 hours in deionized water.

(b) The concrete also had 325 ppm sulfate and other ions including nitrate, formate and acetate.

(c) The specification on leachable C1 in Kaowool is 10 ppm one "archive" sample leached as much as 44 ppm, this value is probably not representative of that in the reactor.

(d) Error bands or uncertainties have not been applied to these values because they are based on leaching single samples. Obviously, the uncertainty would be large, perhaps factor 6 of 2+.4.

Ti sponge and concrete. The fuel rods contain in the range 1 to 20 ppm chlorine. Some of the residual chlorine may be released as HCl gas during heatup or hydrolysis at elevated temperatures. Tests to determine the amounts and sources of the gaseous form are discussed in the phase II work.

3.2 Phase 2 Heatup/Hydrolysis Results

Phase 2 work involves heating candidate materials to their reactor operating temperature in flowing dry and wet helium. The apparatus and test method are shown in Appendix A. The dry helium step would remove volatile chlorine (or HCl) and simulates a normal heatup in the reactor. The wet helium step may cause hydrolysis of metal chlorides creating HCl gas by the reaction.

 $H_20 + MC1_2 = 2 HC1^{+} + MO$

where M = Fe, Mg, etc.

3.2.1 Ti sponge

Titanium sponge was felt to be a likely source because the control rod drive penetrations are purged with purified helium which comes directly from the Ti beds. Furthermore, the manufacture of Ti sponge involves the reduction of TiCl, by Mg

metal. The final product can contain up to several thousand ppm of chlorine as MgCl₂. The MgCl₂ is

subject to hydrolysis via the above chemical reaction, however, it is difficult to create a scenario whereby moisture contacts the sponge while at operating temperature. One possible sequence would be the following.

Following icing in the LTA exchanger, the system is regenerated by purging the LTA backwards into the waste gas system. If the LTA is not completely dried out prior to establishment of normal flow and further, and if the Ti bed is still hot, then some water could contact the sponge while it is in operation. The results of the phase 2 tests on the sponge are shown in Table 4.

Table 4 shows that during initial heatup of the Ti sponge about 0.6 to 3 g of chlorine (tests 1 and 5) could have been released from the 210 lb. getter bed at FSV. Upon longer heating times, the amount released would trickle down to approximately 0.0005 g/hr (average of tests 2 and 7) or in fact to zero (based on the FSV sponge tests). If the sponge were subjected to water vapor, the rate of chlorine release could be about 0.01 g/hr (test 4) or virtually zero (test 12 on FSV sponge). It is

Test No.	Material	Weight (g)	Time Hours	Gas(a)	Chlorine (µg)	µg/hr	FSV Initial Heatup (g)	FSV Continuous Release (g/hr)
Blank	Empty tube		17	Не	21	1.2		
1	Fresh Ti sponge	80.0	5.5	Не	2698		3.2	
2	Fresh Ti sponge	80.0	63.5	Не	99	1.5		0.0004
3	Fresh Ti sponge	80.0	6	He/ H ₂ 0	138	23		0.025
4	Fresh Ti sponge	80.0	18.5	He/ H ₂ 0	157	8.5		0.009
5	Fresh Ti sponge	78.6	2	He/H ₂ (a)	497		0.6	
6	Fresh Ti sponge	78.6	17.5	He/H ₂	57	3		0.002
7	Fresh Ti sponge	78.6	24.5	He/H ₂	41	1.7		0.0006
8	Used FSV sponge	46.8	3.75	He/H ₂	41	10,9	0.02	
9	Used FSV sponge	46.8	67.25	He/H ₂	44	0.65(b)		0
10	Used FSV sponge	46.8	46,25	He/H ₂	36	0.78 ^(b)		0
12	Used FSV sponge	46.8	72.5	He/H ₂ / H ₂ 0	32.8	0.45(b)		0

TABLE 4 RESULTS OF PHASE 2 TESTS ON TI SPONGE (Temperature All Tests - 700°F)

(a) In Run 5 the gas was changed from pure He or helium containing 25,000 ppm water vapor to a mix-ture of He and 1000 ppm H₂ or He/100 ppm H₂/25,000 ppm H₂0. The addition of H₂ was thought to simulate H₂ in the reactor and to maximize the production of HCl gas. (b) Less than background run No. 1.

concluded that initial heatup of the sponge can release a few grams of chlorine (probably less than 3 g) but proglonged heating and/or exposure to moisture has little effect on chlorine release. Furthermore, while short exposures to water vapor may be possible, it is difficult to imagine a long term exposure of the sponge to water vapor. It may be concluded that the Ti sponge is not the major source of chlorine in the primary circuit.

3.2.2 Graphite

HLM graphite and H-327 graphite were coarsely crushed and subjected to heatup in dry helium followed by wet helium. The HLM was heated to 1300°F, simulating the side reflector temperature while the H-327 was heated to 1800°, the fuel element temperature. The results are shown in Table 5.

TABLE 5

RESULTS OF HEATUP AND HYDROLYSIS OF GRAPHITE

							Chlorine Released			
Test	No.	Sample	Weight (g)	Gas	Temp (°F)	Time (Hr)	Total (µg)	g/core ^(a)	G9hr	
4		HLM	66.8	He/H ₂	1300	24	34	ND		
5		HLM	66.8	H3/H2/H20	1300	24 .	29		ND	
6		H-327	145.0	He/H ₂	1800	3	40	ND		

(a) g HC1 released from entire FSV core inventory after furnace blank of 40 µgm subtracted.

ND = not detected or HCl less than blank.

These results show that graphite does not release gaseous chlorine or HCl upon heatup or exposure to water vapor.

3.2.3 Fuel Rods

It was surmised that fuel rods could be a source of chlorine for the following reasons. During fuel manufacturing, particles are coated with SiC by thermal decomposition of methyl trichlorosilane, which results in some residual chlorine in the fuel particles. In addition, fuel rods are leached with HCl gas after the hot press and carbonization steps to remove trapped or uncoated uranium and thorium. The HCl leaching is accomplished during the final high temperature anneal step at 2900° to 3300°F, which effectively removes most of the HCl from the rod. Some residual chlorine remains, however, typically in the low ppm range.

At GA Technologies, as part of fuel production, QA testing, and qualification, finished fuel rods are routinely heated in the high temperature mass spectrometer to measure the chlorine vapor pressure above the rod, and therefore the potential for chlorine release into the primary circuit. When rods are heated up in vacuum in the lab apparatus they invariably release about 1 to 50 µg of HCl gas per rod at around 1000°CF (This is from 0.1 to 5 ppm in the rods).

Since the rods were annealed at up to 3300°F during the HCl leach step the release of HCl gas during the modest heatup in the mass spectrometer was puzzling. It was concluded that either the leach/high fire process contaminated the rods or that the HCl gas was formed during storage in air due to hydrolysis of metal chlorides. Furthermore, if the latter occurred it was expected that hydrolysis in the reactor should also occur during normal operation where a few ppm moisture is available or during shutdowns where large amounts of water are present.

TABLE 6

SUMMARY OF PHASE 2 HEATUP/HYDROLYSIS OF FUEL RODS

				HC1 S Spec.	HC1 Tub	e Furnace			eleased core, g
Test No.	Fuel Segment	Year Service	ppm(a)	No. Rods Tested	Dry He ppm(a)	Wet He ppm/hr	No. Rods Tested	Mass	Tube Furnace (b)
1	Core 1	1	0.28	3	3.7		3		
2	Core 1	2	0.71	5					
3	Core 1	3	0.70	5	3.2	0.06	6		
4	Core 1	4	0,5	5	0,75		2		
5	Core 1	6	0.67	1	0.33		6	20	90
6	Core 7		0.5	1	0.26	0.03	6	3	2
7	Core 8				0.10		6		1
8	Core 9				0.4		6		2
9	Core 10	4	3.5	4	15	-0-	4		
10	Core 10 1	st ^(c)							

Core 10 mid^(c) 11

Core 10 last(c)

12

- (a) 1 ppm HCl = 50g HCl released, calculated by 10^{-6} gm/gmx4x10⁶rodsx11 gms/rod.
- (b) The total released from the tube furnace was divided by 0.79, which was the collection efficiency, prior to calculating the total amount recovered.
- (c) Uncertainties or error bands have not been assigned, a factor of 2 uncertainty might be appropriate.

To verify the results of the HCl observation in the mass spectrometer and to determine the affect of hydrolysis a number of fuel rods have been heated in the Phase II apparatus. The rods included an archive specimens from the initial core loading including 1, 3, 4 and 6 year fuel, and rods from each of the reload segments 7, 8, 9 and 10. The results are summarized in Table 6. Details of these results including all background or blank determinations are given in Appendix B.

The results of Table 6 show that the initial core fuel rods averaged about 0.5 ppm based on averaging 19 mass spectrometer tests. This means a release of about 20 g of Cl from core 1 heatup. In 4 tube furnace tests, on 21 fuel rods, the average HCl found was 1.4 ppm which converts to 90 gm released from the initial core.

In the tests where hydrolysis was tried two rod batches showed small HCl releases, equivalent to 1 to 3 μ gm/hr from the core. This could be important during reactor operation and high moisture concentration.

It is apparent from the table that the initial core released about 90 g HCl upon startup in 1976. Heatup of each reload contributed an additional gram or so. This amount of release is fairly consistent with that speculated to be in the primary circuit, about 50 to 200 g. It may be concluded that HCl gas released from the fuel is a major contributor to the total Cl burden. The mass spectrometer results are known to be nonquantitative on total release. The tube furnace results are much less ambiguous and are more quantitatively correct.

A list of conclusions of Phase 2 Heatup and Hydrolysis Tests is given below.

- Initial heatup of fuel rods in core 1 released about 90 g HCl. Prolonged heating did not increase the release.
- Titanium sponge released 1 to 3 g HCl on initial heatup. Prolonged heating did not increase the release.
- Heat up of HLM side reflector and H-327 fuel element graphite did not release HC1.
- Hydrolysis of Ti sponge, or graphite did not cause HCl release.
- 5. Hydrolysis of fuel at operating temperature and high moisture would cause a small

release of HCl gas, about 1 to 3 gm cl per hour.

3.3

Neutron Activation of Chlorine

Chlorine 35 has a large neutron capture cross section (43 barns) creating Cl-36 which has a halflife of 3 x 10^5 yr and is a pure beta emitter (0.7 MeV). It was surmissed that if chlorine found on the cable (or elsewhere in the primary circuit) contained Cl-36, then it would prove that either the source of the chlorine was the core, or $\frac{1}{2}$ least, the chlorine had circulated in the pr. $\frac{1}{2}$ circuit, becoming activated, prior to plating out in the system.

Accordingly, a number of samples from the primary circuit were analyzed for Cl-36 and total Cl content. The results are given in Table 7.

The results in Table 7 clearly show that the chlorine found on corroded cable, the circulator duct and the circulator bolts has been subjected to a degree of activation equivalent to 24 to 80 days in core at 70% power.

TABLE 7

RESULTS OF CHLORINE 36 ANALYSIS

Sample	Time in Service EFPD	Total Chlo Total Found	orine ugm/cm ²	Chlorine 36 Total Found	<u>µci 36</u> gm 35	Neutron Activation Days at 70%
Cable wire near corroded area	10 yrs 676 EFPD	138 ug/g (a)	10	23 µci/g wire	167	43
30" above corroded an	rea	90 µg/g	6	0.086 uci/g wire	1	0.2
Plateout probe tube sections BE, B1, B4, B6 Tube Sections B-13	5 yrs 408 EFPD	6 μg 8 μg	2	0.7 μci 0.11μci	11.4 14.3	2.9 3.7
Circulator C2102 inlet duct (234cm ²) bolt	7 to (c) 352 EFPD	110 μg 990 μg	2 ^(b) 14	23 µci 309 µci	212 312	54 80
<u>Circulator C2104</u> bolt A bolt B	659 ^(d) EFPD	250 µg 120 µg	3.6 1.7	340 μci 110 μci	92 136	24 35
HPS KO POT water	6/84 ingress	3.8 ppm			10.2	2.6
RSS Balls MID 21 RSS Balls BATT 21	10 yr 10 yr	8 μg/ball 7 μg/ball			0.08 0.8	0.02 0.2

(a) 33 ug surface/gm wire also found.

(b) Analysis of wipe was increased by a factor of 4 reflecting a decon factor of .24.

(c) C2102 was in service for 3 months, 7EFPD, prior to shutdown on June 20, 1984. The total service time was 352 EFPD. The efficiency of decon efforts prior to recent service is unkown.

The chlorine found on the cable 30 inches above the corrosion failure on the plateout probe and in the HPS knockout pot has apparently been subjected to substantially less activation. This is not totally understood. The following is offered in explanation. The water obtained C1-36 from the HPS knockout pot in late October, 1984 ppm total Cl and a ratio of 10.2 µci C1-36/gC1. This low ratio suggests that this water sample contains chlorine which is not representative of that in the primary circuit, or in otherwords, it was contaminated with stable C1. The contamination could have come from the sample storage drum. Or, it could have leached from non activated locations inside the primary circuits, since the water sample was obtained 3 to 4 months after reactor shutdown.

The Cl found in the plateout probe diffusion tube also has a low Cl-36 content. Either these samples were contaminated by handling or storage since November, 1981, or, it suggests the major Cl ingress into the primary circuit occurred after the probe was removed on November 9, 1981 which was 54 days into cycle 3 operation. The low chlorine 36, found on the cable above the corrosion failure, means that this area was inside the shield plug where it was well swept with purified helium, thereby inhibiting contact with primary coolant.

The lowest Cl-36 ratio was found on RSS balls from hopper 21. This shows that the water leaked into the hopper did not carry chlorine from the primary circuit with it.

The C1-36 found on the corroded cable could not have been due to in situ neutron activation because this particular control rod, 21, was in region 7 which was unrodded most of the time. This means that the cable was wound on the drum above the shield canister. The neutron flux in this location would be 4 or 5 orders of magnitude less than in the core. This virtually proves that at least some of the chlorine on the cable came from the primary circuit. Also, chlorine on the circulator could not have been activated in situ because of the low neutron flux in the lower plenum.

The chlorine found on the corroded cable and on the circulators experienced neutron activation equivalent to an average 47 days in core at 70% power. This means that most of the chlorine was not continuously released from the core, because much of it would have experienced up to 1000 days of neutron activation. It is certainly possible that the chlorine found in the circuit is a mixture of that which was released from core 1 and a

smaller amount released much later, which would be highly activated.

Another extreme possibility is that a large portion of the chlorine is in constant circulation. For example, residence time in a core is about 0.3 seconds which is 3% of the total cycle time of 10 seconds. If all of the chlorine has circulated continuously for 1000 days of reactor operation, it would exhibit a Cl-36 ratio equivalent to an activation of 1000 x 0.03 = 30 days. This degree of activation is approximately what was found on the cable and on the circulator. However, if there was continuous circulation, there would have been continuous cleanup by the HPS, and the chloride removed would be many times that in the primary circuit or several thousand grams. This seems to be rather unlikely.

It is concluded that only a small fraction of the Cl is circulating, the larger portion being plated out or concentrated in crevices.

Conclusion of C1-36 Analysis

- The Cl-36 concentrations in the primary coolant show that the source of chlorine is the active core, or if not the chlorine found was in almost continuous circulation. The former is must more likely.
- The core does not continuously release Cl, otherwise the "equivalent activation" would be several hundred days.
- 3. There is another source wihch is low chlorine 36 and has apparently contaminated the upper part of the cable, evidently in and above the shield plug. This chlorine was not well mixed with primary circuit chlorine.
- 4. The Cl-36 ratios in the primary circuit are consistent with a mixture of chlorine activation times: a large fraction of relatively non-activated Cl (either released from the core on initial startup or from leaching of concrete or insulation) and a smaller fraction of highly activated Cl, such as might have been released later.
- Some of the above chlorine mixture would circulate and become activated, thereby increasing the C1-36 ratio.

- The low Cl-36 content of the plateout probe diffusion tube suggests that the major Cl ingress occurred after November, 1981.
- 4.0 Overall Conclusions (consistent with C1-36 analysis and heatup tests).
 - The fuel is not a continuous source of Cl rather it is a transient source upon initial heatup. The initial core could have released about 90 g Cl.
 - Exposure of fuel to high water vapor at operating temperatures causes a relatively small release of Cl, about 1 to 3 g/hr, from the core.
 - 3. Graphite is not a source of HC1.
 - 4. Titanium sponge is a minor transient source, up to 3 g, on initial heatup, and could be the non active chlorine source in control rod drive mechanism compartment above the shield plug.
 - Leachable sources such as concrete or insulation could lead to high salt levels locally but would not necessarily contribute to the circulating inventory.

APPENDIX A

PHASE II TEST APPARATUS AND PROCEDURE

The apparatus for determining the release of HCl gas from FSV materials shown in Fig. A-1.

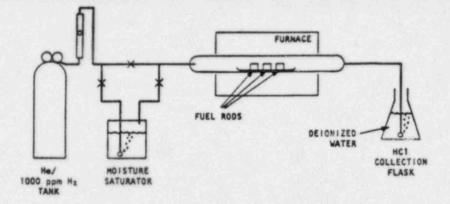


Figure A-1. Heatup and hydrolysis apparatus for measurements of HCl release.

The method is to place the samples in the silica boat in the quartz furnace tube, establish helium flow, turn furnace on to desired temperature (950°C for fuel rods and H-327 graphite, 800°C for HLM and PGX graphite, 370°C for Ti sponge), remove and replace HCl collection flask at 1 to 5 hour intervals, continuing to 24 hours total. If hydrolysis is required, moisture saturator is valved in for additional 24 to 100 hour periods. Furnace background or blank values are determined by performing tests using empty furnace tube prior to addition of the sample, and also by running for long times after the HCl is released from the sample.

Collection flasks are submitted to analytical chemistry for chlorine measurements by means of ion chromatography, the sensitivity of which is below 0.1 ppm chlorine.

A number of standards were run in which known amounts of HCl were added to the furnace, HCl collected in the above method and submitted to analytical chemistry. The results of those calibrations are shown in the table below.

TABLE A-1

HC1 CALIBRATION STANDARDS

HC1 Added (µgm)	Furnace Temp (°C)	Time (hr)	Chlorine Removed (µgm)	Recovery (%)
465	950	4.25	336	72
3650	950	4	2924	80
		20.6	3033	83
785	950	4	518	66
		19.75	584	74

Note: Average recovery: 4 hours = 73%; 20 hours = 79%.

APPENDIX B-1

DETAILS HC1 RELEASED FROM FUEL RODS MASS SPECTROMETER RESULTS

R	od No.	Fuel Segment	HC1 Leached	ppm MS
CR	14-200012-21	Core 1	1x	0.51
CR	14-20024-19	Core 1	1x	0.26
CR	14-30001-0029(1)	Core 1	1x	0.77
CR	14-30001-0029(2)	Core 1	1x	1.81
CR	14-30001-0029(3)	Core 1	1x	0.38
CR	14-30010-0027	Core 1	1x	0.31
CR	14-30019-0026	Core 1	1x	0.20
CR	14-40014-0032	Core 1	1x	0.50
CR	14-2001-24(1)	Core 1	1x	0.69
CR	14-2001-24(2)	Core 1	1x	0.66
CR	14-2001-24(3)	Core 1	1x	1.41
CR	14S-10046-1	Core 1	1x	
CR	145-10050-13	Core 1	1x	
CR	14N-10066-2	Core 1	1x	
CR	14-140013-51-0034	Core 1	1x	
CR	14-4001-51-0037	Core 1	1x	
CR	14-10125-1	Core 1	1x	0.34
CR	16-10125-1	Core 1	2x	0.40
CR	18-10125-1	Core 1	3x	0.10
CR	14N-60078-2	Core 1	1x	0.67
CR	14N-10311-17-00	Core 7	1x	0.52

APPENDIX B-2

DETAILS OF HC1 RELEASED FROM FUEL RODS USING THE TUBE FURNACE METHOD

			Furnace	Dry Heliu	m Purge HC1	Furnace Blank	Wet He HCl	lium HCl
		Fue1	Blank Before	HC1 4 hrs	20 hrs	After	4 hrs	20 hrs
	Rod Number	Segment	μg	μg	μg	μg	ug/hr	µg/hr
2	CR 14-30048-15	Core 1	0.46	173	236		5.6	
2 ea				173	236		5.6	
2 ea	CR 14-30051-1N	Core 1	0.46					
2 ea	CR 14-30053-1N	Core 1	0.46	173	236		5.6	
2 ea	CR 14-60078-2	Core 1	1.8	29.5	56	1.46		
2 ea	CR 14-60080-2	Core 1	1.8	29.5	56	1.46		
2 ea	CR 14-60089-6	Core 1	1.8	29.5	56	1.46		
2 ea	CR 14-10046-1	Core 1	3.0		270	3.0		
2 ea	CR 14-10050-13	Core 1	3.0		270	3.0		
2 ea	CR 14-10066-2	Core 1	3.0		270	3.0		
2 ea	CR 14-10300-00	Seg 7	1.8	21.01	44.2	1.8		
2 ea	CR 14-10318-16	Seg 7	1.8	21.01	44.2	1.8		
2 ea	CR 14-10335-17	Seg 7	1.8	21.01	44.2	1.8		
2 ea	CR 14-20001-24	Seg 8	1.86	10.22	21.8	1.0		
2 ea	CR 14-20024-19	Seg 8	1.86	10.22	21.8	1.0		
2 ea	CR 14-20012-21	Seg 8	1.86	10.22	21.8	1.0		
2 ea	CR 14-30001-0429	Seg 9	1.45	24.5	39	0.72		
2 ea	CR 14-30010-0027	Seg 9	1.45	24.5	39	0.72		
2 ea	CR 14-30019-0026	Seg 9	1.45	24.5	39	0.72		

APPENDIX C

CALCULATIONS OF CHLORINE - 36 FORMATION

Calculate the formation of C1-36(\pm 1/2 = 3x10⁵yr) from 1 gm of stable C1 by neutron activation in FSV at 70% power.

uci Cl 36/gcl = $-\lambda N35\phi\sigma + /3.7 \times 10^4$ dps/uci Where: N_{35} = atoms Cl 35 = $\frac{1 \text{gm} 6 \times 10^{23} \times .75}{35 \text{g/mole}}$ = 1.3×10^{22} 0.75 = fraction 35 in Cl ϕ = neutron flux at 70% power 4×10^{13} λ = 7.5x10⁻¹⁴ σ = cl -35 cross section, $43 \times 10^{-24} \text{cm}^2$ \pm = time, seconds assume 1 day = 8.64×10^4

In one day at 70% power in core a gram of stable C1 yields -

 $\frac{\mu ci 36}{gcl-day} 7.5 \times 10^{-14} 1.3 \times 10^{22} 4 \times 10^{13} 43 \times 10^{-24} 8.64 \times 10^{4} / 3.7 \times 10^{4} = 3.9$

The cable with leach found 167 $\frac{uci 36}{gcl}$: 3.9 = 43 days activation at 70% power.