Long Term Iodine Control In Reactor Containment Buildings Using Combustion Engineering Iodine Removal System

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I. Introduction - General Information on Long-Term Iodine Control

Confirmatory Item 12 of the CESSAR-F Safety Evaluation Report addresses the adequacy of the C-E supplied Iodine Removal System (IRS) to provide long term iodine control inside the containment building. The IRS design was questioned by the staff on the basis of the post-accident sump water pH range over which the hydrazine chemistry effectively retains the iodine in solution. Related concerns were raised regarding scenarios of iodine release to the containment atmosphere which would not be affected by sump water pH and which were applicable to containment spray systems in general. The conclusions drawn in this report are: first, that the chemistry of the hydrazine IRS is such that evolution of iodine from the containment sump is not substantial within the required pH range, and secondly, following the initial iodine release, the IRS has the capability to be manually restarted to enhance long term iodine control.

This package provides a discussion of long term iodine control for the CESSAR IRS. Section II provides the changes to the CESSAR interface requirement that will insure an adequate hydrazine supply is available for IRS restart and subsequent long term control of iodine inside containment. Section III discusses operational requirements for the IRS for both short term and long term system operations. This also describes how the system can be manually operated from the control room. Therefore, the operator should not be burdened by periodically operating the system for long term iodine control. Section IV, V, and VI provide results of analyses to describe the effects of the containment environment on hydrazine concentrations. Also discussed are the results of experiments performed using hydrazine.

In the course of addressing NRC concerns on long-term iodine control, certain points were made on the merits of restarting the IRS for longterm iodine control in the containment atmosphere. The merits of re-initiating the containment sprays are discussed below.

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- 1. The IRS is required to start and run automatically for the necessary length of time based on the Design Basis Event. There are however a number of event scenarios that may not cause activation of the containment sprays and IRS. Certain events will initiate containment sprays, but only for a relatively short period of time normally insufficient for long term iodine control. In such instances as these, the IRS will require manual restart to decrease iodine levels in the containment atmosphere. A description of the restart capability for the CESSAR IRS is contained in this package.
- 2. The IRS may also require restarting in the event of long-term iodine buildup in the containment atmosphere. Since this buildup will most likely be due to volatilization of iodine that has plated out on containment surfaces, repeated operation of the containment sprays will be the only effective method for iodine control. Another case in which the IRS will require restart would be after a delayed release from the Reactor Coolant System. For example, a delayed release may be due to the operation of the Reactor Vessel Head Vent System. Included in this package is a description of the CESSAR IRS and the capability for manual restart for long term iodine control.
- 3. Sump pH control for the hydrazine IRS is controlled by storage of dry chemicals (typically tri-sodium phosphate) in the containment sump. This method provides a passive mechanism that does not require sump pH buffering by a pumped system. This is especially important since some recent events (e.g., Crystal River) have caused the containment sump to fill with water containing boric acid without actuation of the IRS. Where the chemical buffering agent is physically located in the sump area, the acidic RCS fluid can be neutralized without actuation of the containment spray system, hence the sump fluid pH is raised to inhibit materials corrosion.

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II. Interface Requirements Revisions for CESSAR, Appendix B of Chapter 6

This section identifies the proposed changes to the IRS Interface Requirements in Appendix B of Chapter 6 of the CESSAR-F document. These changes will be included in a future amendment to CESSAR-F. Note that only those paragraphs affected are listed under the appropriate section.

- A. Amend Appendix 6B, Section 7.13.23 as follows:
 - 7.13.23 Access to the SCST shall be provided following a LOCA such that the concentrated hydrazine solution can be replenished prior to reaching a minimum level of 5%. Consideration shall be given to radiological and hydrazine vapor hazards, and to alignment of the hydrazine fill apparatus.
- B. Amend Appendix 6B, Section 3.1 (third paragraph) as follows:

3.0 DESIGN DESCRIPTION

3.1 INTRODUCTION

The spray chemical addition pumps and the SCST are located outside containment to permit personnel access for inspection, testing, and maintenance during normal plant operation. Access is also provided post-LOCA for refilling the SCST in the event additional hydrazine is required for long-term iodine control. The pumps and addition lines are physically separate such that a single failure in one train will not cause the loss of the redundant train.

C. Amend Appendix 6B, Section 4.1.2 (fourth paragraph) as follows:

4.1.2 OPERATION DURING PLANT ACCIDENT CONDITIONS

Hydrazine addition is maintained through recirculation at a fixed flowrate. The system will be automatically isolated after four hours of operation, assuming two train operation. Manual isolation is acceptable after four hours of operation. The IRS has the capability of being manually restarted as necessary to provide long-term iodine control.

III. IRS Operational Requirements and Human Factors Considerations

Provided in this section are operational requirements for the System 80 IRS. Included are details of operator actions required to manually initiate the IRS. That is, the necessary switches and instrumentation for manually restarting the IRS for long-term iodine control are located in the control room.

A. IRS AUTOMATIC CHEMICAL ADDITION MODE

Description of Operation

The IRS is actuated from a standby condition to the chemical addition mode by a Containment Spray Actuation Signal (CSAS). The CSAS is initiated by two out of four high-high containment pressure signals of 10 psig. Also it can be initiated manually by the operation of two separate switches in the control room. This signal starts the Spray Chemical Addition Pumps (SCAPs) and opens both the SCST and the IRS isolation valves. The chemical additive stored in the SCST and normally isolated from the atmosphere is pumped into the CSP suction. The chemical additive is transferred into the containment atmosphere, via the spray headers and nozzles, by the Containment Spray System (CSS). Since the SCST is isolated from the atmosphere during system operation, it is supplied with vacuum breakers to protect the SCST and supply proper NPSH for the SCAPs. When pressure in the SCST drops to approximately negative 2 psig during chemical addition, the vacuum breakers open allowing air into the SCST.

The SCST is supplied with a low pressure alarm at approximately 2 psig and a low liquid level alarm at approximately 90%. These may alarm in the control room during the chemical injection mode but have no effect on system operation.

The IRS components are aligned to the Electrical Distribution System according to the availability of power sources. If the preferred plant electrical sources are unavailable, the components will be supplied by the emergency diesel generator (started on a Safety Injection Actuation Signal, SIAS) and energized in sequence.

The chemical addition mode is automatically terminated by a SCST low-low liquid level at approximately 45%. If both trains operated, the IRS will be isolated from the CSS in approximately 4 hours. However, after 4 hours of IRS operation with only one train, the operator may elect to terminate IRS operation manually before the SCST low-low level is received. He does this by stopping the SCAPs and shutting the SCST and IRS isolation valves. If terminated manually, a CSAS override alarm is indicated in the control room.

The IRS has the capability to be restarted as necessary to provide long-term iodine control.

Initial Conditions

a. A SIAS has been initiated.

- A CSAS has been initiated (either automatically or manually by the operator).
- c. The CSS is aligned to the containment atmosphere and operating.

Operational Requirements

No operator actions are required for the automatic chemical addition mode unless it has been determined to manually terminate chemical addition according to one or the other of the following conditions:

- a. No fission products have been released to the containment atmosphere following a CSAS. Such could be the case for a Main Steam Line Break which would not require the IRS.
- b. Fission product levels are below an acceptable limit and can be maintained at these levels by cleanup systems such as the Containment Building Ventilation System.

If manually terminating chemical addition, the following operations are required:

- a. Verify SCST level and the amount of time the IRS has operated.
- b. Stop the SCAPs and isolate the SCST and the IRS.
- B. LONG-TERM IODINE CONTROL

Description of Operation

The IRS may be manually restarted if necessary by the operator to provide long-term iodine control. An example of a typical spray scheme is provided in Figure III-1. The SCST level will be at approximately 45% if chemical addition was automatically terminated. If the IRS was terminated manually after 4 hours of operation of one



TYPICAL SPRAY SCHEME FOR LONG TERM IODINE CONTROL



NOTES: (1) Initial 4 hour IRS operation with two trains.

- (2) Restart one train for one-half hour duration as necessary.
- (3) Refill SCST.

train, the SCST level will be approximately 70%. If the IRS was terminated automatically, the SCST low-low level signal must be overridden to manually restart the system.

Based on the hydrazine depletion rate of the typical hydrazine management scheme presented in Figure III-1, the SCST liquid volume will not be reduced below five (5) percent of the tank capacity before five days following a LOCA.

Initial Conditions

- a. A Safety Injection Actuation Signal (SIAS) has been initiated.
- A CSAS has been initiated (either automatically or manually by the operator).
- c. The CSS is aligned to the containment atmosphere and operating.
- d. The chemical addition mode has been terminated (either automatically or manually by the operator).
- e. If required, the IRS has been inspected and is in the standby mode.

Operations Requirements

To manually restart chemical addition, the SCST and IRS isolation valves are opened and the SCAPs are started.

IV. <u>Chemistry Summary of Hydrazine Concentrations and Interactions with</u> Iodine in Containment

The following paragraphs provide a summary analysis of the hydrazine available for iodine removal based on long-term intermittent operation of the IRS.

The IRS receives hydrazine from the SCST and sprays the contaminant atmosphere to remove the initial iodine inventory. The hydrazine added from the IRS becomes diluted in the containment sump and may be insufficient in concentration to effect iodine retention in itself. Re-evolution of iodine species from the sump, however, would be anticipated only upon oxidation of the iodide which was originally formed in the reaction between hydrazine and iodine in the spray. Sufficient quantities of hydrazine are available for airborne I₂ removal during subsequent operation of the IRS.

A. Hydrazine Concentration in the Sump

Hydrazine concentrations in the containment sump, following a 30 minute period during which the containment spray system is operated, would range from 5 to 14 ppm. This concentration range is dependent on the LOCA scenario in which various quantities of water enter the sump. Subsequent decrease in the hydrazine concentrations will occur from the effects of radiolysis and oxidation.

Long-term availability of hydrazine in the sump would not be sufficient to react with the design basis LOCA iodine inventory, if this were the only mechanism of iodine capture. The containment spray, however, contains sufficient quantitites of hydrazine to effect the initial iodine capture and the control of subsequent releases of iodine (from the core, or re-evolution from surfaces) should they occur.

B. Hydrazine Concentration in Containment Spray

Hydrazine is blended with recirculated sump water to produce a minimum concentration in the spray header of 53 ppm. The initial concentration of hydrazine in the spray droplets decreases to a minimum of 48 ppm, due to the reaction between hydrazine and oxygen in the sump water. Further reaction with oxygen during the droplet transit time causes this concentration to decrease by an additional 0.4 ppm.

Energy deposition from radionuclide decay in the sump water causes radiolysis of the hydrazine; another mechanism to decrease the hydrazine concentration. The hydrazine, added to the containment spray, is degraded through radiolysis at a rate of approximately 40% or 20 ppm per hour. This loss rate is insignificant when compared to the 7-8 second transit time for each drop, which represents the period of iodine capture.

With a continuous feed of hydrazine into the recirculated sump water, the containment spray is capable of capturing the entire inventory of core iodine released following the design basis LOCA. The total quantity of hydrazine delivered during a 30 minute spray period is 40 times the stoichiometric amount needed to react with all the iodine released following the design basis LOCA.

C. Iodine Partitioning from the Sump

The partitioning of iodine from the sump into the containment atmosphere is predicted from partition coefficients, defined as the ratio of the total iodine species concentration in liquid to the concentration of I_2 in the vapor. The values of the partition coefficients depend on the equilibrium concentrations of iodine from the hydrolysis reaction between I_2 (aq) and water. This equilibrium is pH-dependent as the following equation illustrates:

 $I_2 (aq) + H_20 + HOI (aq) + I^{-} (aq) + H^{+} (aq)$

In this reaction, iodine does not ungergo a net reduction or oxidation. The hydrolsis, is therefore, reversible and depends only on the presence of both $I^{-}(aq)$ and HOI(aq).

When hydrazine is present in solution, HOI(aq) is reduced to $I^{-}(aq)$. This means that water which contains hydrazine produces a net reduction of captured I_2 to I^{-} . Evolution of I_2 from such a solution is not expected unless other mechanisms are available to produce sufficient concentrations of oxidized iodine species to react with $I^{-}(aq)$ and form $I_2(aq)$.

Experiments performed in simulated containment vessels, in which hydrazine sprays were used to capture I_2 from the vapor space, demonstrated a long-term retention of iodine in sump liquid which contained boric acid at a pH of 7.0.⁽¹⁾ This implies that oxidation of reduced iodine species (I⁻) proceeds at a slow rate, which thereby limits the partitioning of iodine to the containment atmosphere.

Radiolysis of $I^{(aq)}$ solutions is expected to produce chemical changes which could influence the extent of I_2 formation, and subsequent evolution from solution. Radiolysis experiments performed on $I^{(aq)}$ solutions demonstrate that I_2 formation is insignificant at neutral to alkaline pH. These results are presented in the next section.

V. Summary of Radiolysis Experiments of Iodine Solutions

Experiments have been performed on iodide and iodate solutions irradiated with cobalt 60 radiation.⁽²⁾ at 25°C. The pH was adjusted with H_2SO_4 or NaOH and ranged from 2 to 10. The aqueous solutions were either scrubbed with helium to deaerate, or scrubbed with air to fully aerate. Initial iodide concentrations were either 10^{-3} to 10^{-4} molar, or $\leq 10^{-11}$ molar. The absorbed doses ranged from 10^3 to 10^8 rads.

The following ouservations from this study are considered significant:

- 1. Iodide (I⁻), when extremely dilute ($\leq 10^{-11}$ molar), is quantitatively converted to iodate ($I0_3^-$). This conversion is only slightly affected by pH.
- 2. Moderate concentrations of I⁻ $(10^{-3} 10^{-4} \text{ molar})$ are mostly converted to I₂ at low pH (pH = 2-3), and mostly unreacted at, or above pH = 5.
- 3. Indine (I_2) concentrations after 22 hours of irradiation were greater by a factor of 2 to 3 than after 1 hour of irradiation.
- There were no significant differences in solution composition whether completely aearated or deaerated.
- 5. The kinetics of the radiolysis reactions are considered to be rapid; the evolution of I_2 from an irradiated solution is expected to be limited by mass transfer of the I_2 rather than the radiolytic production rate.
- 6. The presence of a free radical scavengers such as Cu^{2+} have a significant effect on the production of I_2 from I^{*}. The percentage of I_2 at pH = 7 ranged from 0.3 to 38.1% as the concentration of copper ranged from 5 x 10⁻⁵ to 5 x 10⁻⁴ molar. Similar behavior is anticipated with other free radical scavengers.

Table V-1 summarizes the solution composition as a function of such variables as pH, initial I^{\circ} concentration, absorbed dose and dose rate. For comparitive purposes, a post LOCA containment sump with 4 x 10⁶ lbs. of water is expected to contain up to 59 x 10⁶ curies of I-131. The total sump concentration of I^{\circ}, including I-127, would be approximately 1 x 10⁻⁵ molar.

Variables	<u>рн</u>	(I ⁻)initial, <u>Molarity</u>	dose, <u>rads</u>	Distribution of Iodine, Post-Irradiation, %		
рН	3 4 7.3 9	10 ⁻³ 10 ⁻³ 10 ⁻³ 10 ⁻³	4.5 x 10^{6} 4.5 x 10^{6} 4.5 x 10^{6} 4.5 x 10^{6}	I ⁻ 18.0 92.3 95.9 96.2	103 0.2 1.1 2.9 3.5	I ₂ 81.8 8.6 1.2 .3
exposure time	5	10 ⁻³ 10 ⁻³	4.5 x 10^{6} (1 hr.) 99 x 10^{6} (22 hrs.)	97 93	.3 .5	2.4 6.9
Aeration of Solution He Scrubbed Air Scrubbed	6.7 6.9		4.5 x 10 ⁶ 4.5 x 10 ⁶	1.5 2.2	98.5 97.4	0.4
dose	7 7 7		3.7×10^{3} 4.5×10^{4} 1.2×10^{5}	84.7 78.0 5.0	13.4 19.8 94.5	1.9 2.2 0.4
Initial (I ⁻), pH	7.3 6.6 6.7	10^{-3} 10^{-4} $\leq 10^{-11}$	4.5×10^{6} 4.5×10^{6} 4.5×10^{6}	95.9 95.1 1.5	2.9 1.2 98.5	1.2
	4	10 ⁻³ < 10 ⁻¹¹	4.5×10^{6} 4.5×10^{6}	92.3 1.1	1.1 98.5	8.6 0.4

Table V-1

Partition Coefficients

Partition coefficients from the radiolysis experiments are calculated from the concentration date listed in Table V-1 and compared with partition coefficients based on non-irradiation hydrolysis conditions $^{(3)}$ at 25°C. These are shown in Table V-2.

Table V-2

Irradiation	[I ₂] (total, 1	iq.) <u>pH</u>	Partition Coefficient
No Yes No	5×10^{-4} m 5×10^{-4} m 5×10^{-4} m	5 5 1 7	76 1,100 87
Yes	5 x 10 ⁻⁴ m	1 7	6,250
No	5 x 10 ⁻⁶ m	n 7	200
Yes	5 x 10 ⁻⁶ m	1 7	3,750
No	5 x 10 ⁻⁴ m	ı 9	234
Yes	5 x 10 ⁻⁴ m	1 9	25,000

As the partition coefficient is increased, the tendancy for iodine to evolve from solution is decreased. The radiolysis experiments show that the concentrations of I_2 that result from irradiation of I^- solutions are consistently lower than the equilibrium I_2 concentrations that exist in non-irradiated aqueous iodine solutions.

VI. Summary of Coolant Release at Crystal River Unit 3

An incident at Crystal River Unit 3 on February 26, 1980 caused approximately 40,000 gallons of coolant to be released from the RCS and enter the containment sump.⁽⁴⁾ The liquid released included reactor coolant and refueling water, added through the high pressure safety injection pumps. Containment spray was not initiated nor were any adjustments made in the pH of the coolant entering the sump. Although measurements were not available, it is estimated that the final pH of the sump liquid was below 6.0.

Iodine concentrations were measured in the sump liquid and the containment atmosphere. The results of these measurements are shown in Table VI-1 and Figures VI-1 and VI-2. The chemical forms of the iodine were not determined. I-131 in the atmosphere peaked at 4 x 10^{-5} uCi/cc approximately 84 hours following the releases of coolant. The I-131 activity in the sump liquid immediately following the release was between .25 and .45 uCi/cc. The partition coefficient decreased to a stable, minimum value of 2,000, 5 days following the release.

Although the chemical forms of iodine were not determined, the implication of the activity measurements following the release of coolant was that there was no significant, long-term evolution of iodine from the sump liquid, even at relatively low pH.

Table VI-1

REACTOR COOLANT RADIOCHEMISTRY CRYSTAL RIVER UNIT 3

Sample		Total Activity	Dose Eq. I	I-131	I-133	Cs-124	Co-58	H-3
te	Time	uCi/cc	uCi/cc	uCi/cc	uCi/cc	uCi/cc	uCi/cc	uCi/cc
-26	0010	2.29	0.322	0.246	0.233	1.77E-2	7.64E-2	0.27
	1423 - 1428	Discharge of Coolan	t					
	1615	2.41	0.593	0.454	0.429	4.46E-2	2.31E-2	
	1904	1.55	0.566	0.447	0.383	4.15E-2		
	2135	1.93	0.831	0.664	0.548	5.75E-2	5.19E-2	
-27	0058	2.63	1.45	1.19	0.884	8.91E-2		0.13
	0615	1.97	1.10	0.924	0.574	8.47E-2		0.113
	0855	1.78	0.979	0.833	0.506	1.04E-2		
	1255	1.60	0.944	0.818	0.437	7.71E-2		
	1755	1.75	1.07	0.949	0.416	9.37E-2	9.99E-3	
	2110	1.31	0.818	0.736	0.288	7.06E-2	1.12E-2	
- 28	0110	1.12	0.755	0.686	0.245	4.97E-2	2.0E-3	0.112
	0815	0.97	0.620	0.575	0.160	6.76E-2	9.6E-3	
	2020	0.77	0.526	0.525		5.52E-2	5.3E-2	



Figure VI -1 Radio-lodine in reactor coclarit versus time.



Figure VI -2 Xe-133 and lodine-131 levels in containment atmosphere.

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