Demonstration of Methanol Injection During Startup at LaSalle-1

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AREVA

BWRVIP Mitigation Committee
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Radiolysis Fundamentals

- There are primary radiolysis products, and secondary radiolysis products.
- Primary radiolysis are produced very rapidly. They are sometimes called “direct yields.” They would result within the first $\sim 10^{-6}$ seconds after radiation interacts with water. These are: $e_{aq}^-, H, H_2, OH, H_2O_2, HO_2, H^+$
- $O_2$ is not a primary radiolysis product (Neither is $OH^-$)
- Secondary products result from the reactions of these primary radiolysis products with each other and with water.

G-values: tell production rates of primary products

Water Reaction Sets: tells how radiolysis products react with each other, water, and hydrogen

Methanol Reaction Set: tells how methanol reacts with radiolysis products. When combined with water reaction sets, and g-values can predict oxidant depletion and some of the products

[Jarvis, Doctoral Thesis, MIT, 2015]
Understanding H₂ and O₂ concentrations: looking at methanol reactions

- Mechanism(s) causing oxygen depletion:
  - Methanol or its intermediates react directly with the OH radical, thus lowering one source of O₂ formation
  - Methanol or its intermediates react with H₂O₂, thus lowering one source of O₂ formation
  - Methanol or its intermediates react directly with O₂, reducing it directly
  - Methanol can decompose to H₂, and the H₂ can react with O₂

- Source of hydrogen:
  - Methanol can decompose, forming H₂ directly
  - Radiolysis: if methanol reacts with primary radiolysis products like OH, then less H₂ produced directly from radiolysis may be consumed (meaning the H₂ is able to exist longer). However, there is a limit on how much H₂ can be produced from radiolysis under specified dose rates and flow rates (If all the resulting hydrogen is from radiolysis, adding more methanol past a certain level would not result in higher hydrogen concentration)

- It is not yet known which mechanism(s) are most influential on the oxygen and hydrogen concentrations

Mechanism for hydrogen production from methanol

Mechanism for OH reduction directly by methanol

Mechanism for O₂ and H₂O₂ reduction by formaldehyde (methanol intermediate)

Table 3: Radiation chemical reactions for methanol system

<table>
<thead>
<tr>
<th>Reaction</th>
<th>25°C</th>
<th>300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>4.5 x 10⁹</td>
<td>7.8 x 10⁹</td>
</tr>
<tr>
<td>M2</td>
<td>8.4 x 10⁹</td>
<td>1.5 x 10¹⁰</td>
</tr>
<tr>
<td>M3</td>
<td>1.7 x 10⁹</td>
<td>2.9 x 10⁹⁹</td>
</tr>
<tr>
<td>M4</td>
<td>2.7 x 10⁹</td>
<td>4.7 x 10⁹⁹</td>
</tr>
<tr>
<td>M5</td>
<td>4.4 x 10⁹</td>
<td>7.6 x 10⁹⁹</td>
</tr>
<tr>
<td>M6</td>
<td>1.6 x 10⁹</td>
<td>2.4 x 10⁹⁹</td>
</tr>
<tr>
<td>M7</td>
<td>1.9 x 10⁹</td>
<td>3.3 x 10⁹⁹</td>
</tr>
<tr>
<td>M8</td>
<td>1.0 x 10⁹</td>
<td>1.7 x 10⁹⁹</td>
</tr>
<tr>
<td>M9</td>
<td>6.9 x 10⁹</td>
<td>1.2 x 10¹⁰</td>
</tr>
<tr>
<td>M10</td>
<td>4.2 x 10⁹</td>
<td>7.3 x 10⁹⁹</td>
</tr>
<tr>
<td>M11</td>
<td>3.4 x 10⁹</td>
<td>5.9 x 10⁹⁹</td>
</tr>
<tr>
<td>M12</td>
<td>5.9 x 10⁹</td>
<td>1.0 x 10⁹⁹</td>
</tr>
<tr>
<td>M13</td>
<td>1.3 x 10⁹</td>
<td>2.2 x 10⁹⁹</td>
</tr>
<tr>
<td>M14</td>
<td>3.8 x 10⁹</td>
<td>6.6 x 10⁹⁹</td>
</tr>
<tr>
<td>M15</td>
<td>1.0 x 10⁹</td>
<td>1.7 x 10⁹⁹</td>
</tr>
</tbody>
</table>

Overview of Data: 3 startups

3/08-3/09 (L1R16)
Methanol Injection: variable rate
Rx Critical (2nd attempt): 3/9 4:06
MVP data: analyzer and manual readings
RWCU O₂ data: 3/9 02:30- 3/9 15:55 (+2.3 to 11.8 hrs after criticality)
HWC started: after oxygen data collection concluded. (~24 hours after criticality)

3/15-3/16 (L1F42)
Methanol Injection: None
Rx Critical: 3/16 1:05
MVP data: analyzer
RWCU O₂ data:
   3/15 11:00- 3/16 15:45
   (-14 to 14.67 hrs after criticality)
HWC started: 3/16 15:30 (14.4 hrs after criticality)

3/21-3/22 (L1F43)
Methanol Injection: 49 mL/min constant
Rx Critical: 3/21 20:26
MVP data: not collected
RWCU O₂ data:
   (+2.7 to 16.48 hrs after criticality)
HWC started: 3/22 9:30 (13.1 hrs after criticality)
How to measure Mitigation effectiveness at Noble Metal plant?

- Reactor water oxidant (DO)
  - Used for HWC
  - However, low levels do not always indicate effectiveness
  - Trends are valuable
- Excess reactor water hydrogen (DH)
  - Used for HWC
  - Valuable to show molar ratio of oxidants to hydrogen has been met
- Electrochemical corrosion potential (ECP)
  - Used for HWC, but temperature and ECP probe-type dependent
  - Platinum probes effective when excess hydrogen is present
Comparison of DO measurements

First Injection 3/9: has the highest increase in DO when the reactor reaches 350°F. First startup attempt, so \( \text{H}_2\text{O}_2 \) was higher.


The lowest DO achieved during 3/21 startup with MeOH, 22 ppb.

AREVA indicated the demonstration goal was <10 ppb DO.

<table>
<thead>
<tr>
<th>Date</th>
<th>Highest DO prior to Criticality (ppb)</th>
<th>Lowest DO after Criticality and before 350°F (ppb)</th>
<th>Highest DO after Rx 350°F (ppb)</th>
<th>Lowest DO after Rx 350°F and before HWC (ppb)</th>
<th>Increase in DO at/after 350°F (ppb)</th>
<th>Decrease in DO after 350°F (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/9</td>
<td>N/A</td>
<td>128</td>
<td>320</td>
<td>52 (MeOH)</td>
<td>192</td>
<td>26 (MeOH)</td>
</tr>
<tr>
<td>3/16</td>
<td>6680</td>
<td>133</td>
<td>191</td>
<td>47</td>
<td>58</td>
<td>144</td>
</tr>
<tr>
<td>3/21</td>
<td>N/A (MeOH)</td>
<td>44 (MeOH)</td>
<td>123 (MeOH)</td>
<td>22 (MeOH)</td>
<td>79</td>
<td>101 (MeOH)</td>
</tr>
</tbody>
</table>
Measured reactor water hydrogen was ~1 ppb. Therefore, changes in excess DH are driven by the oxygen concentration.

In all 3 startups, excess DH was always <0 ppb prior to the start of normal HWC.

This means that the coolant at wetted catalytic surfaces was always oxidizing based on an $\text{H}_2:\text{O}_2$ molar ratio less than 2.
Increase in reactor conductivity observed with methanol injection. This is likely due to CO$_2$ produced by methanol and possibly other intermediates. (DATA STILL NEEDED)

For 3/21 startup, the conductivity increases for ~1.8 hours following the start of methanol injection, and then decays for ~1.2 hours, returning to the pre-methanol injection values.

For 3/9, the increase and decrease are slower, and the conductivity is still slightly elevated compared to the pre-methanol values at the conclusion of the injection.
CDI conductivity is higher during the 3/9 and 3/21 startups with methanol, than during the 3/16 startup without methanol.

Note that the conductivity on 3/16 increases following reactor criticality.

CO$_2$ produced by methanol will be transported with steam to the condenser.

The generally higher CDI conductivities during methanol injection may be a result of this CO$_2$. 
ECP Data Overview

- Iron/Iron Oxide Electrode **was failed**.
- Pt electrode can only provide ECP results when there is excess hydrogen (MR > 2, or Excess DH > 0).

ECP measured with Fe/Fe-oxide probe is inconsistent with changes in excess DH-minimal change when HWC starts. ECP should be > -230 mV(SHE) when coolant is oxidizing.

Same behavior observed for the 3/16 startup (no methanol): ECP < -600 mV SHE prior to HWC.
Here the raw potential measurements using the Pt probe are shown vs hours after reactor criticality. Raw measurements are very similar for the three startups. In all cases, the electrodes are not activated until after normal HWC is started. For the 3/9 startup, HWC is started later, and consequently the Pt electrode is not activated. These results suggest that there was insufficient methanol to prove mitigation during the 3/9 and 3/21 startups.
Comparison of MVP %H2 with and without Methanol

(Axes are adjusted to approximately match in scale)

In both cases, the %H2 decreases towards the end of MVP operation.

For startup without methanol, the maximum %H2 is ~0.26%

For startup with methanol, the maximum %H2 is ~0.45%
Summary of Results from LaSalle-1 Methanol Injection during Startup

- **Dissolved Oxygen:**
  - RWCU Dissolved oxygen concentrations never lowered below ~20 ppb during methanol injection.

- **Excess Hydrogen**
  - Positive values of reactor coolant excess hydrogen were not achieved during methanol injection.
  - Excess hydrogen only achieve after normal HWC was placed in service.

- **Mechanical Vacuum Pump (MVP) Hydrogen**
  - Measured MVP hydrogen concentrations were below 1% with and without methanol.

- **Reactor Water Conductivity**
  - Reactor water conductivity was generally higher under methanol injection, peak values were 0.27-0.28 μS/cm.

- **MMS ECP**
  - Ground-Pt potential difference did not indicate activation during methanol injection, but did indicate activation after normal HWC was placed in service.
Future Thoughts:

- Is a methanol:oxygen molar ratio of 2 sufficient to achieve mitigation?
  - Some tests under irradiation have achieved a sufficiently low ECP.
  - Tests without irradiation have not achieved sufficiently low ECP until the molar ratio is very high.
  - Target molar ratio will likely depend on the core dose rates; a higher molar ratio may be required during startup compared to full power.

- Is UV light required on the surface to achieve mitigation with a molar ratio ~2? For example, can the recirculation piping be mitigated? How much UV or irradiation is required?

- Is it necessary to have excess hydrogen under methanol injection in order to achieve mitigation?
Data Gaps

- MSLRM dose rates: are there any changes in the MSLRM dose rates? (may be more significant if higher injection rates are used)
- Analysis of reactor coolant samples for MeOH and organic reaction products still outstanding
- Reactor water metals needed to review for indications of any crud restructuring due to the methanol injection
- For future consideration:
  - ECP using a probe that does not require excess DH (something other than Pt). Note that Fe/Fe oxide probes cannot provide reliable ECP below ~ 446 °F/230 °C.
  - Hydrogen Peroxide measurements early in the startup, prior to 350 °F.
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