RADIOLYTIC DECOMPOSITION OF COOLANT WATER IN CIRUS REACTOR

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I. INTRODUCTION

Water is extensively used as coolant and/or moderator in various types of nuclear reactors. Its choice and suitability was decided by its abundant supply, wide experience with conventional water technology and good heat exchange property. Its drawbacks are (a) high neutron absorption cross-section and (b) decomposition when subjected to radiation fields. The first drawback can be offset by using heavy water instead of light water; but heavy water being very costly, a compromise is sometimes achieved, when light water is used as coolant and heavy water as moderator.

Radiolytic decomposition of water leads to the formation of hydrogen, hydrogen peroxide and oxygen as end products. The formation rates of these products are required to be known, so that any corrective action such as installation of degassifiers or recombination units (in case of heavy water) can be carried out. Radiolytic decomposition rates of light water and heavy water with comparable purity are of the same order and their characteristic reactions are also similar.

II. EXPERIMENTAL

To understand the phenomenon of radiolysis of water and know the equilibrium concentration of end products, experiments were
carried out in CIRUS reactor at various power levels to estimate the concentrations of end products in coolant water.

CIRUS is a 40 MW (th) natural uranium fuelled, heavy water moderated and light water (D,M. water) cooled reactor. The reactor operation was started and the reactor power was stabilised at different power levels such as 4 MW, 10 MW, 20 MW, 30 MW and 40 MW respectively. At each power level, coolant water was analysed for its H2O2 content and dissolved H2 content at various time intervals till the equilibrium conditions were reached.

Coolant water specifications were maintained as follows:

pH = 6.0; Sp. conductance = 1.0 µmhos/cm. Dissolved oxygen = <1 ppm and T.D.S. = <2 ppm.

III. RESULTS AND DISCUSSION:

Large amount of investigations has been carried out on the radiolysis of water and aqueous solutions. The principal radiolytic reactions involved in water radiolysis, as a result of reactor irradiation are as follows (1), (2).

\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H} + \text{OH} \\
\text{H}_2\text{O} + \text{OH} & \rightarrow \text{H} + \text{H}_2\text{O}_2 \\
\text{H}_2\text{O} + \text{H} & \rightarrow \text{OH} + \text{H}_2 \\
\text{H}_2\text{O}_2 & \rightarrow \text{H} + \text{O}_2 \\
\text{H}_2\text{O} + \text{O}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{OH} \\
\text{H} + \text{H} & \rightarrow \text{H}_2 \\
\text{OH} + \text{OH} & \rightarrow \text{H}_2\text{O}_2
\end{align*}
Reactions from (1) to (5) are decomposition reactions and those from (6) to (9) are recombination reactions. All these reactions are considered to be taking place in the coolant water of nuclear reactors. However, the equilibrium concentrations of the species formed depend on the power and flux of nuclear reactors and other coolant conditions such as dissolved gases, impurity levels, temperature and pressure.

1) $H_2O_2$ build up and its formation rates:

If before start up of the reactor, the dissolved oxygen concentration in coolant is higher, $H_2O_2$ formation in reactor coolant is more. Hence, dissolved oxygen in coolant water is brought down to less than 1 mg/litre by deaerators, before the reactor is taken to power. In this experiment, to study the rate of $H_2O_2$ build up, reactor power was raised in stages and data were collected till equilibrium was attained at each stage. $H_2O_2$ formation and its build up rate at different power levels of the reactors are shown in Figures 1, 2 and 3. Part of the $H_2O_2$ formed in the coolant gets removed by anion exchange resin, as well as due to atomisation or scrubbing in the deaerator at elevated temperature. The rate of build up of $H_2O_2$: $\frac{d[H_2O_2]}{dt} (mg/hr)$
is given by
\[ \frac{d{H}_2O_2}{dt} = v \times S_{H_2O_2} - (\sigma_i v_1 C_{H_2O_2} + \sigma_d v_2 C_{H_2O_2}) \]

where
- \( S_{H_2O_2} \) = Amount of \( H_2O_2 \) produced in mg/litre-Hr
- \( v \) = Volume of coolant in litres
- \( \sigma_i \) = Efficiency of \( H_2O_2 \) removal by ion exchanger
- \( \sigma_d \) = Efficiency of \( H_2O_2 \) removal by deaerators.
- \( v_1 \) = Amount of coolant flow in litres through ion exchangers per hour
- \( v_2 \) = Amount of coolant flow in litres through deaerators per hour.
- \( C_{H_2O_2} \) = Equilibrium concentration of \( H_2O_2 \) in coolant in mg/litre.

At a particular reactor power, the equilibrium condition is considered to have reached when the rate of removal of \( H_2O_2 \) by ion exchangers and deaerators becomes equal to the rate of formation of \( H_2O_2 \). Hence it is necessary to evaluate the efficiency of these two agencies which are responsible for removing the system \( H_2O_2 \). Samples were collected from the outlet of deaerators and ion exchange beds and their \( H_2O_2 \) contents were determined to arrive at their efficiency factors at various power levels.
From the knowledge of the flow rates through these and equilibrium concentration of $\text{H}_2\text{O}_2$ in coolant water, the specific formation rates of $\text{H}_2\text{O}_2$ in gms, $\text{H}_2\text{O}_2$/MW-Hr. were calculated and are plotted in Figure 3.

At higher reactor power (i.e. above 30 MW) the decrease in equilibrium concentration of $\text{H}_2\text{O}_2$ is due to higher coolant temperature ($>65^\circ\text{C}$) when $\text{H}_2\text{O}_2$ decomposition rate is high compared to the formation rate. Our observations are similar to those obtained at JMTR by Hirohito Tone et al.

Increase in the build up rate of $\text{H}_2\text{O}_2$ at higher dissolved oxygen concentration can be explained considering the reactions.

\[
\begin{align*}
2 \text{H} + 2 \text{O}_2 & = 2 \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 & = \text{H}_2\text{O}_2 + \text{O}_2
\end{align*}
\]

ii) Hydrogen formation rates:

Hydrogen formation in water under irradiation, takes place according to the equations (3) and (6). The rate of build up of $\text{H}_2$ can be written as

\[
\frac{dS_{\text{H}_2}}{dt} = S_{\text{H}_2} - v_2 c_{\text{H}_2}
\]

where $S_{\text{H}_2}$ = Amount of $\text{H}_2$ produced in litres/hr.

$v_2$ = Amount of coolant flow through deaerator in litres/hr.

$c_{\text{H}_2}$ = Equilibrium concentration of $\text{H}_2$ in litres/kg of water.
In the reactor, hydrogen gas formed is removed by online deaerators. After passing through deaerator, it is found that almost all hydrogen dissolved in water gets removed. Hence at equilibrium, the rate of removal of hydrogen by deaerators will be the rate of formation of hydrogen. From the knowledge of amount of hydrogen, the amount of water decomposed can be calculated. The \( \text{H}_2 \) formation rates and decomposition rates of water with respect to power are plotted in Figures 4 and 5.

Rate of formation of hydrogen depends on dissolved oxygen content in water, impurity level in water, temperature and energy deposition in the coolant at the core. Figure 5 indicates that decomposition rate per \( \text{MW-Hr} \) is high at lower reactor power, but decreases at higher power.

As \( \text{H}_2 \) and \( \text{H}_2\text{O} \) starts building up the recombination reaction becomes predominant and consequently the specific decomposition rate decreases at higher power levels. While comparing the decomposition rates of water in CIRUS with that of JMTR reactor, decomposition rates are higher in JMTR, due to high dissolved oxygen content in its coolant.

The determinations of \( \text{H}_2 \) concentration in water were carried out by the method described by Vartak et al.\(^3\).
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References:


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