Abstract

Fuel crud deposits on Callaway Cycle 9 once-burnt high-axial offset anomaly (AOA \( \approx -15\% \)) feed assemblies revealed a complex 4-phase matted-layered morphology of a new type that is uncommon in pressurized water reactors [1–3]. The up to 140-\( \mu \)m-thick crud flakes consisted predominantly of insoluble needle-like particles of Ni-Fe oxyborate \( \text{Ni}_2\text{FeBO}_5 \) (bonaccordite) and granular precipitates of \( m-\text{ZrO}_2 \) (baddeleyite), along with nickel oxide \( \text{NiO} \) (bunsenite) and minor amount of nickel ferrite \( \text{NiFe}_2\text{O}_4 \) (trevorite). Furthermore, boron in crud flakes showed that the concentration of \( ^{10}\text{B} \) had depleted to 10.2\( \pm \)0.2\%, as compared to its 20\% natural isotopic abundance and its 17\% end-of-cycle abundance in bulk coolant. The form and depth distribution of \( \text{Ni}_2\text{FeBO}_5 \) and \( m-\text{ZrO}_2 \) precipitates, as well as substantial \( ^{10}\text{B} \) burn-up, point to a strongly alkaline environment at the clad surface of the high-duty fuel rods.

This paper extends a nuclear chemistry model of heavily borated fuel crud deposits first proposed in Ref. [4]. The paper shows that the local nuclear heat and lithium buildup from \( ^{10}\text{B}(n,\gamma)^7\text{Li} \) reactions may help to create hydrothermal and chemical conditions within the crud layer in favor of \( \text{Ni}_2\text{FeBO}_5 \) formation and a \( \text{ZrO}_2 \) dissolution-reprecipitation mechanism. Consistent with the model, the hydrothermal formation of \( \text{Ni}_2\text{FeBO}_5 \) needles was recently proved to be possible in laboratory tests with aqueous \( \text{NiO-Fe}_2\text{O}_3-\text{H}_3\text{BO}_3-\text{LiOH} \) slurries, at temperatures only slightly exceeding 400\°C.

Introduction

As is generally known, thermal neutron capture by \( ^{10}\text{B} \) occurs at a high rate and at a substantial energy yield, that is,

\[
^{10}\text{B} + n \text{(thermal)} \rightarrow ^7\text{Li} + \gamma
\]

\( \gamma = 3,840 \text{ b} \left( 10^{-24} \text{ cm}^2 \right) \text{ at 25 meV} \)

\( \gamma = 2,000 \text{ b} \text{ at the deposit temperature} \)

\( Q = 2.79 \text{ MeV} \left( 4.46 \times 10^{-13} \text{ J} \right) \)

In a thermal flux \( \phi = 10^{14} \text{ n/cm}^2\text{s} \), the \(^{10}\text{B}-n \) reaction rate is

\[
R = \phi \gamma = 2,000 \times 10^{24} \times 10^{14} = 2 \times 10^7 \text{ s} (1.73 \times 10^{-2} \text{ d})
\]

The nuclear, thermal and chemical effects of \(^{10}\text{B}-n \) reaction in boron-bearing deposits and some of their consequences are listed below:

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<th>Processes</th>
<th>Effects</th>
<th>Possible consequences</th>
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<td>(^{10}\text{B} ) burn-up</td>
<td>(^{10}\text{B} ) depletion</td>
<td>saturation temperature and concentrations rise</td>
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<td>(^{7}\text{Li} ) build-up</td>
<td>( \text{pH} ) elevation</td>
<td>( \text{Ni, Fe, B, Li} ) concentrate in hot spots</td>
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<td>energy yield</td>
<td>local heat</td>
<td>( \text{Ni}_2\text{FeBO}_5 ) forms in hot/high pH areas</td>
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<td>radiolysis</td>
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<td>( \text{ZrO}_2 ) dissolves/precipitates along ( T/\text{pH} ) gradients</td>
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Added local power

At the \(^{10}\text{B}-n \) reaction rate \( R \) given above, 1.73\% of \(^{10}\text{B} \) is converted to \(^{7}\text{Li} \) per day; for 20\% \(^{10}\text{B} \) natural boron, the rate is 0.35\% of boron mass per day. Thus, in the absence of any isotopic exchange with fresh (not depleted) boron, depletion of the \(^{10}\text{B} \) concentration from 20\% to 10\% would occur in about 40 days.
The kinetic energy of $^7\text{Li}$ recoils and $\beta$ particles is absorbed in close proximity to each reaction point (i.e., <10 $\mu$m). Let us assume that only about 50% of reaction energy $Q$ is deposited within the crud layer. At the reaction rate $R = 2 \times 10^{-7}$/s, the average deposited power $P$ per individual $^{10}\text{B}$-n reaction is

$$P(^{10}\text{B}) = 0.5 QR = 2.23 \times 10^{-13} \times 2 \times 10^{-7} = 4.46 \times 10^{-20} \text{ W}.$$ 

One mole of natural boron contains $n(^{10}\text{B}) = 0.2 \times 6.0 \times 10^{23} = 1.2 \times 10^{23} \text{^{10B} nuclei/gram.}$ The deposited power per mole of boron is $P(M) = n(^{10}\text{B}) QR = 1.2 \times 10^{23} \times 4.46 \times 10^{-20} = 5.4 \text{ kW},$ which corresponds to 500 W per gram of boron.

In order to visualize the microscopic nature of the quantities at hand, consider from this point on a 100-um-thick fuel crud deposit 1 cm x 1 cm in area, i.e., 0.01 cm$^3$ in volume. Assume that—as in the Callaway Cycle 9 crud flakes—the crud is 80% porous and that Ni$_2$FeBO$_5$ comprises 50% of its weight. At the density of Ni$_2$FeBO$_5$, 5.17 g/cm$^3$, such a “unitary” deposit would contain 0.5 x 5.17 x 0.01 = 26 mg of Ni$_2$FeBO$_5$; for a B/Ni$_2$FeBO$_5$ mass ratio = 4.1%, this amounts to 1.07 mg of boron in a 0.01 cm$^3$ sample of crud. Thus, at the end of the cycle (10% $^{10}\text{B}$), the power added by $^{10}\text{B}$-n reactions would be 0.27 W/cm$^2$, or, for a 0.91-cm-diameter pin, 0.77 W/cm.

In the beginning of the cycle, and as long as the boron concentration in the coolant is high, the pores in the deposit may be filled by lithium metaborate LiBO$_2$—a currently assumed root cause of AOA. The maximum mass of LiBO$_2$ (density 1.4 g/cm$^3$) in 0.01 cm$^3$ of deposit would be 0.8 x 1.4 x 0.01 = 11.2 mg. For the mass ratio B/LiBO$_2$ = 21.7%, this gives 2.43 mg of boron. Since $^{10}\text{B}$ is at the 20% level at the beginning of the cycle, the power added by LiBO$_2$ locked in pores would be 1.22 W/cm$^2$ and 3.49 W/cm for the power flux and power for a 0.91-cm-diameter pin, respectively. If Ni$_2$FeBO$_5$ was quickly formed on fuel in the amount observed at the end of the cycle and starting from fresh 20% $^{10}\text{B}$, then the power output would be further increased by 0.54 W/cm$^2$ (1.54 W/cm), totalling 1.76 W/cm$^2$ (5.03 W/cm).

Thus, subject of the microstructure and the heat transfer capability of the deposit, the power added by $^{10}\text{B}$-n reactions in volume of the deposit may not be negligible compared to the average thermal power of fuel—in Callaway, this average power is 106.5 W/cm (for 3,565 MW(th) total power and 193x7x7 6-m-long fuel pins). One should also bear in mind that there is always substantial heat deposited in the crud by the intense gamma and beta fields in core. Therefore, when the heat flow from crud to coolant is obstructed by highly structured matted crud, one can expect a significant increase in temperature within the deposit, particularly in the zone near the clad surface, in regions of sealed pores and in material between wick boiling chimneys.

**Lithium build-up**

$^7\text{Li}$ from $^{10}\text{B}$-n reactions may also considerably raise the alkalinity of coolant in the deposit. Let us start from the end-of-cycle estimate of lithium production. For our unitary 0.01 cm$^3$ (80% porous, 50 wt% Ni$_2$FeBO$_5$, 10% $^{10}\text{B}$) deposit, we get 0.5 x 1.07 mg x 1.1 x 10$^{23}$ = 5.9 x 10$^{19}$ $^{10}\text{B}$ nuclei in the 0.01 cm$^3$ volume. The $^{10}$B-n reactions would produce 1.2 x 10$^{12}$ $^7\text{Li}$ atoms/s in this volume, or 5 x 10$^{15}$ $^7\text{Li}$ atoms/day. If the volume of all the pores were taken up by water, then the 0.01 cm$^3$ deposit would contain 1.6 x 10$^{20}$ H$_2$O molecules. Hence, Li would be added at a rate of about 260 mg/kg per day. If all of the 5.9 x 10$^{19}$ $^7\text{Li}$ atoms produced during the burnup of boron from 20 to 10% $^{10}\text{B}$ were to remain in the volume, then the concentration of Li in water would become 14.3 g/kg.

The build-up of Li may have an even more dramatic effect in concentrated LiBO$_2$ or B$_2$O$_3$ locked in the pores (i.e., in 80% of the 0.01 cm$^3$ deposit volume). In particular, for 2.43 mg of boron in fresh LiBO$_2$ (20% $^{10}\text{B}$), the rate of $^7\text{Li}$ production would be 1.8 g/kg per day. Hence, Li concentrations of 1 to 2 M could be built up in closed pores within a period of 1 to 2 weeks. Therefore, the lithium produced locally in deposits by $^{10}\text{B}$-n reactions can be far more concentrated than that produced from bulk pH control, and is likely comparable to concentrations built up during boiling (dryout).

Both pH elevation and added heat are conducive for observed zirconium oxide dissolution and its reprecipitation along pH and temperature gradients formed in the crud. The calculations presented here purposefully overstate the effect of the boron conversion reaction by ignoring the kinetics of heat transfer and mass transfer. The locally produced heat and lithium may be quickly dissipated to yield a rather small net perturbation to the temperature and chemistry in the crud layer. Indeed, if the corrosion product layer did in fact impede the flow of heat and lithium ions, one would expect that fuel integrity under deposits could well be compromised. The fact that fuel performs just fine, even with the type of deposits seen in high-duty PWRs, confirms that the fuel crud comprises a minor barrier, if any, at least to heat transfer.

Note that the effects of radiolysis in a borated aqueous medium are also remarkable and ought to also be included in the AOA model. The initial LET for the $^{10}\text{B}$-n reaction is 6 times larger than that for neutrons, and
about $10^5$ ion-electron pairs are formed per $^{10}$B fission near each reaction point, resulting in a high ionization rate of water. The resultant greatly elevated concentration of $\text{H}_2\text{O}_2$ must create oxidative conditions in the crud. This is consistent with the observation of only ferric ($\text{Fe}^{3+}$) species in the examined deposits. The high density of radiolytic species may also accelerate reaction processes, leading to the formation of $\text{Ni}_2\text{FeBO}_5$. The modeling of all of the micro-thermohydraulic and radiolytic processes in borated crud is in progress.

**Formation of $\text{Ni}_2\text{FeBO}_5$**

The heat and alkaline/oxidative conditions produced by $^{10}$B-n reactions in fuel crud are needed to promote the transformation of $\text{NiO}/\text{NiFe}_2\text{O}_4$ into $\text{Ni}_2\text{FeBO}_5$. In the laboratory, we have readily produced $\text{Ni}_2\text{FeBO}_5$ by hydrothermal reactions at caustic conditions and temperatures, starting from 400 $^\circ$C. Up to this point, we have found that $\text{Ni}_2\text{FeBO}_5$ can be best obtained from an oxygenated aqueous slurry of $\text{NiO}$, $\text{Fe}_2\text{O}_3$, $\text{H}_3\text{BO}_3$ and LiOH, at about 1 to 2 $M$ LiOH concentrations. Figure 1 presents the temperature dependence of $\text{Ni}_2\text{FeBO}_5$ formation for two of these tests.

**Remarks**

In summary, we suggest that $^{10}$B-n nuclear reactions may play a prominent role in modifying the microchemistry of water in deposits on high-duty reactor fuel. In the core, the synthesis of $\text{Ni}_2\text{FeBO}_5$ can start to occur early in the fuel cycle, in the presence of high power density on high span first feed assemblies, high Ni and Fe species transport at high Ni/Fe mass ratios, and high concentrations of B and Li near the fuel surface. Conditions leading to the accumulation of Ni and Fe oxides at Ni/Fe mass ratios larger than 1 may lead to the fixing of large amounts of boron in $\text{Ni}_2\text{FeBO}_5$ on fuel. Such adverse conditions should be avoided in high boiling duty cores.

![Figure 1](image)

Figure 1. Hydrothermal production of $\text{Ni}_2\text{FeBO}_5$ (BA) as a function of temperature for two different compositions of slurry. Red (gray) points – high Ni/Fe ratio; blue (black) points – lower Ni/Fe ratio.

**References**


