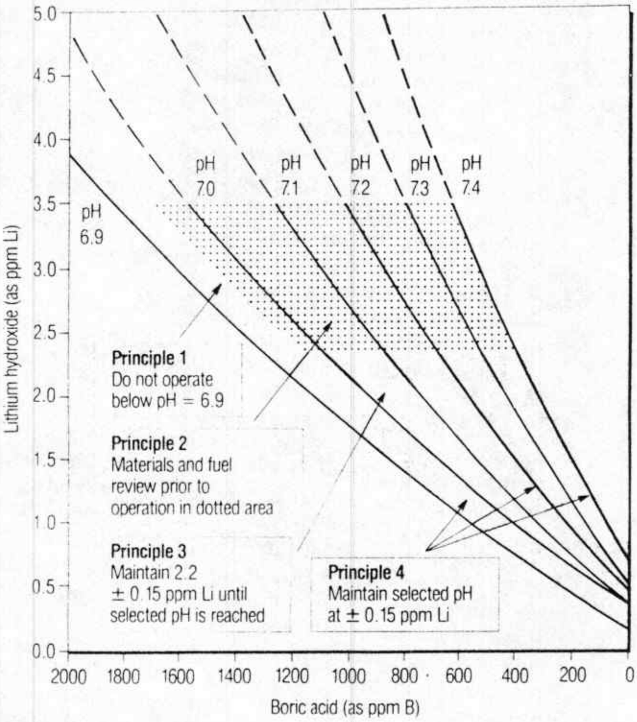
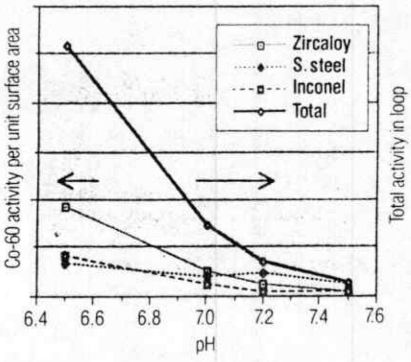
PWR primary coolant chemistry: the view from the USA

By Howard Ocken

Data now coming from US plants confirm that there are effective primary coolant chemistry regimes which reduce shutdown radiation fields without creating accelerated corrosion of Zircaloy fuel rod cladding or primary side stress corrosion cracking of Alloy 600 SG tubing.



◀ **The latest recommendations for optimising PWR primary chemistry.**



▼ **Activity in a PWR primary loop versus pH. The data are from experiments performed by MIT using an in-pile loop.**

The first step in the buildup of radiation fields is the release of cobalt from surfaces contacting the primary coolant. Activation to the gamma-emitting isotope cobalt-60 requires incorporation of the released cobalt into the corrosion products that form on the Zircaloy-clad fuel rods.

Variations in pH can significantly affect the transport of corrosion products around the primary circuit. Laboratory studies using magnetite to model the transport of corrosion products showed that operation at a pH of at least 6.9 at 300°C corresponded to the zero temperature coefficient of solubility. This is the pH value at which corrosion products would tend to deposit on out-of-core surfaces, rather than the fuel, thereby reducing the formation of cobalt-60. Analyses of corrosion products on fuel rods showed them to be nickel ferrite of varying stoichiometry. Solubility measurements on nickel ferrites as a function of pH, temperature, and dissolved oxygen showed that a pH of about 7.4 is required to obtain zero or positive temperature coefficients of solubility.

These results have been confirmed by data obtained from experiments performed at MIT using an in-pile loop that simulates a PWR primary circuit. The total activity produced in the loop as a function of pH is shown right. Reduced formation of Co-60 was observed as the pH increased. Operation at pH 6.5 was found to be especially detrimental; pH 7.2 was significantly superior to 7.0, but only a small further improvement was observed at pH 7.5.

However, long-term plant operation using lithium concentrations above 2.2 ppm to effect higher pH presents possible concerns about increased Zircaloy fuel cladding oxidation. Laboratory and loop tests show that elevated lithium concentrations above 10 ppm in the coolant increase Zircaloy corrosion rates.

Thus, the desire to increase pH to reduce radiation fields must be tempered by the need to minimise possible degradation of the fuel cladding by excessive corrosion. Also, the effect of lithium on the stress corrosion cracking of Alloy 600 steam generator tubing remains an open issue. Some laboratory data suggest that lithium concentrations above 2.2 ppm reduce the time required to initiate primary side stress corrosion cracking.

The most recent recommendations for optimizing PWR primary chemistry are discussed by Wood (*Nuclear Engineering International*April 1991) and shown in the diagram above.

These recommendations, in order of priority, are:

- Do not operate below pH 6.9.
- Perform a plant-specific fuel and materials review if operation above 2.2 ppm lithium is required, and decrease the lithium concentration to 2.2 ppm as soon as possible.
- Maintain 2.2 ± 0.15ppm lithium until the selected pH is reached. And then
- Maintain the selected pH at ±0.15 ppm lithium.

These procedures are designed to reduce radiation fields, while minimising the potential for corrosion-induced damage

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