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The Benefits of Using Enriched Boric Acid in Commercial Nuclear Power Plants

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Abstract

The economics of operating pressurized water reactors (PWRs) demand increased fuel economy, which in turn places increasing demands on the primary coolant chemistry. Higher energy production can be achieved by using increased enrichment of the nuclear fuel, higher fuel burn-up and longer fuel cycles, requiring increased amounts of neutron poison (^{10}B isotope) to maintain reactivity control. However, addition of increased amounts of boric acid leads to increased addition of alkali materials such as lithium hydroxide. This can lead to a variety of issues that can be satisfactorily addressed through the use of ^{10}B enriched boric acid (EBA). Furthermore, it is shown that the return EBA expense relative to natural boric acid is expected to be substantial.

Issue	Principle	Remedy with EPA
Operational radiation exposure (dose rate)	Desired operation at optimum pH for as much of the fuel cycle as possible	Allows the expected pH from beginning of fuel cycle and within acceptable Li limits
Corrosion of fuel cladding	Fuel vendors impose maximum Li concentration	Lower total Boron means lower Lithium
Axial offset anomalies	Boron deposition on fuel	Lower risk of B precipitation
Corrosion of alloy 600	Sensitive to high Li content	Lower total B means lower Li
Stainless steel 304 corrosion	May occur with high Li assay	Lower total B means lower Li
Increase boric acid tank volume	Depends on fuel requirements	Lower volume with EBA
Need to heat safety tank	H_3BO_3 precipitation if high B	Lower concentration with EBA
Compensation of ^{10}B depletion	Inject a small amount of EBA	Lower addition as compared to natural boron

Keywords: Enriched Boric Acid, boron, water chemistry, enriched boron, chemical shim, shutdown

1 Introduction

Boron has a variety of uses in commercial nuclear power plants, including use as a chemical shim in the primary coolant of PWRs, use as a burnable absorber and emergency control of reactors. The use of boron in these applications is due to the high absorption cross section for thermal neutrons of ^{10}B (>3800 barns).

$$^{10}_{5}B + ^{1}_{0}n \longrightarrow ^{7}_{3}Li + ^{4}_{2}He$$

The ^{10}B isotope only comprises ~19.6 at% of natural boron, with the balance essentially consisting of the neutron transparent ^{11}B isotope. The ~80% of ^{11}B isotope is of little use in the nuclear power industry and is in fact undesirable, as it increases the total boron concentration. Isotope enrichment has no effect on solubility, but it does dramatically increase the content of the desired ^{10}B isotope at a given total boric acid concentration. In other words, with judicious choice of enrichment, one can maintain the necessary ^{10}B concentration while decreasing total boron concentration relative to natural abundance boric acid. Bulk properties such as water solubility, solution pH and solution density of ^{10}B enriched boric acid (EBA) are essentially indistinguishable from that of natural boric acid. Commercial isotope enrichment processes can concentrate the ^{10}B isotope to greater than 99 at%, making this valuable isotope readily available to the commercial nuclear power market.

The PWR reactor coolant system pH is temperature dependent[1], and at 300°C the pH of both water and aqueous boric acid is less than 6. Even though boric acid is weakly acidic, this environment is unacceptable, since it increases the general corrosion of materials and adversely affects material integrity by initiating and accelerating stress corrosion cracking, resulting in increased activation and transport of corrosion products in the system. For this reason, fuel vendors have established a preferable pH = 7.2. Therefore, it's necessary to elevate pH with the addition of an alkaline reagent, such as lithium or potassium hydroxide. However, above a certain concentration, lithium will also have an adverse effect on the reactor materials. The desire to extract more energy from nuclear fuel plants magnifies these issues by increasing demands on plant materials and primary coolant chemistry. Fuel performance trends, including longer operating cycles, higher fuel burn-up and increased average rod power, require a higher concentration of ^{10}B during the fuel cycle and, in turn, increase the concentration of total boron and lithium. This paper details the issues resulting from non-optimal water chemistry conditions in PWRs.

2 Impact of EBA on Material Behavior

2.1 Fuel Cladding Corrosion

High Li concentrations are not normally acceptable due to the risk of concentrating lithium hydroxide on fuel cladding and increasing corrosion product deposition, which may result in fuel failures and high dose rates. This is of high concern due to the potential release of highly energetic and noxious actinides, fission products and alpha particles. PWRs in some cases have operated with Li up to 6 ppm; however, the maximum value is typically ~3.5 ppm as defined by most fuel manufacturers, utilities and regulatory bodies.

At a 3.5 ppm Li limit, the pH at 300°C can be equal to 7.0 and even lower during some parts of the fuel cycle, which is a non-optimal pH level. For example, Figure 1 shows that the amount of iron and nickel deposited on Zirlo at a pH < 6.9 was more than 5 times the amount than at pH = 7.2 at 307 °C (2.8 µg/cm^2 vs 0.5 µg/cm^2).[2]

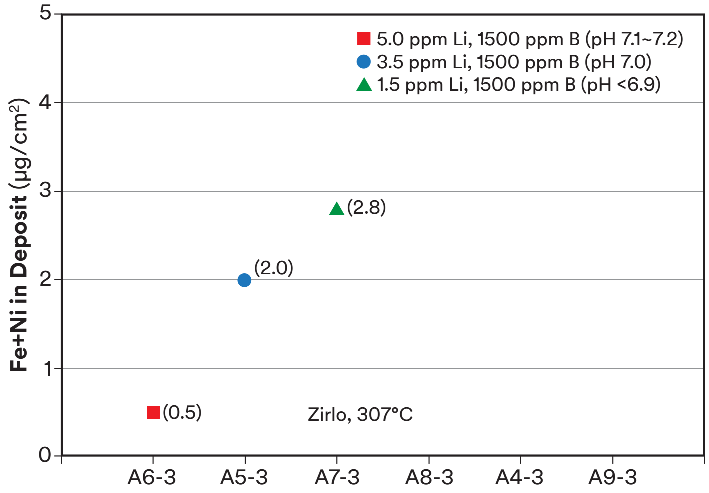


Figure 1: pH Influence on Fuel Cladding Deposit. Optimization of Water Chemistry to Ensure Reliable Water Reactor Fuel Performance at High Burnup and in Ageing Plant (FUWAC), IAEA, 2009.

However, in order to achieve the lowest deposit levels in this study, 5.0 ppm of lithium was added, which is above the typical maximum value. The only solution to the problem is use of EBA, which allows optimal pH within the maximum acceptable Li limit of 3.5 ppm.[3]

2.2 Steam Generator Tubing and Other Alloy 600 Components

The sensitivity of nickel-based alloys such as Alloy 600 to Stress Corrosion Cracking (SCC) is well known and has been the cause of the most important and frequent component failures in operating units. Alloy 600 may crack in pure water under high stress conditions, but will crack even more easily in alkaline conditions. Consequently, Li values are frequently limited to 3.5 ppm (similar for fuel corrosion) in order to avoid accelerating Crack Growth Rate or initiation time. The risk of SCC in Alloy 600 is a primary concern with steam generator tubing, as well as many other components of the RCS where Alloy 600 is not easily replaced. Figure 2 illustrates the detrimental influence of increasing Li content from 2.4 to 3.5 ppm on SCC initiation time (decreased 50% for the higher Li content).[4]

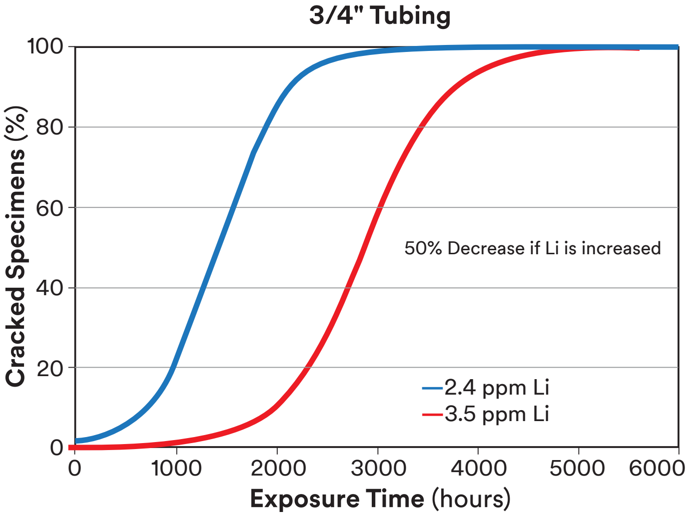


Figure 2: Lithium Effect on Stress Corrosion Cracking Initiation. K. Norring and J. Engstrom, "Initiation of PWSCC in Nickel Base Alloys in Primary PWR Environment. Overview of Efforts at Studsvik Since mid-1980s" in *The European Corrosion Conference EUROCORR 2007*, Freiburg, 2007.

Decreasing SCC may mitigate primary to secondary leaks and thus the presence of undesirable quantities of radioactive compounds in the secondary system. Additionally, reduced SCC may also decrease the need for extensive maintenance expense and plant downtime due to tube repair, tube plugging or in-service inspection.

The issues associated with steam generator degradation have a significant impact on nuclear power plant operation, impacting plant availability and potential lifetime. The most common form of failure is stress-corrosion cracking.[5] As a result, utilities with degrading steam generators must weigh the trade-off of replacing the steam generator or operating with higher operation costs, higher maintenance costs, higher worker exposure rates and increased forced outages from tube ruptures. For sensitive or hard-to-replace components, the use of EBA may increase useful life before replacement.

2.3 Stainless Steel

Recently, EDF (France) asked VTT (Finland) to perform tests on 304 Stainless Steel to investigate the risk of Irradiation Assisted SCC (IASCC) for Li concentration increases from 2.2 ppm to 3.5 ppm.[6] The integrity of some 304 Stainless Steels components in the reactor core can be of high importance for safety. The risk of IASCC on stainless steel was found to increase with increasing concentration of Li. The use of EBA solves the problem by allowing for reduced Li concentration and not increasing stainless steel 304 IASCC risk.

3 Impact of EBA on Dose Rate and Waste Reduction

3.1 Necessity of Optimum pH of Primary Coolant for Dose Rate

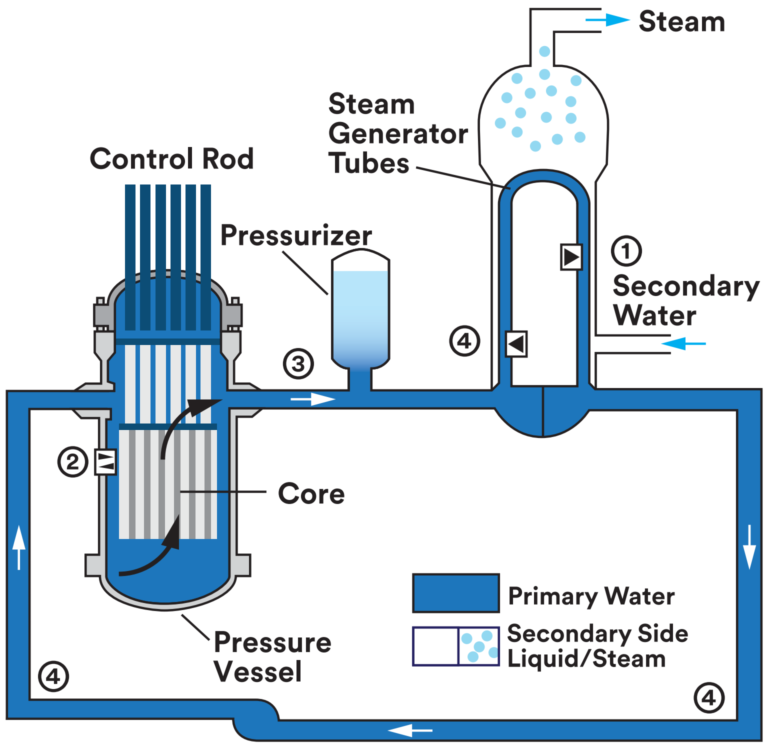
Occupational Radiation Exposure (ORE) can result when even a small amount of released corrosion product is deposited and activated in the reactor core. Corrosion products may be produced from the critical components in the primary coolant system, which can include stainless steel, zircalloy, M5, Zirlo™, SG tubing and chromium containing steels. Once deposits are formed, activated radionuclides can be transported throughout the reactor coolant system (RCS), resulting in radiation field increases and increased personal dose rates. Of highest concern is ORE during maintenance activities.

While materials exposed to primary coolant generally have high corrosion compatibility,[1] even an extremely small amount of released corrosion product can be deposited and activated in the reactor core. Due to its large surface area, steam generator tubing (with ~70% of total Reactor Coolant System surface area) is the main source of corrosion product generation as shown in Figure 3.[6]

The most important radioactive isotopes are ^{58}Co, which originates from nickel activation in many components, including the steam generator, and ^{60}Co, which originates from cobalt contained either on some metals (such as stellite) or as an impurity in steels used throughout the coolant system. Corrosion deposits consist of nickel ferrites, nickel oxide and metallic nickel as determined by reactor coolant system materials.

The optimal pH control strategy seeks to minimize oxide solubility throughout the entire RCS and to minimize structural component corrosion. The coordination of lithium hydroxide with boron should be maintained to achieve a pH value close to at least 7.2 to minimize the solubility of nickel ferrite at various temperatures. Progressive improvement of optimum pH, Li control and other modified practices drastically decreased worldwide dose rates from 1990 to 2006.[7]

The use of EBA is particularly recommended for PWR units where the initial boron concentration would be higher than 900 ppm with natural boric acid. This corresponds to a $pH_{300^\circ C} = 7.2$ and a Li concentration limit of 3.5 ppm as shown on Figure 4.[6] If the Li content should be limited to 2.2 ppm, then the maximum Boron content becomes 500 ppm for a $pH_{300^\circ C} = 7.2$ and about 900 ppm for a $pH_{300^\circ C} = 7.0$.



① Materials corrosion and release of corrosion products in the primary water

② Deposition and activation of the corrosion products under neutron flux:

$$^{58}Ni + n \rightarrow {}^{58}Co + \rho$$
$$^{59}Co + n \rightarrow {}^{60}Co + \gamma$$

③ Transport of the corrosion products

④ Deposition in the primary system induces out-of-core radioactive contamination

Impacts:
→ Increase of radiation dose rates
→ Increase of AOA[1] potential (CIPS[2])

Source term reduction ways:
→ Optimization of materials
→ Optimization of primary water chemistry

[1] AOA: Axial Offset Anomaly

[2] CIPS: Crud Induced Power Shift

Figure 3: Radioactive Corrosion Product Transport in PWR Coolant Systems. S. Taunier et. al., "Corrosion Products Behavior and Source Term Reduction: Guidelines and Feedback for EdF PWRs, Concerning the B/Li Coordinations and Steam Generator Replacements," in *Nuclear Plant Chemistry Conference 2010*, Quebec, 2010.

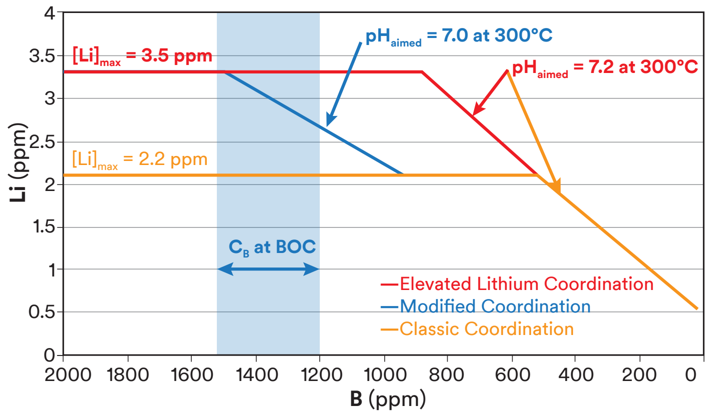


Figure 4: Relation Between [Li]-[B] and $pH_{300°C}$. S. Taunier et. al., "Corrosion Products Behavior and Source Term Reduction: Guidelines and Feedback for EdF PWRs, Concerning the B/Li Coordinations and Steam Generator Replacements," *in Nuclear Plant Chemistry Conference 2010*, Quebec, 2010.

The necessary enrichment of EBA may be easily defined based on the boron concentration at the beginning of fuel cycle for natural boron, the maximum allowed Li concentration and the target $pH_{300°C}$. In the example shown, an EBA enrichment of 40 at% B-10 would allow a reduction in CB from 1400 to 700 ppm providing a $pH_{300°C}$ of 7.2 at a maximum Li concentration of 2.7 ppm, which is more advantageous for safety requirements and fuel behavior. Additionally, a constant $pH_{300°C}$ of 7.2 may be kept throughout the entire fuel cycle without modifying the solubility of oxides, which is favorable for ORE mitigation. Operation with natural boric acid and with the safety requirements limiting the duration of operation at 3.5 ppm Li, the same plant needs to operate with an initial $pH_{300°C}$ of 7.0 for a significant duration of the fuel cycle. Boron enrichment by a factor of 2 is typically sufficient to reach the target $pH_{300°C}$ without exceeding the upper Li concentration limit. For this reason, the EPR™ (Areva Generation III PWR) has been designed with EBA with a ^{10}B enrichment of ~40 at%.

3.2 Impact of EBA on Waste Reduction

As the ^{10}B isotope is progressively consumed through neutronic reaction, there is some decrease of ^{10}B isotopic proportion that may become unacceptable from a safety point of view. When natural boron is used, the only solution to compensate for this depletion is to release boron solution into the environment and to replace it with fresh boric acid solution.

An alternate course of action would be to add a small quantity of EBA of sufficient enrichment to recover the ^{10}B proportion within the specified range. This reduces waste and reduces the associated consequences of waste disposal and release. In some cases, the replacement of the contents of the refueling water storage tank may also be avoided by simply adding EBA to recover the target range of ^{10}B. Whatever the situation, the use of small quantities of EBA will more efficiently solve the problem of progressive depletion of ^{10}B when compared to replacement of large quantities of water by solution of natural boric acid.

4 Impact of EBA on CRUD and Axial Offset Anomalies

Corrosion product deposits which precipitate on and cover fuel rods during operation can lead to fouling of the fuel, loss of heat transfer efficiency, fuel failures, increased radiation fields and neutronic disturbances in the core. If localized boiling occurs, CRUD (~80% porous) that contains elevated amounts of boron can form and induce CRUD induced power shifts (CIPS) or axial offset anomalies (AOA). AOA occurs when the distortion in the measured axial offset in an operating reactor reaches 3% with safety consequences.[8] Crud Induced Power Shift (CIPS) is used to describe the axial distortion of the power shape due to CRUD deposition and the subsequent local accumulation of boron. In case of severe AOA, the plant must be shut down for safety reasons, demonstrating the importance of this phenomenon on plant operation and on selecting chemistry conditions that may avoid its appearance.

There are three conditions that are believed necessary for CIPS to occur: (1) Sub-cooled nucleate boiling at fuel rod surfaces; (2) CRUD deposition on fuel rod surfaces; and (3) Boron deposition on fuel rod surfaces or adsorption in the CRUD. CIPS is clearly associated with the presence of nickel in the CRUD, favoring boron precipitation in nickel ferrite.

Figure 5 highlights the potential benefit of reduced boron concentrations and, therefore, the value in EBA usage on AOA mitigation. Boron content of the deposits decreases with decreasing boron concentration, decreasing lithium concentration as well as decreasing nickel concentrations.[2]

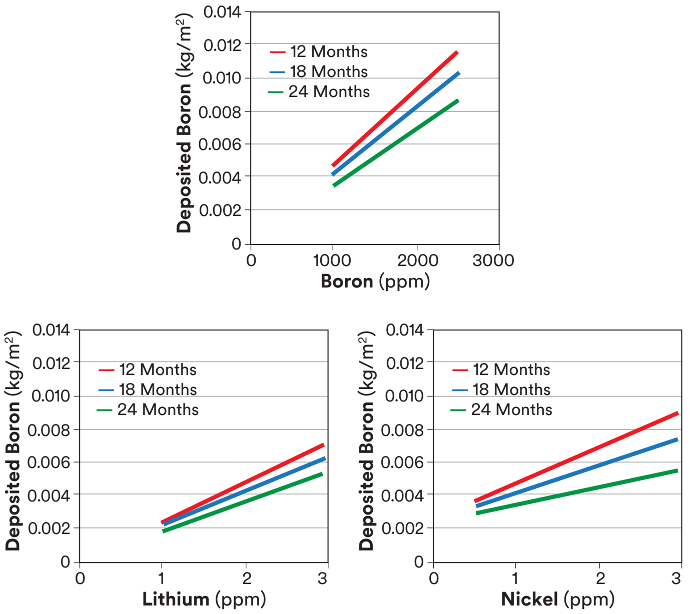


Figure 5: Boron Deposition on Fuel Rods Due to Boron, Lithium and Nickel Concentrations. Optimization of Water Chemistry to Ensure Reliable Water Reactor Fuel Performance at High Burnup and in Ageing Plant (FUWAC), IAEA, 2009.

5 Safety and Economic Evaluation of EBA Use

5.1 Safety Issues

The reduction in boric acid and lithium concentration resulting from the use of EBA has a positive impact on critical safety areas:

- Decreases risk of corrosion product deposition on fuel cladding and elsewhere
- Reduces potential fuel failures
- Reduces CRUD induced power shifts
- Decreased direct corrosion of fuel cladding corrosion in the presence of high alkaline reagent concentration (> 3.5 ppm Li)
- Decreases risk of stress corrosion cracking of reactor coolant system and steam generator
- Decrease in occupational radiation exposure

In addition, the advantages of using EBA or ^{10}B enriched sodium pentaborate are clear. Using a ^{10}B enriched product leads to a significantly greater concentration of the functional ^{10}B isotope, which can increase safety factors, decrease total boron concentrations, eliminate concerns resulting from boric acid precipitation and even decrease the footprint of the emergency pools.

5.2 Plant Life Extension

As outlined in the above discussion, use of EBA allows a plant to limit Li concentration, decreasing the risk of stress corrosion cracking of sensitive and/or hard-to-replace components. Corrosion-related issues are often complex and affected by many factors in plant design and operation; however, it is possible to approximate the excellent return on the additional cost of EBA by looking at a plant life extension benefit. Consider an example PWR unit:

- The additional cost of 40 at% EBA compared to natural boric acid is $6.5 MM for initial system filling + $460k/year make-up. 10 years of EBA usage is a cost of $11.1 MM.
- Yearly plant earnings are ~$365 million.
- Cost of 10 years of EBA usage is 1.7% of the earnings from one operational year.
- Each additional year of plant life owing to reduced Li and boron concentrations would realize an additional $365 MM of yearly earnings. This clearly demonstrates the low financial risk and potential value of applying EBA in plants with SCC and other issues attributable to higher lithium and boron concentrations.

5.3 Plant Availability

The beneficial result of EBA for plant availability is rather difficult to quantify in the same way as it is difficult to quantify the plant life extension. The plant availability may be increased according to the following positive impacts of EBA due to reductions in prolonged shutdown and reductions in necessary maintenance:

- Decreased stress corrosion cracking of metals
- Reduced risk of fuel failure
- Decreased risk of axial offset anomalies

In order to illustrate the return EBA usge may bring, consider a 900 MWe PWR unit as above:

- The incremental 10 year cost of EBA in place of natural boric acid is $11.1 MM.
- A one day plant availability increase saves $1,000,000/day earnings.
- The cost of using EBA for 10 years is largely compensated by saving 1 day of operation every year.

6 Conclusion

Primary coolant water chemistry for PWR units can be difficult to apply in a manner which ensures all safety issues are taken into account. A key issue is operating at an optimal pH in order to minimize dose rates; however, this means a sufficiently high lithium concentration has to be selected. Increasingly higher fuel performance factors necessitate incompatible maximum lithium concentrations for the behavior of various components of the reactor coolant system; thus, EBA is the only solution to the limitations of natural boric acid.

Indeed, high lithium and boron concentrations result in:

- Increased fuel cladding corrosion and possible fuel failures with noxious radioactivity release
- Increased SCC of various components, including steam generators and core components
- Axial Offset Anomalies induced by precipitation of boron in CRUD deposits. The deposits are increased with increasing lithium and boron concentrations
- Increased waste releases in the boron recovery system

The solution to these problems is the use of EBA, which allows a reactor to operate at the optimal pH with significantly decreased lithium and boron concentrations. Considering all the advantages of EBA, any new plant where total boron concentration would exceed 900 ppm using natural boric acid (i.e. 19.6 at% ^{10}B) should instead use EBA in the design.

In operating plants where the fuel option modifications are inducing high natural boron concentration that is not compatible with the maximum acceptable Li limits and optimal operating pH, conversion to EBA should be strongly considered. In particular, EBA can be used to compensate for ^{10}B depletion from neutronic absorption. EBA, or other similar ^{10}B enriched products, should also be given strong consideration for emergency pools.

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