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A Study on the Changes of Primary Coolant Chemistry and CRUD generation at PWR for Long Term Fuel Cycle

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ABSTRACT

Nuclear power plant operation practice shifts to long-term fuel cycle such as from 12 month operating cycle to 18~24 month operating one. It is important to emphasize that the current trend to longer fuel cycle has complicated the dilemma of finding optimum pH range for the primary coolant chemistry. And long term fuel cycle has a possibility to occur AOA(axial offset anomaly). Although CRUD is not a high level waste, it is very important products because CRUD is the major source of ORE (occupational radiation exposure) and its transport mechanism is not specified exactly yet. To analyze the generation mechanism of CRUD at the long-term fuel cycle, the COTRAN code used, which simulate the behavior of the CRUD based on double layer concept model and solubility difference. It turned out that the activities of CRUD decreases as the pH of the coolant increases, and for the same period of different fuel cycle, the generation of the CRUD increases as the operating fuel cycle duration increased. In this paper, enriched boric acid (40% enriched B^{10}concentration) for the reactivity control is adopted for the simulation as the required chemical shim rather than natural boric acid.

1. INTRODUCTION

Light water reactors (LWR) have been commercially deployed for four decades and currently account for approximately 85% of the installed nuclear capacity in the world. The historical design burn-ups of Pressurized Water Reactors (PWRs), 33MWd/kgU, although based on much earlier optimization studies, were suggested and used from the late 1970s because of fuel supplier warranties and assurances of licensing and performance, however no longer represented an economic optimum[1].

The discharge burn-ups of nuclear fuel for PWRs have been substantially increased the levels prevalent from fifteen to twenty years ago. Currently the average design discharge burn-ups that are commercially available for PWRs are in the range 40-50 MWd/kgU. Economic incentives may exist for extending burn-up even further, at least 60 MWd/kgU. It is of interest to identify the conditions under which such incentives may comply. Long-term fuel cycles require higher initial enrichment and/or more fresh fuel to provide the additional reactivity to support the longer operation, and this higher initial reactivity requires a greater quantity of controlled neutron absorbers in the core at the beginning of the cycle.

These days, nuclear power plant operation practice shift to long-term fuel cycle, so new operational method which can satisfy long-term safety is required. For this purpose, increasing the boron concentration in the primary coolant may be required. However to satisfy reactor kinetic condition we should also increase the Li concentration initiates and elevates Lithium-Zirconium stress corrosion cracking. At the same time, fuel duty should be increased and the need to avoid increased cladding oxidation is greater than before because Zr-clad thickness can be reduced to undesirable level.

It has been a well-known practice that pH of about 6.9 is required in the primary coolant of PWRs to optimize corrosion product deposition, which is the major source of ORE, on the primary loop. It was based on the assumption that the corrosion product was mostly composed of magnetite (Fe_3O_4). However, more research reveals that corrosion product is mainly composed of nickel-ferrite ($Ni_xFe_{3-x}O_4$), so the corresponding modification on the existing theoretical modeling has been followed.[2] Several laboratories' experimental measurements for the solubility of corrosion product have concluded that the pH level of 7.4 is more suitable compared to the pH level of 6.9.(Fig 1) It is now generally believed that the minimized corrosion product build-up can be achieved in steam generator with the high pH value.

2. LONG-TERM FUEL CYCLE

2.1 Influence of Long-Term Fuel Cycle

The International Nuclear Fuel Cycle Evaluation in 1980 and many national studies supporting long term fuel cycle have identified a large potential for fuel cycle improvements which reduce uranium and separative work requirements and fuel cycle cost[1]. Among these, extended burnup was identified as one of choice. Goals of extended burnup were discharge batch average burnups of 45MWd/kgU for PWRs and 40 MWd/kgU for BWRs. In the years 1982-1985 the first fully successful results of the LWR fuel extended burnup programs were obtained no significant unexpected phenomena or trends were encountered; good design and licensing data were obtained up to high burnup levels and very good fuel reliability was reported. As a result, many utilities have moved ahead with a series of small steps towards these target extended burnups.

In case of applying long term fuel cycle(18month cycle)[3];

- Increase of capacity power : 3~7%

- Additional fuel fabrication cost : 5~7%
- Reduction of fixed charge : ~5%
- Decrease of electric power generation cost

In addition, the long-term fuel cycle contributes to the more stable supply of electric power and reduce uranium consumption and spent fuel. In case of 24month fuel cycle operation, mid cycle outage that checks the component integrity temporally, is needed. This outage period is very important because this could be a dominant factor in the economic evaluation.

It is now important to emphasize that the current movement to long-term fuel cycles has increased the difficulty of pH optimization. Typically, 12-month fuel cycles begin with no more than 1200ppm boron at a start of a cycle, so the maximum of 2.2ppm lithium is required to satisfy the requirement of pH 6.9 (Fig 2). Long-term fuel cycles of 18 or 24months have forced chemistry personnel to select an operating pH regime that minimizes "negative effects" rather than maximizes "the benefits." [4]

As an adequate reserve supply of reactivity it might necessary to start operation with a corresponding higher boron concentration at the beginning of a cycle. Due to the upper limitation of Li concentration, the high temperature-pH (pH_{300}) of the coolant will require the pH value below the accepted minimum of 6.9 during a certain period of time.[5] In this period, an increased influence on the release rate of various metal ions and on the solubility of corrosion products is obvious and AOA(axial offset anomaly) may be occurred[6][7] since the pH and corrosion process of the activity will buildup and the dose rate of the components could be increased. For this reason, we were confined to adopt which of the following possibilities we should use during long-term cycles:

- Toleration of a little, temporarily limited pH lowering
- Enhancement of the upper lithium limitation
- Reduction of the boron concentration by the use of enriched boric acid with B-10
- Use of mixed fuel with an increased amount of gadolinium oxide to minimize the boron concentration at the beginning of a cycle

2.2 Primary Coolant Chemistry

In the early 1980s, many plants began to employ Coordinated Chemistry in which lithium is coordinated with boron to maintain a pH of 6.9. More recently, some plants have increased the coolant steady-state pH from 6.9-7.4 to minimize CRUD deposition on the core and reduce radiation fields in out-of-core regions. Solubility studies suggest that operating with pH=7.4 will minimize nickel ferrite precipitation in the core. In the late 1980s, several PWRs implemented a 3.5ppm Li(max.)/pH=7.4 (Elevated Lithium) scheme to reduce out-of-core radiation fields. The Elevated Lithium chemistry programs were terminated due to concerns over the potential effects of prolonged exposure to 3.5ppm lithium on primary water stress corrosion cracking (PWSCC) of

Alloy 600 and Zircaloy cladding corrosion. Instead, a Modified Chemistry regime with ~2.2ppm lithium/pH=7.2~7.4 has been adopted by many plants. Maintaining lithium concentrations at a maximum of 2.2ppm during startup, however, can result in a pH<6.9 for plants operating with an initial boron concentration exceeding ~1200ppm. Depending on the cycle length and fuel design, the startup boron concentration may exceed 2000ppm, which will significantly lower the pH. Therefore in the Modified Chemistry regime, the startup lithium and boron are coordinated to maintain pH>6.9 until the required lithium concentration decreases to 2.2ppm. At this point, the pH is permitted to increase with constant 2.2ppm lithium, until it reaches 7.2~7.4. It is important to note that extended fuel cycle chemistry may require significant concentrations of lithium for the early portion of the cycle. "Modified pH chemistry" involves operation at pH 6.9 in the initial part of the cycle, until the lithium level drops to 2.2ppm. This level is maintained until the pH rise to 7.4, which is the recommended value till the end of cycle. The modified pH chemistry reduces the possibility of enhanced Zircaloy oxidation, compared to elevated lithium.[4]

2.3 Use of Enriched Boric Acid[8][9]

In the nuclear plant, typically natural boric acid (NBA) dissolved in a PWR primary coolant is used as a soluble reactivity control agent. The dissolved boric acid is referred to as a soluble poison or chemical shim due to its high capacity for thermal neutron absorption capability (3837barn) exhibited by Boron-10 (B-10). However, natural boron contains only 20 atom percent of the B-10 isotope with the remaining 80% being the B-11 isotope. The B-11 isotope has little thermal neutron absorption cross section(0.005barn). Since B-11 makes up the bulk of the total boron present, it is necessary to eliminate or reduce this isotope composition from total boric acid inventory to produce enriched boric acid B-10 isotope (EBA). Through this process, the boric acid concentration in the operating PWR plants could only be a small fraction of that present level. Natural boric acids have large portion in liquid waste and boric acids recycled through BRS(boron recycle system) have much impurities, which may raise bad influences in plant operation.

The benefits of EBA are related to the corresponding changes in the primary coolant chemistry that reduces the required concentration of boric acid for operation. The use of EBA will allow the plant operation at significantly reduced boric acid concentrations. Consequently, an elevated coolant pH of 7.4 can be achieved by using an acceptable maximum of 2.2ppm lithium during the entire 18-24 months of long-term fuel cycles. Operating under these conditions for the whole fuel cycle can reduce the amounts of corrosion products transport and the amounts of radiocobalts deposited on ex-core surfaces, thus reduce plant dose rates.

As the evaluation based on chemistry parameters was typically used to quantify the man-rem (ALARA) saving and ultimately dollar savings resulted from plant operation with enriched boric acid, the decrease in overall plant exposure rates can be related directly to man-rem savings for maintenance and inspection activities.

2.4 Modification of Simulation Code

The primary coolant system is divided into soluble, particulate products of coolant, inner oxide layer and outer oxide layer in the simulation model of our computer code, COTRAN. It should be noticed that in a PWR with recirculating flow, coolant temperature and pH can change the solubility of the CRUD such that reactor core and steam generator surface can be in either a release or deposit mode of soluble ions[10]. It is important to understand that net activity transport can take place even when there is no mass transport[11]. The driving force for mass transfer is the mass concentration gradient, and the direction of net mass transport is to the lower mass concentration. However the driving force for the activity transfer can be the concentration gradient of the particular radionuclide relative to the total mass of that element in a given volume.

The COTRAN code is developed in KAIST to estimate CRUD only for one cycle. However, our purpose of this study is to predict the amount of corrosion product not for only one cycle, but for multi-cycle. In order to predict the generation of CRUD for long-term, the COTRAN code is required to be modified with decontamination and refueling process. It is assumed that 40% of CRUD is decontaminated and one-third of the fuel is refueled at every cycle. This simulation code has been developed to provide the amounts of CRUD at each component like the CRUDSIM.

3. RESULTS AND DISCUSSION

3.1 Input Data

In this study, data are established to estimate relative amount of corrosion product at long-term fuel cycle for different cycle duration (12month, 18month, NBA 24month, EBA-40% 24month). The EFPD (Effective Full Power Days) of each cycle are 300, 450 and 567 EFPD for 12, 18 and 24 month cycle respectively. As the EFPD increase, initial boron concentrations also increase, and the concentration will decrease rapidly up to xenon saturation. Each initial boron concentration is assumed to be 1200, 1500, 1900 and 950ppm for the above cases. The water chemistry assumed is modified chemistry regime that is applied to the PWR of Korea. Thus, lithium concentration is correspondingly controlled in order to maintain pH 6.9 or over. The run time of each cycle is up to 1800 EFPD to predict saturation time of corrosion product. These data are shown at Table 1. The reactor type applied with these conditions is ABB CE's SYSTEM 80+ which is model of APR1400.

3.2 Results and Discussion

3.2.1 CRUD Buildup

Deposition and release of CRUD occurs by the solubility change of the coolant water, which depends on both pH and temperature. The chemical change of 24 month cycle is shown Fig 3. As the pH levels increase from low to high values, the magnitude of solubility become lower and the temperature coefficients of solubility shift from negative to positive(Fig 1). Thus, it can be found out that reduction of corrosion product transport into the core and radiation field at out of core can be accomplished with higher pH levels. Activity decreases as pH increases, and for the same period of the different fuel cycles, as the fuel cycle period increased, the generation of the CRUD increases (Fig 4, 5 and 6). Consequently, the generation of CRUD increases linearly at steam generator and increases exponentially at core. The pH dependence appears to be larger at core than at steam generator. As the operation time is increased, the ratio of Co^{58}/Co^{60} becomes small (Fig 7).

3.2.2 Effect of EBA

The effect of the use of enriched boric acid is that the neutron absorption capability of the chemical shim is maintained while decreasing the overall boron concentration in the reactor coolant system. It can reduce not only initial boron concentration but also lithium concentration. From the results applied to 24month-cycle operation(Fig 4), we can see that the generation of CRUD shows tendency to decrease up to 18 month-cycle operation level with natural boric acid(Fig 5, 6). If the concentration of B^{10} is higher, the amount of CRUD is expected to reduce considerably.

3.2.3 Verification of Results

The result of the COTRAN code was verified by applying and comparing PCCL of MIT during one cycle that is relatively short period in previous study[10]. However, rarely the measured data of long term and multi-cycle is available. Thus, code outputs are compared with data of Millstone Point 3 PWR[12] where average cycle length is about 450 EFPD(49 MWd/kgU) and capacity is 1150MWe. The measured values of steam generator tube surface activity shows similar trends to those of 18-month cycle simulation result (Fig 8 and 9).

4. CONCLUSION

In order to increase the capacity factor to improve the economy of NPP, power plant operation practice shifts to long-term fuel cycle from typical 12 month operating cycle to 18~24 month, so new operational methodology which can satisfy the corresponding long term safety is desirable and required. For this purpose, increasing the boron and lithium concentrations in the primary coolant should be recommended.

From the result of the simulation code, the following conclusions are obtained :

(1) The fuel cycle length and pH values are important parameters to control the generation of CRUD at core.

- The amounts of CRUD generation increase linearly at the steam generator region and increases exponentially at reactor core as the cycle length is extended.
- High pH values from 6.9 to 7.4 reduce the corresponding radiation fields at in-core and out of

core surface.

(2) With the application of enriched boric acids, the amounts of the generated CRUD shows reducing tendency because of the extended high pH operation periods. At the long-term fuel cycle, initial boron and lithium concentrations have to be high compared to the current cycle to perform as chemical shim agents. This reactor chemistry scheme will come up with several another safety problems such as CRUD buildup, PWSCC etc. Usage of enriched boric acid and zinc injection can be considered to be option of the potential applications to solve those problems.

The result of computer code simulation is still quite preliminary to be applicable to the experimental and plant real data. Thus, more extensive studies and experiments are required to simulate the more accurate and real reactor CRUD behaviors at the coolant system.

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Table 1. Input Data of Each Cycle

Cycle (month)	12	18	24 (NBA)	24 (EBA-40%)
EFPD	300	450	567	567
Initial Boron . (ppm)	1200	1500	1900	950
Boron Con. After Xe Buildup	850	1200	1560	780
Chemistry Regime	Modified Chemistry Regime			
Initial Li. (ppm)	2.2	2.7	3.5	2.2
Run Time (cycle)	6	4	3	3
Reactor Type	KNGR (System 80+)			

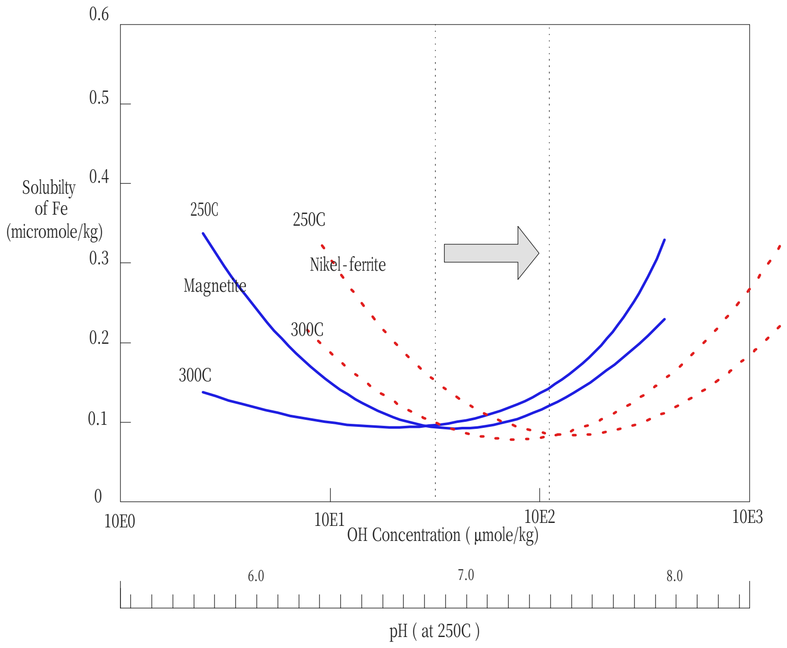


Fig 1. Solubility of Fe

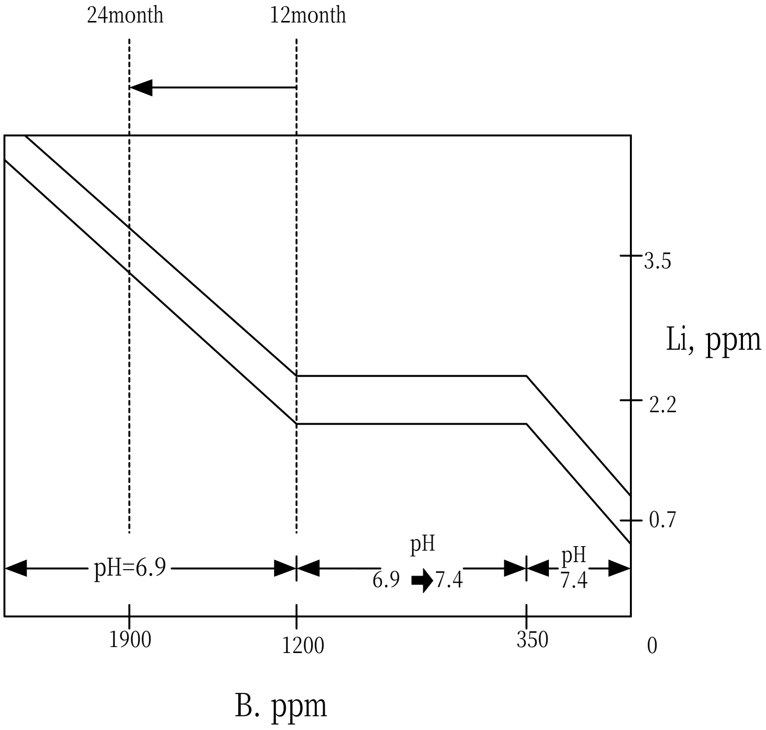
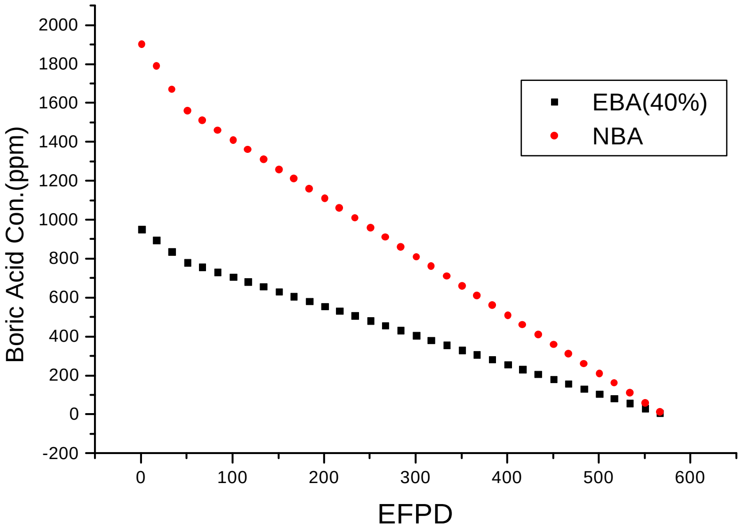
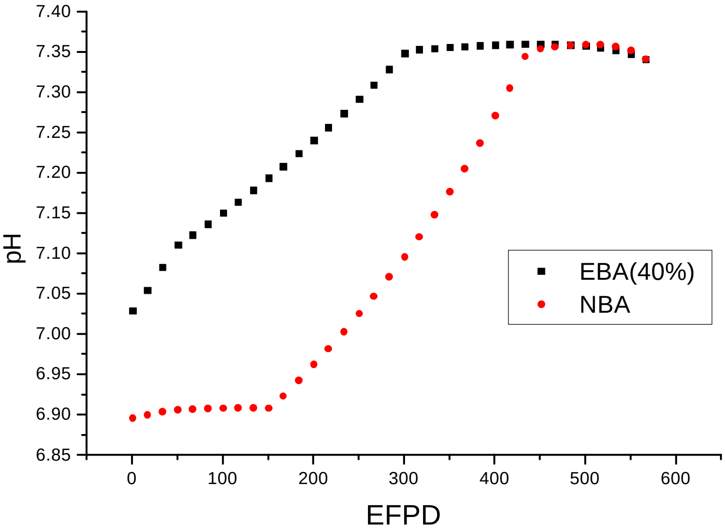


Fig 2. Chemical Change at Modified Regime



(a) Boron Concentration



(b) pH

Fig 3. 24-month cycle chemistry (NBA & EBA)

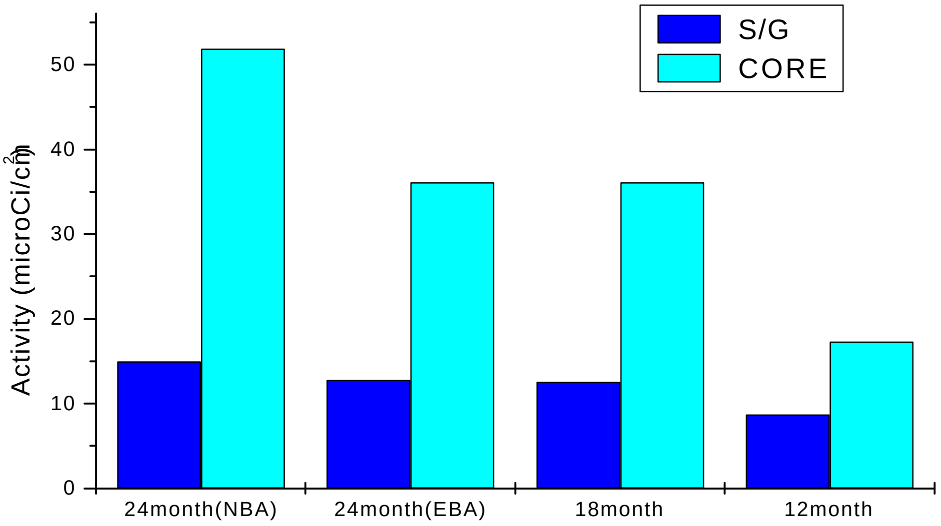


Fig 4. Activity of Co^{58} after 1800 EFPD

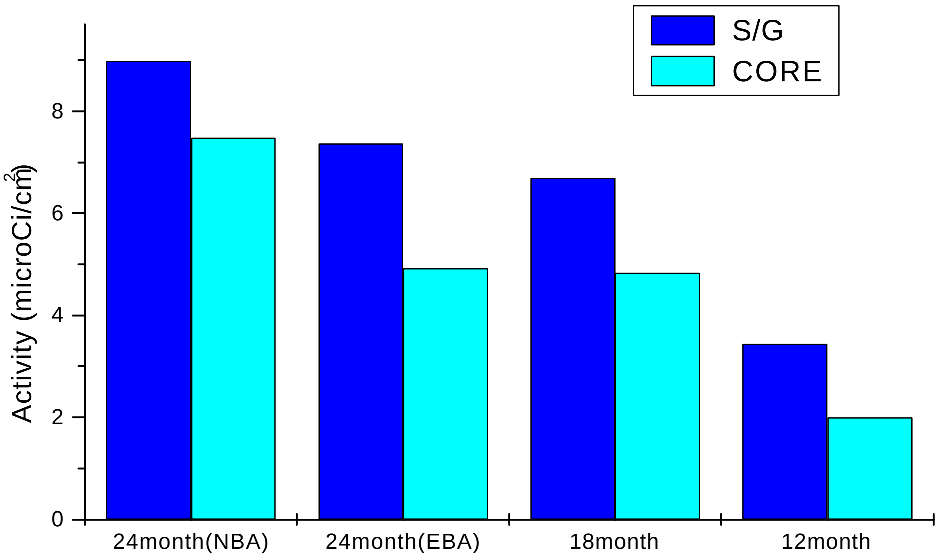


Fig 5. Activity of Co^{60} after 1800 EFPD

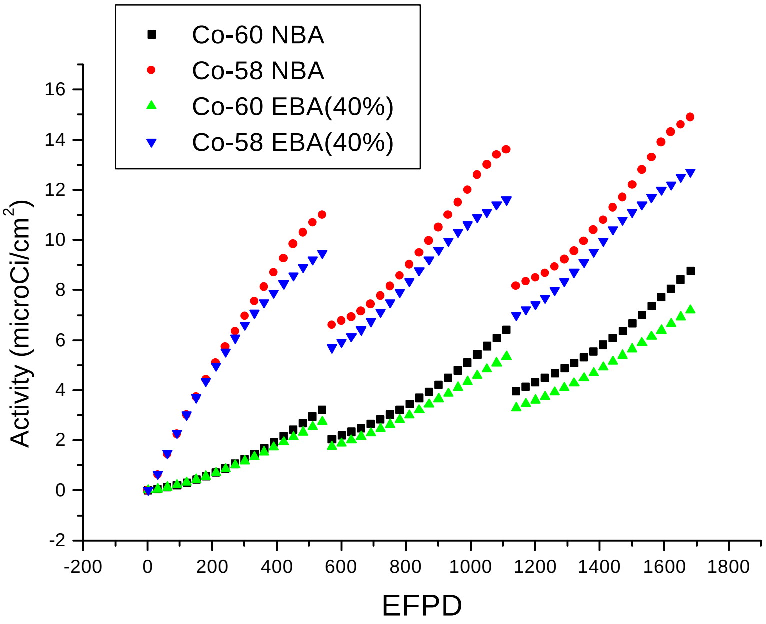


Fig 6. Activity of CRUD at 24-month cycle (S/G)

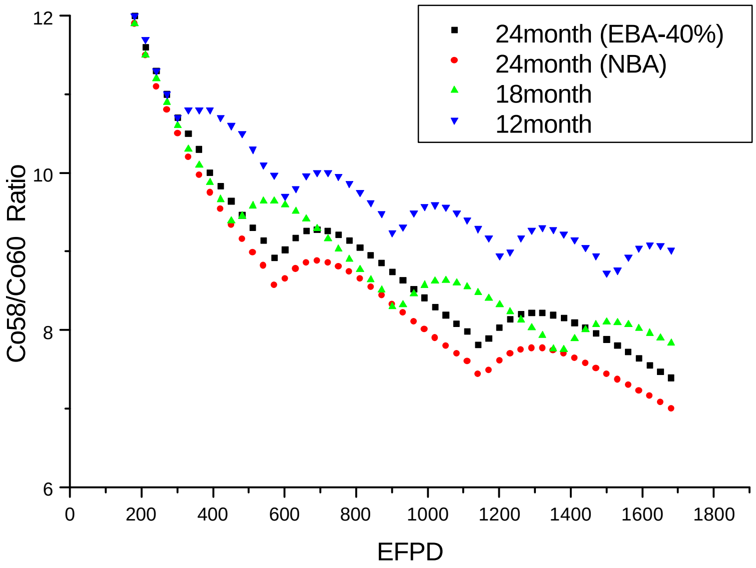


Fig 7. Co^{58}/Co^{60} Ratio at Core

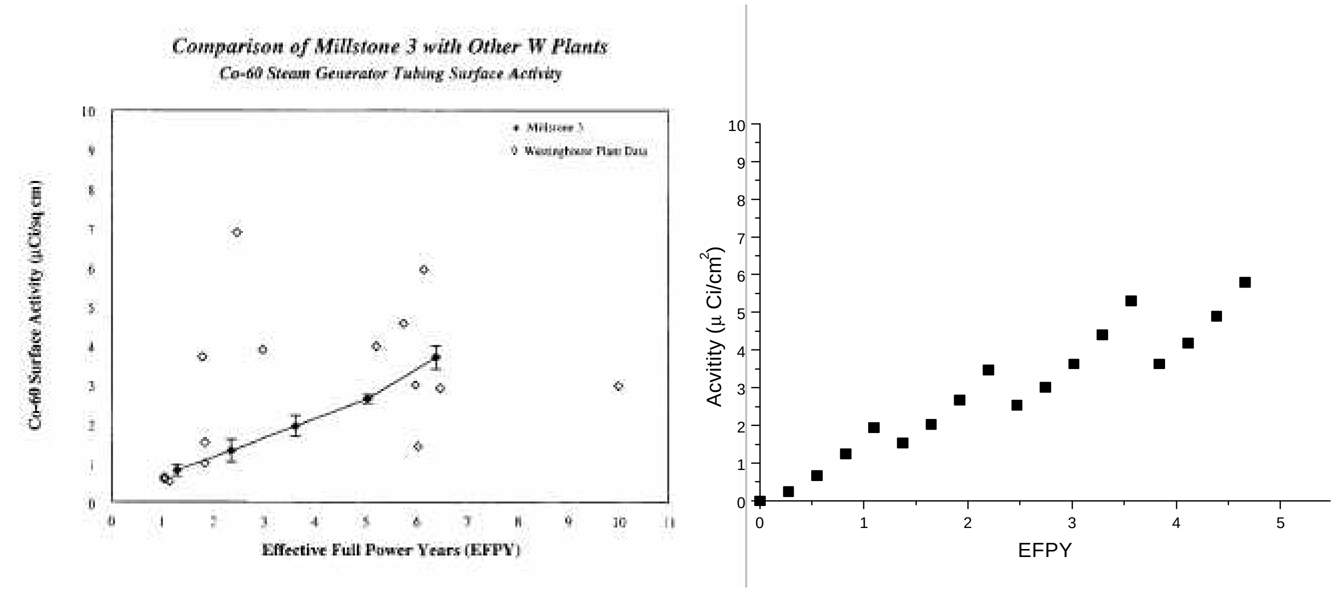


Fig 8. Millstone Point 3 PWR Measured Values & Code Results at S/G (Co-60)

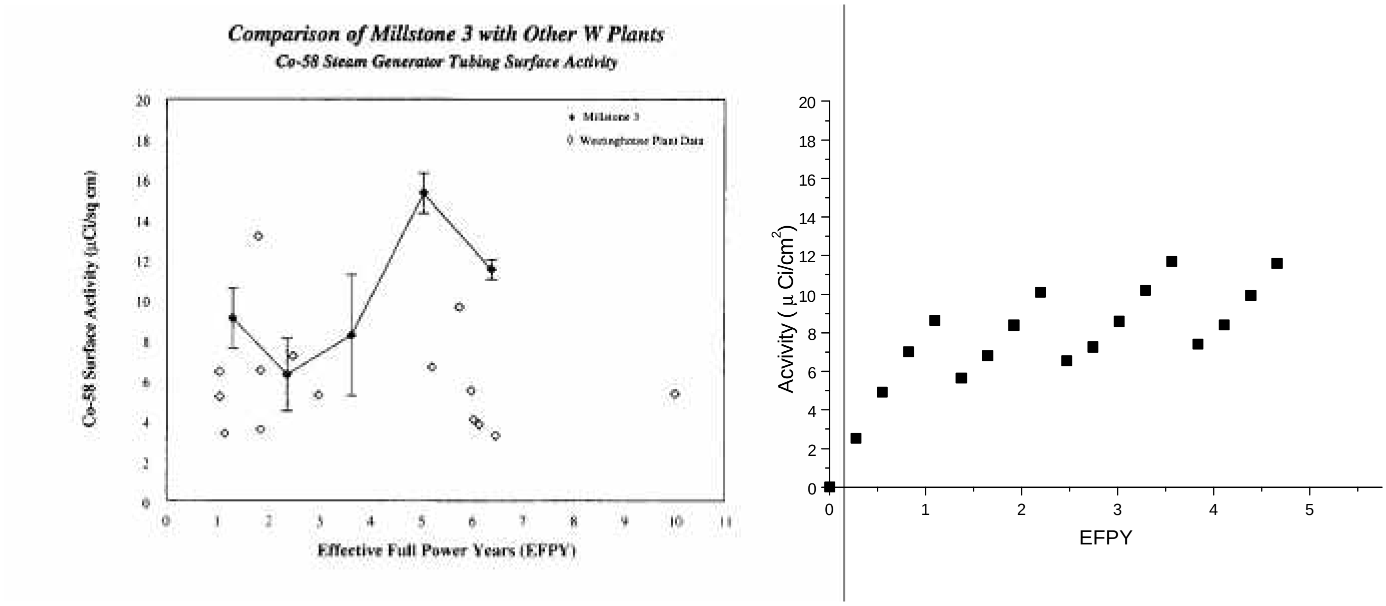


Fig 9. Millstone Point 3 PWR Measured Values & Code Results at S/G (Co-58)