K/OP-241

URANIUM PRODUCTION IN THORIUM/DENATURED URANIUM FUELED PWRS

W. B. Arthur

Operations Analysis and Planning

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UNION CARBIDE

OAK RIDGE GASEOUS DIFFUSION PLANT
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ABSTRACT

Uranium-232 buildup in a thorium/denatured uranium fueled pressurized water reactor, PWR(Th), was studied using a modified version of the spectrum-dependent zero dimensional depletion code, LEOPARD. The generic Combustion Engineering System 80^{TM} reactor design was selected as the reactor model for the calculations. Reactors fueled with either enriched natural uranium and self-generated recycled uranium or uranium from a thorium breeder and self-generated recycled uranium were considered. For enriched natural uranium, concentrations of ^{232}U varied from about 135 ppm ($^{232}U/U$ weight basis) in the zeroth generation to about 260 ppm ($^{232}U/U$ weight basis) at the end of the fifth generation. For the case in which thorium breeder fuel (with its relatively high ^{232}U concentration) was used as reactor makeup fuel, concentrations of ^{232}U varied from 411 ppm ($^{232}U/U$ weight basis) at discharge from the first generation to about 512 ppm ($^{232}U/U$ weight basis) at the end of the fifth generation. Concentrations in freshly fabricated fuel for this later case were 20-35% higher than the discharge concentration.

These concentrations are low when compared to those of other thorium fueled reactor types (HTGR and MSBR) because of the relatively high ^{238}U concentration added to the fuel as a denaturant. Excellent agreement was found between calculated and existing experimental values. Nevertheless, caution is urged in the use of these values because experimental results are very limited, and the relevant nuclear data, especially for ^{231}Pa and ^{232}U, are not of high quality.

I. INTRODUCTION

The search for a nuclear fuel cycle which makes more difficult the task of diverting fissile material suitable for weapons has led to more active consideration of thorium based fuel cycles using "denatured" uranium.* It was assumed that the first reactor designs to implement these new fuel cycles will resemble PWRs currently in use. One such design is Combustion Engineering's System 80^{TM} reactor which is claimed to accommodate thorium, uranium and plutonium based fuels. A secondary, yet important, consideration in assessing the viability of this fuel cycle is ^{232}U production. Alpha and gamma radiation from ^{232}U decay chain daughters dominates other actinide radiation sources. Thus, ^{232}U concentrations in the fuel cycle provide a potential hazard during fuel reprocessing and fabrication.

The fuel management scheme used to obtain the data presented later is detailed elsewhere.[1] This scheme uses self-generated recycle of uranium initially bred in UO_2/ThO_2 fuel assemblies in which the fissile uranium content is denatured. In this study, denatured uranium has a fissile fraction equal to a denaturant limit (D), i.e.,

$$D = \frac{M_3+M_5}{M} \quad .$$

The denaturant limit was defined by the following expression:

$$D = \frac{0.12\ M_3 + 0.20\ M_5}{M_3 + M_5}$$

where: D = Denaturant limit

M_3 = Mass of ^{233}U in a fuel assembly

M_5 = Mass of ^{235}U in a fuel assembly

M = Mass of all uranium isotopes in the fuel assembly

Thus, a fuel whose fissile material is all ^{233}U or ^{235}U must have a fissile component in the total uranium no greater than 12 or 20%, respectively. The plutonium bred in the reactor is separated from spent fuel, but it is not recycled into this reactor. However, recycle of bred uranium continues throughout the reactor operating history. Bred uranium is mixed with either highly enriched natural uranium or uranium from a thorium breeder blanket to bring its fissile content up to the denaturant limit after each recycle.

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*Denaturing in this context means the dilution of the fissile uranium (^{233}U or ^{235}U) with ^{238}U such that the fissile content of the mixture is too low for weapons use.

The LEOPARD[2] computer code was modified to perform the necessary calculations. This code was selected because: (1) its results are well validated for PWR designs, (2) its basic cross section library was recently updated using ENDF/IV nuclear data,[3] (3) numerous calculations can be performed at moderate computational cost, (4) it allows recomputation of the neutron spectra at user selected intervals during fuel lifetime, and (5) the basic code was already implemented in Oak Ridge. A detailed description of the modified code will be available shortly.[4]

II. PRODUCTION ROUTES TO ^{232}U

The principal production/depletion routes to ^{232}U in LWRs are shown in Fig. 1. In currently operating low enriched ^{235}U PWRs, route D is the dominant production route, although discrepancies between experimental measurement and calculations seem to weaken this conclusion somewhat.[5] For the case of a PWR fueled with Th, route A is the predominant path to ^{232}U due to the large thorium inventory in these reactors. The percentage contributions to the ^{232}U concentration from these production paths vary with assumptions about the ^{230}Th concentration in thorium. Values from 0 to 100 ppm ($^{230}Th/Th$) appear plausible.[6]

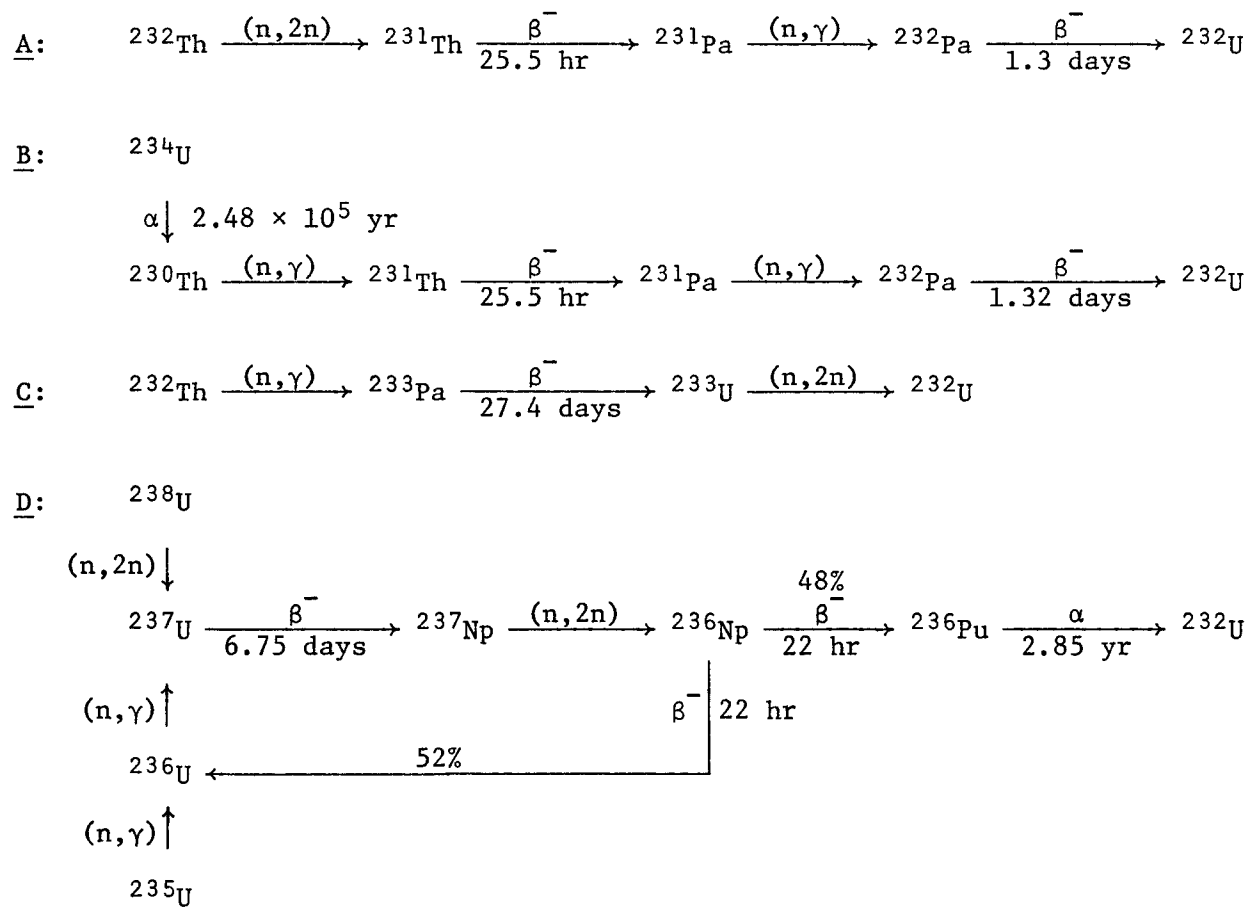
III. BASIC NUCLEAR DATA AND METHOD OF CALCULATION

The versions of LEOPARD available from EPRI[3] or the Argonne Code Center (ACC) do not consider ^{232}U production and they do not contain the relevant nuclear data. LEOPARD employs a 54-group fast cross section library and a 172-group thermal library with an 0.625 eV. thermal cutoff. (The thermal library is created in a subprogram from a 246-group library.) Where possible, ENDF/B-IV or V data were added to the basic cross section libraries. Unfortunately, several cross sections of importance in ^{232}U production are not in the ENDF/B system. These include $^{230}Th(n,\gamma)$, $^{231}Pa(n,\gamma)$ and $^{232}U(n,\gamma; n,f)$. Cross section sets for these nuclides were developed from literature referenced in CINDA 75 using methods of Full Information Maximum Likelihood Parameter Estimation Via Extended Kalman Filtering.[7] (While these methods are relatively new, they generate better validity statistics for non-linear models than are available with generalized least squares data fitting.) In coalescing data, strong weighting was given to General Atomic[8] "evaluations" of ^{231}Pa and ^{232}U and data with a 1000 barn resonance integral and 40 barn 2200 m/sec cross section for ^{230}Th. The collapsed 1-group cross section used in the depletion/production subroutines of the code was recomputed from the multi-group cross sections at 2000 MWd/MTHM intervals.

A few modifications to the basic LEOPARD code available from EPRI or ACC were necessary to model ^{232}U production in thorium/denatured uranium reactors. These modifications included: (1) treatment of the (n,2n) reaction type for ^{232}Th and ^{233}U, (2) addition of production/depletion chains leading to ^{232}U,

Figure 1

^{232}U PRODUCTION ROUTES



(3) insertion of a well documented ^{232}Th integral resonance correlation* to allow shielding of thorium resonance cross sections, and (4) insertion of a ^{238}U integral resonance correlation for low density uranium fuel mixtures.[9] More detailed information on the nuclear data and code modifications will be available shortly.[4]

IV. RESULTS OF CALCULATIONS

Tables 1 and 2 summarize the generation data for a CE System 80™ reactor. (Generation data presented are for the isotopics of the fuel assemblies using recycled fuel, and *not* for the average reactor isotopics.) In Table 1 makeup fuel is 93 wt % ^{235}U enriched natural uranium. In Table 2 makeup fuel is assumed to be available from a thorium breeder blanket[11] with composition:

Nuclide	%
^{232}U	0.392
^{233}U	92.481
^{234}U	6.651
^{235}U	0.448
^{236}U	0.028
^{238}U	0

To achieve the necessary denaturing of uranium in the zeroth generation for this makeup, the breeder blanket material was mixed with depleted uranium (0.2 wt % ^{235}U) as might be available from tails at an enrichment plant. We note from the tables that at the end of five fuel recycles in the 93 wt % ^{235}U makeup case, ^{232}U has not quite reached its equilibrium concentration. A reasonable extrapolation of the data suggests an equilibrium concentration of about 0.064 kg/MTHM at discharge from the reactor. This corresponds to about 265 ppm ($^{232}U/U$ weight basis). In the case in which a thorium breeder supplies the makeup feed, the ^{232}U concentration is almost at equilibrium and has a concentration of ^{232}U equal to about 512 ppm ($^{232}U/U$ weight basis) at discharge from the fifth generation. In this case ^{232}U is burning out in the reactor and its changing concentration over the life of the reactor is "driven" by the initial dilution of breeder fuel ^{232}U with the depleted uranium added as a denaturant in the initial fuel loading. If it were assumed that pure ^{233}U were available from some source without the ^{232}U, LEOPARD calculations showed that the ^{232}U concentration increases in each cycle were about 12 to 17% higher than found in the enriched natural uranium case.

The tables do not show the effect of a significant ^{230}Th concentration in the fuel. Assessment of ^{230}Th's contribution to ^{232}U production requires some

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*The version of LEOPARD available from ACC or EPRI has a correlation developed by Westinghouse. Because it was not possible to verify the basis of the correlation, a correlation developed by Combustion Engineering[10] was used.

Table 1

INVENTORIES FOR ThO_2 (DENATURED RECYCLED U) RODS

(Assemblies with 93 wt % ^{235}U Makeup)

	Generation					
	0*	1	2	3	4	5
			Initial Inventories (kg/MTIHM)**			
^{232}U		2.9×10^{-2}	4.5×10^{-2}	5.6×10^{-2}	6.1×10^{-2}	6.4×10^{-2}
^{233}U		10.95	14.16	14.92	15.37	15.42
^{234}U	0.35	1.27	2.75	3.97	4.88	5.52
^{235}U	44.00	30.75	27.84	27.68	28.53	29.58
^{236}U		5.36	8.46	10.73	12.85	14.73
^{238}U	175.65	184.60	189.47	190.34	193.69	195.42
^{232}Th	780.00	767.04	757.27	752.30	744.62	739.27
TOTAL	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
$^{232}U/U$		124 ppm	185 ppm	226 ppm	239 ppm	245 ppm
			Discharge Inventories (kg/MTIHM)**			
^{232}U	2.7×10^{-2}	4.3×10^{-2}	5.3×10^{-2}	5.8×10^{-2}	6.1×10^{-2}	6.2×10^{-2}
^{233}U	10.04	13.25	14.24	14.52	14.70	14.77
^{234}U	0.98	2.36	3.56	4.38	5.03	5.48
^{235}U	15.87	11.81	10.71	11.75	12.59	13.39
^{236}U	4.92	7.92	10.24	12.14	14.04	15.77
^{238}U	168.52	176.44	180.66	182.06	185.36	187.09
^{232}Th	762.31	749.86	741.42	735.85	728.56	723.51
TOTAL	962.67	961.68	960.88	960.76	960.34	960.07
$^{232}U/U$	135 ppm	203 ppm	242 ppm	258 ppm	263 ppm	262 ppm

*No recycled fuel.
**Metric tons initial heavy metal.

NOTES:
1. Figures at discharge show ^{233}Pa combined with ^{233}U.
2. Discharge burnup is 33,000 ±500 MWd/MTHM.
3. Reactor type is CE System 80™.
4. Reprocessing losses are assumed equal to zero.
5. ^{230}Th concentration assumed equal to zero.

Table 2

INVENTORIES FOR ThO_2 (DENATURED RECYCLED U) RODS

(Assemblies with Thorium Breeder ^{233}U Makeup)

	Generation				
	1	2	3	4	5
			Initial Inventories (kg/MTIHM)*		
^{232}U	0.13	0.16	0.17	0.17	0.18
^{233}U	31.22	31.22	31.36	31.50	31.74
^{234}U	2.24	5.22	7.23	8.46	9.69
^{235}U	0.61	1.28	2.14	2.82	3.46
^{236}U	0.01	0.20	0.53	0.94	1.47
^{238}U	229.19	226.77	226.38	228.71	229.44
^{232}Th	736.60	735.21	732.20	729.01	723.98
TOTAL	1000.00	1000.00	1000.00	1000.00	1000.00
$^{232}U/U$	494 ppm	604 ppm	635 ppm	627 ppm	652 ppm
			Discharge Inventories (kg/MTIHM)*		
^{232}U	0.10	0.11	0.12	0.12	0.13
^{233}U	18.47	18.72	19.27	19.39	19.49
^{234}U	4.22	6.11	7.44	8.25	9.15
^{235}U	1.18	2.00	2.69	3.17	3.67
^{236}U	0.19	0.50	0.91	1.36	1.89
^{238}U	219.30	217.01	216.71	218.15	219.79
^{232}Th	718.86	717.80	715.18	712.01	707.61
TOTAL	962.32	962.25	962.32	962.45	961.73
$^{232}U/U$	411 ppm	450 ppm	486 ppm	479 ppm	512 ppm

*Metric tons initial heavy metal.

NOTES:
1. Figures at discharge show ^{233}Pa combined with ^{233}U.
2. Discharge burnup is 33,000 ±500 MWd/MTHM.
3. Reactor type is CE System 80™.
4. Reprocessing losses are assumed equal to zero.
5. ^{230}Th concentration assumed equal to zero.

knowledge of the isotopics of the uranium and thorium which is mined for use in reactor fuel. If thorium were isolated from uranium in nature, we would expect negligible amounts of ^{230}Th in ^{232}Th since the principal source of ^{230}Th in nature is the alpha decay of ^{234}U (as shown by route B in Fig. 1). The equilibrium concentration of ^{230}Th in uranium is about 17 ppm.* Since Th:U ratios in monazite sands, a major thorium resource, are typically about 20:1,[6] we could expect the $(\frac{^{230}Th}{Th})$ ratio to be less than 1 ppm. LEOPARD results indicate that in PWRs about 18% of the original ^{230}Th in the fuel becomes ^{232}U at fuel burnups of about 33,000 MWd/MTHM. Because the Th:U ratio in the System 80^{TM} reactor is about 3.65:1, the ^{230}Th contribution to ^{232}U would be only about 3-4 ppm $(\frac{^{232}U}{U})$.

Monazite sands are not our only thorium resource, however. If we assume requirements for thorium are initially met by uranium mine tailings, the Th:U ratio might be about 1:5 (as at Blind River, Canada).[6] With this ratio, the expected ^{230}Th concentration is 85 ppm $(\frac{^{230}Th}{Th})$. Again recognizing that 18% of this ^{230}Th will be transmuted to ^{232}U in the reactor, we can expect a near maximum impact of ^{230}Th to be a 56 ppm increase in ^{232}U concentration. Thus, the importance of ^{230}Th concentration upon the ^{232}U production is based on knowing the Th:U ratio in the mined thorium used in the reactor. Table 3 summarizes the percentage contributions from each production route at 0 and 85 ppm $(\frac{^{230}Th}{Th})$ concentrations.

These results assume that the Th:U ratio in a given deposit has remained constant for thousands of years so that ^{230}Th reached its secular equilibrium concentration. Some evidence suggests that thorium deposits are fairly transient by geological standards.[12] Under transient conditions, it is necessary to make actual isotopic measurements of the thorium to accurately estimate ^{230}Th concentrations in a specific deposit.

V. EVALUATION OF CALCULATED RESULTS

The extreme paucity of good experimental data and reservations about the accuracy of the basic nuclear data make the task of validating the computational results difficult. One experimental study[13] performed a postirradiation examination (PIE) of ThO_2-UO_2 fuel pins from Indian Point Core A [265 MW(e)]. This

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*Assuming ^{230}Th is in secular equilibrium with ^{234}U:

$$\frac{^{230}Th}{U} = \left(\frac{\text{half life of } ^{230}Th}{\text{half life of } ^{234}U}\right) \text{ (a/f } ^{234}U \text{ in natural uranium)}$$

$$= \left(\frac{7.7 \times 10^{4} \text{ yr}}{2.44 \times 10^{5} \text{ yr}}\right) (5.5 \times 10^{-5}) = 17 \text{ ppm}$$

Table 3

PRODUCTION ROUTE CONTRIBUTIONS TO
^{232}U CONCENTRATION IN AN LWR(Th)

	A	B	C	D
^{235}U Initial Fissile No ^{230}Th	98-99%	0%	1-2%	0.001%
^{235}U Initial Fissile 85 ppm $^{230}Th/Th$	70-71%	28%	1-2%	<0.001%
^{233}U Initial Fissile No ^{230}Th	95-96%	0%	4-5%	<0.0001%
^{233}U Initial Fissile 85 ppm $^{230}Th/Th$	71-72%	25%	3-4%	<0.0001%

NOTES: 1. Values derived from mass balance edit of a modified version of the LEOPARD code.
2. Reactor design modeled: CE System 80™.
3. Discharge burnup: 33,000 MWd/MTIHM (metric tons initial heavy metal).

core was not denatured, but used 93 wt % ^{235}U uranium dioxide in thorium dioxide fuel. This difference should not significantly invalidate comparisons with denatured fuels if ^{232}U concentrations are compared as fractions of ^{232}Th loadings. Unfortunately, the particular fuel rods selected for the PIE were not representative of most fuel rods in the core. For ease in removal, only irradiated rods at the fuel assembly outer edge and near large water slots during irradiation were selected. As a consequence, the neutron spectrum in the selected fuel pins should be significantly more "thermal" than in most of the reactor core. The effect of this difference on ^{232}U production is difficult to assess without performing a two-dimensional reactor calculation (which was not done here). The reaction rate from ^{232}Th to ^{231}Th would be reduced, but the ^{231}Pa to ^{232}Pa rate might well increase. Over all, one might expect ^{232}U concentrations a little less than the core average at comparable fuel burnup. Figure 2 shows ^{232}U buildup calculated for the CE System 80^{TM} reactor (having an initial fuel loading of 20% ^{235}U in uranium and diluted with thorium to yield a reactivity lifetime of 33,000 MWd/MT) as a function of burnup. For comparison, experimental concentrations are presented at the burnups determined in the PIE for Indian Point fuel. The agreement is surprising and possibly somewhat coincidental. The experimental samples were taken from fuel pellets in different positions in 13 fuel rods. Uranium isotopics were measured by mass spectrometry with the exception of ^{232}U which was found as a function of ^{233}U concentration using alpha spectrometry.

The results presented here agree well with *calculations* performed by other organizations. For a case comparable to that considered in Table 1, Combustion Engineering[14] calculates values at discharge from the zeroth and fifth generations of 146 ppm and 251 ppm ($^{232}U/U$ weight basis), whereas our results show 135 ppm and 262 ppm, respectively. Considering the different calculational tools (CE uses their proprietary CEPAK code) and cross section sets, the agreement is remarkable. Results calculated for standard PWRs compare favorably with Westinghouse results for the same PWR design. Here, calculations of the ^{232}U contributed by ^{232}Th impurities in the standard fuel agree with Westinghouse values[15] to within about 10%.

VI. CONCLUSIONS

1. LEOPARD calculations of ^{232}U production in PWR(Th)s using denatured uranium show:

   a. Concentrations of ^{232}U in total uranium vary from 135 ppm out of the zeroth generation to 260 ppm out of the fifth generation when highly enriched uranium is used as the makeup fuel.

   b. Concentrations of ^{232}U in total uranium vary from 411 ppm out of the first generation to 512 ppm out of the fifth generation when thorium breeder bred uranium is used as makeup fuel. Initial ^{232}U loadings were somewhat higher and varied from 494 ppm to 652 ppm.

2. Limited experimental work and the calculational results of other organizations appear to corroborate the results presented here. However, the quality of the nuclear data suggests caution in the use of these results.

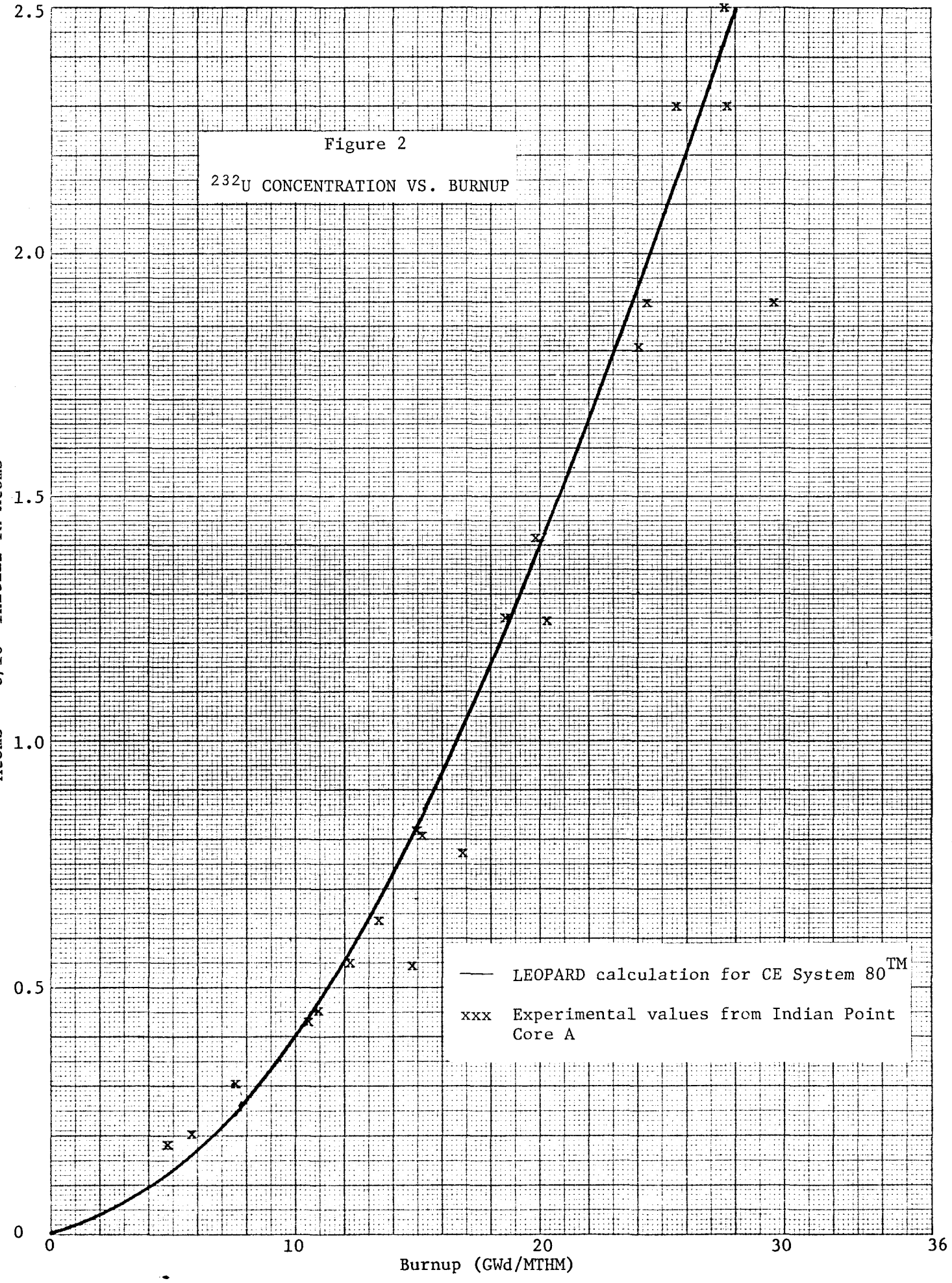
Figure 2
^{232}U CONCENTRATION VS. BURNUP
Atoms $^{232}U/10^5$ Initial Th Atoms
2.5
2.0
1.5
1.0
0.5
0
0
10
20
30
36
Burnup (GWd/MTHM)
—— LEOPARD calculation for CE System 80™
xxx Experimental values from Indian Point Core A

3. The ^{232}U concentrations reported here should only be applied directly to denatured uranium fueled PWR(Th)s. The high ^{238}U concentrations necessary to achieve denaturing make $^{232}U/U$ ratios in these reactors low when compared to other thorium fueled reactor types (high enriched HTGR and MSBR).

4. Buildup of ^{232}U in other thermal reactors using initial fuel mixtures of ^{232}Th, ^{238}U and ^{235}U probably compares reasonably well with the results shown in Fig. 2, but only when compared on the basis of $(\frac{^{232}U \text{ atoms}}{^{232}Th \text{ atoms}})$.

VII. ACKNOWLEDGMENT

The author wishes to acknowledge the substantial help of J. C. Cleveland of the Engineering Technology Division in developing modifications necessary to model thorium/denatured uranium fueled reactors and in providing several test cases for evaluating the quality of the modified code's results.

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