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SUBJECT: Desirability of Chemical Decladding  
 from the Waste Disposal Viewpoint

TO: H. E. Goeller

FROM: A. R. Irvine

#### ABSTRACT

Chemical decladding of stainless steel and Zircaloy jacketed fuel is discussed with respect to cladding activation, capacity for storage of decladding waste in existing concrete tanks at ORNL, and waste disposal cost as compared with a total dissolution process.

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## INTRODUCTION AND SUMMARY

Recent observations of the gamma activity found in de-clad solutions has caused concern over the validity of the assumption that these solutions can be treated as medium-activity wastes and stored, or otherwise disposed of, in a less expensive manner than can first cycle solvent extraction raffinate. It is the purpose of this paper to present what is known about cladding activation, to review the Laboratory's capability to store de-clad solutions, and to establish under what conditions a de-clad flowsheet results in lower waste cost than does a total dissolution flowsheet.

The neutron absorption of both stainless steel and zirconium results in appreciable activation. However, with the exception of Co-60, the radioisotopes in the cladding have half-lives shorter than one year and consequently decay rapidly as compared with gross fission product activity and will generate relatively small quantities of heat at 180 days after reactor discharge. Cobalt-60 will normally be present in very low concentration, except possibly in the cladding of fuels from reactors which do not use water as coolant. The heat generation expected in the cladding of a typical fuel having a cobalt content of 0.03 wt % is about 0.5% of the heat generation of the gross fission products at 180 days decay. Further, Co-60 will decay considerably faster than will the long-lived fission product heat contributors, Cs-137 and Sr-90. Also, the activated cladding represents approximately  $10^5$  times less biological hazard than does the Sr-90 contained in the core material. It therefore appears that the relative biological hazard of de-clad solution as opposed to solvent extraction first cycle aqueous raffinate will be controlled entirely by the fission product contaminants.

The existing concrete waste storage tanks appear to be adequate without modification to dissipate heat generated by activated cladding and up to 1% of the fission product activity from fuels presently assigned to ORNL, provided two tanks can be used for this purpose. Their adequacy as to containment is a matter for a management committee to decide; however, de-cladding wastes are expected to be less hazardous than wastes previously stored in these tanks.

The mode of waste storage, treatment, or disposal actually determines whether chemical de-cladding is economically desirable. Some of the more liberal thoughts on waste disposal could possibly reduce the cost of this operation to a very low value; hence, any savings in waste cost achieved by flowsheet adjustment would be negligible. The prudent course, however, is to assume current technology with allowances made for foreseeable developments. Under these ground rules, the economic desirability of Sulfex de-cladding of  $UO_2$  fuels as opposed to Darex total dissolution depends on (1) the ability to store Darex-Purex waste in the neutralized condition and (2) the feasibility of cheaply solidifying or otherwise disposing of Sulfex de-clad solution. If Sulfex de-clad solution cannot be volume-reduced and solidified cheaply and if Darex-Purex wastes can be stored in the neutralized condition, the latter process will yield the lower waste storage cost. If Darex-Purex wastes cannot be stored in an alkaline condition or if Sulfex wastes can be disposed of more economically than by storage in mild steel tanks, Sulfex has the advantage from the waste viewpoint.

### ACTIVATION OF CLADDING

Calculations made to determine the degree of neutron activation of stainless steel reveal a heavy dependence on cobalt content. Water-cooled thermal reactors do not demand the use of low cobalt stainless steel for nuclear reasons; however, corrosion products from stainless steel are carried throughout the coolant circuit and deposited more or less uniformly. Therefore, a high cobalt content will result in high background activity in otherwise nonradioactive heat exchangers, etc. For this reason, one can expect a low cobalt content in the cladding of water-cooled reactor fuels. Normal stainless steel can be expected to contain up to 0.7% cobalt by weight. The APPR used a steel having 0.005% cobalt, which was obtained by careful selection of materials. Babcock and Wilcox is currently specifying cobalt contents ranging from 0.04 to 0.01%, maximum, for reactors which they are designing. The EGCR, on the other hand, has a 0.2% maximum cobalt specification.

Ullmann has calculated the activity to be expected in the cladding of CETR fuel, assuming a cobalt content of 0.03 wt %. The results of his calculations are shown in Table 1 and Figs. 1 and 2. Figure 3 is a plot of the heat generation of 1% of the fission product activity and of the cladding activity in CETR fuel as a function of decay time. It can be seen that with the expected maximum cobalt content (0.03%) the heat generation of the activated cladding is less than one-half per cent of the total fission product heat generation at 200-day decay. The weight ratio of clad-to-core is ~ 0.375:1 and total irradiation is 25,000 Mwd/T.

Neutron activation of Zircaloy cladding will yield approximately 5% as much  $Zr^{95}$  as will fission in natural uranium core material. Because  $Zr^{95}$  has only a 65-day half-life, it is not seen as especially significant. The assumed clad-to-core weight ratio was 1:5.

### FEASIBILITY OF STORAGE OF DECLAD WASTES IN EXISTING CONCRETE TANKS

The utility of the six existing 170,000-gal concrete waste tanks is presently being considered by Management and any comments made here are preliminary and subject to reversal.

The concrete storage tanks are not equipped with a means for secondary containment and dissipation of radioactive-decay heat must take place by means of conduction to the environment. Jury has calculated that approximately 18,000 Btu/hr can be dissipated from each waste tank if all tanks are full and are at the boiling point. It is assumed that wastes can be stored in these tanks if the wastes have a maximum heat generation at time of entry of the order of 0.1 Btu/gal-hr. It is highly unlikely that all the tanks will be releasing large quantities of heat simultaneously.

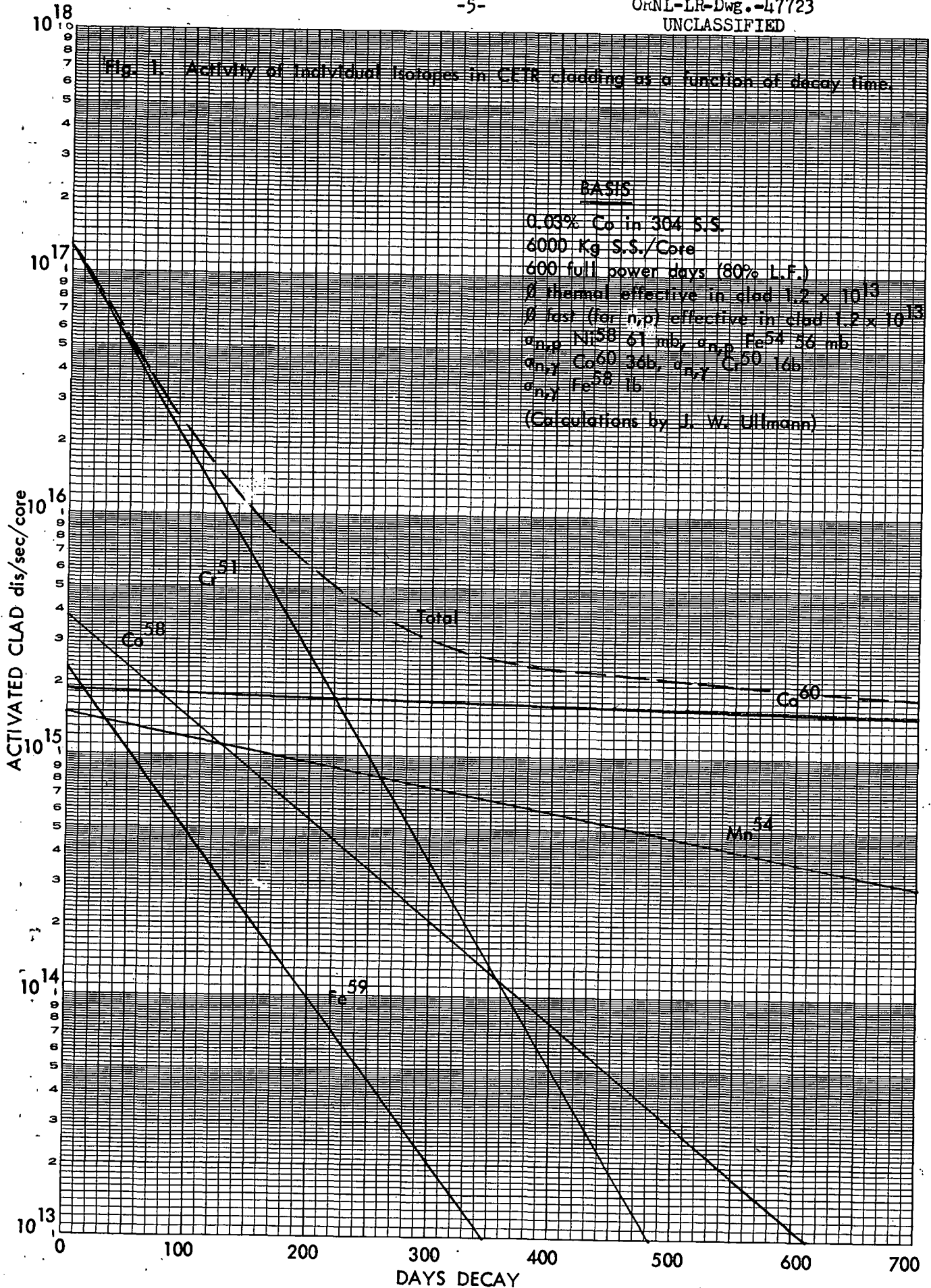
The heat generated by activated cladding constituents of various reactor fuels scheduled for processing at ORNL has been estimated and are tabulated in Table 2. The heat generation from this source is seen to be relatively small. If there are no other significant sources of heat, one tank could easily reject all the heat generated in the declad solutions. If all the reactors were to be discharged and processed simultaneously, the total decay heat from activated cladding would be ~ 33,000 Btu/hr.

Table 1. Activation of CETR Cladding

	<u>Days Decay</u>					
	<u>~ 0</u>	<u>60</u>	<u>120</u>	<u>180</u>	<u>300</u>	<u>600</u>
<u>Activated Clad, d/s/core x 10<sup>15</sup></u>						
Cr-51	125	40	12	3.8	0.37	-
Co-58	3.75	2.1	1.15	0.65	0.2	0.01
Co-60	1.89	1.82	1.8	1.76	1.7	1.5
Fe-59	2.3	0.9	0.35	0.14	0.02	-
Mn-54	1.5	1.2	1.15	1.0	0.75	0.38
<u>Activated Clad, Btu/hr/core</u>						
Cr-51	51,200	16,400	4,280	1,570	170	-
Co-58	1,970	1,100	600	340	110	-
Co-60	2,690	2,600	2,560	2,510	2,420	2,140
Fe-59	1,720	670	260	100	16	-
Mn-54	<u>1,110</u>	<u>890</u>	<u>850</u>	<u>740</u>	<u>550</u>	<u>280</u>
	58,690	21,660	8,850	5,260	3,266	2,320

(Calculations by J. W. Ullmann)

Fig. 1. Activity of Individual Isotopes in CTR cladding as a function of decay time.



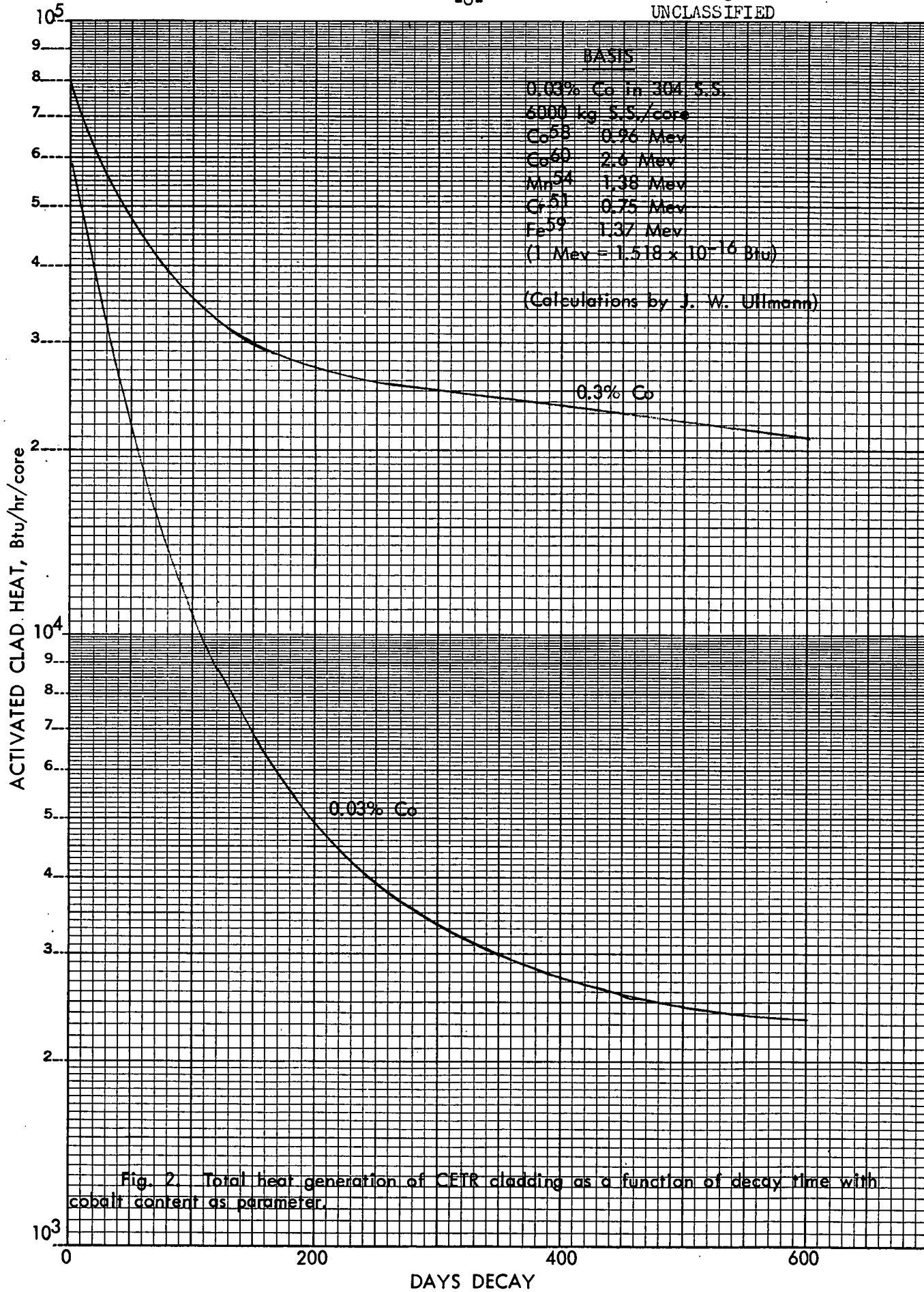


Fig. 2 Total heat generation of CFR cladding as a function of decay time with cobalt content as parameter.



200 20%

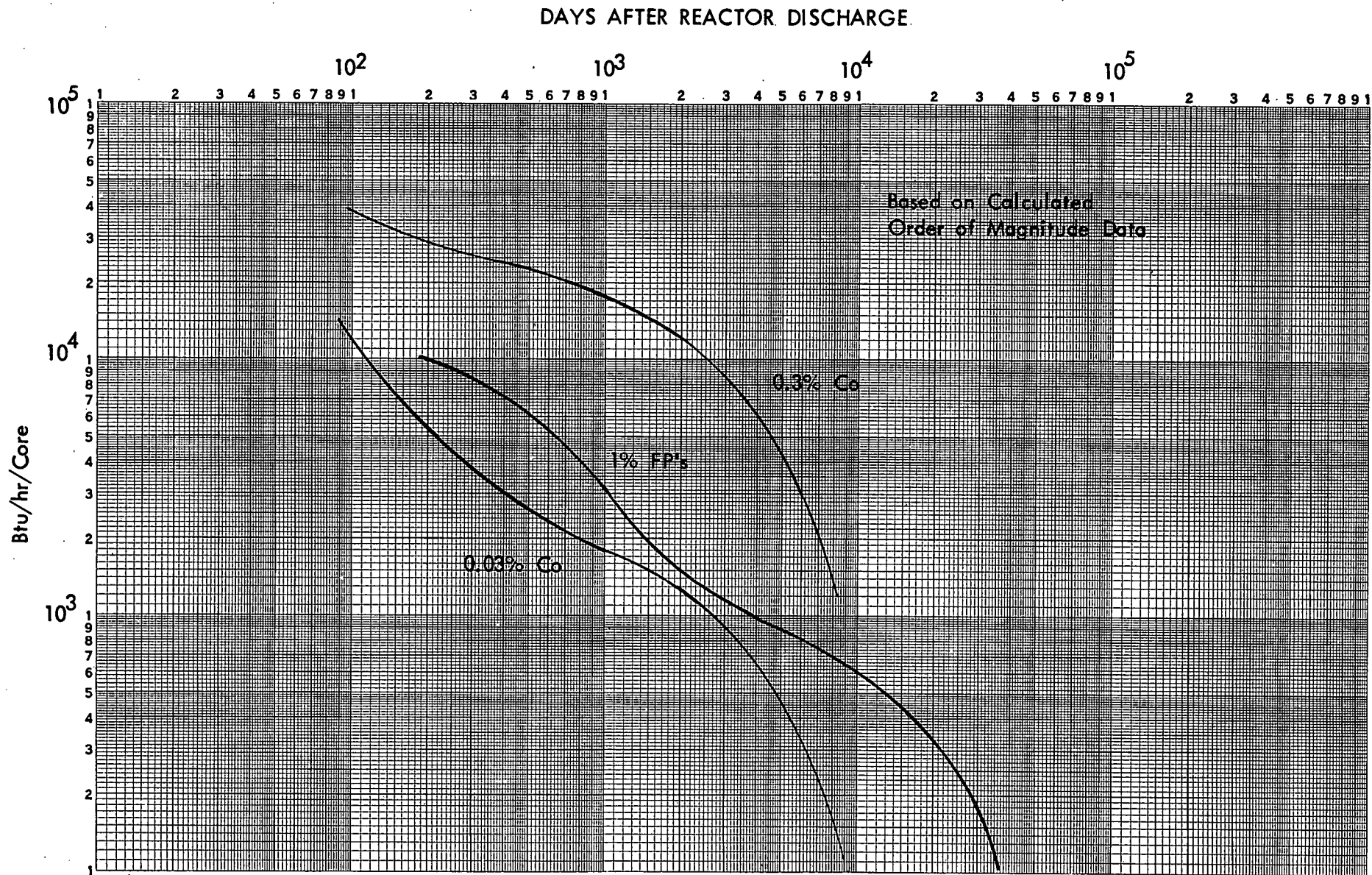


Fig. 3. Heat generation of activated clad and 1% fission products in CETR core as a function of decay time.

Table 2. Estimated Heat Generation of Declad Solutions

<u>Source of Fuel</u>	<u>Processing Date</u>	<u>Wt Cladding, 10<sup>3</sup> kg</u>	<u>Cobalt Content, %</u>	<u>Heat Generation<sup>a</sup></u>	
				<u>Cladding</u>	<u>1% FP's</u>
Elk River - Core 1	1963	1.15	0.03 <sup>c</sup>	0.5 x 10 <sup>3</sup>	0.9 x 10 <sup>3</sup>
NMSR - Core 1	1963	3.1	0.02 - 0.05	2.0	1.6
CETR - Core 1	1964	6	0.03	5	10
FWC-EC	1964	1.8	0.03 <sup>c</sup>	1.5	2.3
CPPD (Hallam)	1964	2.0	0.2 <sup>c</sup>	2.3	5.4
Elk River - Core 2	1965	1.15	0.03 <sup>c</sup>	0.5	0.9
EGCR	1965	2.0	0.2	7	1.4
PRDC Blanket	1965	2.3	0.2 <sup>c</sup>	8 <sup>b</sup>	0.5
CETR	1966	6	0.03	5	10
NMSR - Core 2	1966	3.1	0.005 - 0.01	1.5	1.6

<sup>a</sup> At 200 day decay.

<sup>b</sup> This is ~ 60% 71d Co-58 and 40% 300d Mn-54; presume that there should be relatively little direct activation of Co because of neutron energy spectrum.

<sup>c</sup> Based purely on guess.

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Losses of fission products to de-clad solution still appear to be a direct function of fissile loss, although it might be argued that experimental results as yet do not confirm or deny this statement. Table 2 also shows the heat generation of 1% of the gross fission products. It is hoped that actual plant losses will be  $\leq 0.3\%$ , in which case no difficulty would be expected from heat generation if the de-clad solution could be stored in two of the concrete tanks. Even with a 1% loss, storage in two tanks probably would be permissible.

With regard to the biological hazards of the various radioactive isotopes in the wastes, the total activity in curies and the relative hazard in number of MPC's for water were calculated for a CETR core cooled 180 and 600 days. These data are given in Table 3. Since the amount of plutonium in  $\text{ThO}_2\text{-UO}_2$  fuel is very small, the amount present from a natural or low-enriched uranium fuel irradiated to 5000 g of Pu per tonne is also given in Table 3 for comparison. These data indicate that the Sr-90 activity in the waste is initially the most hazardous isotope and that after very long cooling Pu-239 is the major hazard. Initially the Sr-90 is more hazardous than Pu-239 by a factor of  $10^3$ . The hazard involved in the radionuclides of Mn, Fe, Cr, and Co from the cladding was shown to be  $\geq 10^6$  less significant than the Sr-90 activity and  $\geq 10^3$  than the Pu-239 activity for any practical cooling time. Sr-90 is, for many years, the controlling contaminant in the clad solution from the standpoint of biological hazard even if fission product and fissile loss are as low as 0.1%.

The Sr-90 content of de-clad solution will probably be orders of magnitude greater than that of second cycle solvent extraction raffinates, yet considerably less than that of first cycle raffinate from processing of low burnup fuels which have been processed at ORNL in the past. Therefore, storage of de-cladding solution should certainly be less hazardous than storage of first cycle raffinates that have previously been routed to these tanks.

#### COMPARISON OF WASTE COSTS FOR CHEMICAL DECLADDING AND FOR TOTAL DISSOLUTION PROCESSES

There are many unknowns and intangibles involved in the determination of the relative cost of storage of waste produced when processing stainless steel--clad  $\text{UO}_2$  by a chemical de-cladding technique as opposed to a total dissolution process. One of the intangibles is the number of precautionary measures required as a function of waste composition. If the fission product content of one solution is a factor of 1000 lower than that of another solution, it appears that a considerably different treatment should be permissible. Solidification and storage in dry caves becomes more attractive as fission product content and heat generation decrease. Shipment of solid wastes to favorable geological storage areas may be acceptable, whereas it is fairly generally agreed at this time that shipment of highly active solutions is too hazardous to attempt. But there are no rules, no precedent, and little cost data to support or refute arguments for segregating mildly contaminated cladding solution from the bulk of the activity.

Arnold, Blomeke, and Stockdale estimated that the cost of permanent tank storage for neutralized de-cladding type waste will be approximately 1/3 to 1/4 as much per gallon as storage for neutralized waste from the Thorex process, which uses an aluminum nitrate salted scrub. Because the ANN-containing Thorex

Table 3. Activities in and Relative Hazard of Various Isotopes in CETR Fuel Clad and Core

Isotope	Curies/Core		MPC, µc/ml Water	Relative Hazard	
	180 Day Cooled	600 Day Cooled		180 Day Cooled	600 Day Cooled
Cr-51	$1 \times 10^5$	2	0.5	-	-
Co-58	$1.8 \times 10^4$	$3 \times 10^2$	$2 \times 10^{-2}$ a	$9 \times 10^5$	$1.5 \times 10^4$
Co-60	$4.8 \times 10^4$	$4 \times 10^4$	$2 \times 10^{-2}$	$2.4 \times 10^6$	$2 \times 10^6$
Fe-59	$3.8 \times 10^3$	6	$1 \times 10^{-4}$	$3.8 \times 10^7$	$6 \times 10^4$
Mn-54	$2.7 \times 10^4$	$1 \times 10^4$	$1.5 \times 10^{-3}$ b	$1.8 \times 10^7$	$6 \times 10^6$
Sr-90, Y-90	$3.2 \times 10^6$	$3 \times 10^6$	$8 \times 10^{-7}$	$3.75 \times 10^{12}$	$3.75 \times 10^{12}$
Cs-137	$1.1 \times 10^6$	$1.1 \times 10^6$	$1.5 \times 10^{-3}$	$7 \times 10^8$	$7 \times 10^8$
U-233	$1.4 \times 10^3$	$1.4 \times 10^3$	$1.5 \times 10^{-4}$	$9.5 \times 10^6$	$9.5 \times 10^6$
Pu-239 <sup>c</sup>	$5 \times 10^3$	$5 \times 10^3$	$1.5 \times 10^{-6}$	$3.3 \times 10^9$	$3.3 \times 10^9$

<sup>a</sup> No value given in NBS-52; used same as for Co-60, which is probably too conservative for this isotope.

<sup>b</sup> Used 100 times value for Mn-56 because of longer half-life.

<sup>c</sup> Plutonium-239 is present in very small quantities in CETR fuel. Figures shown are for 5000 g/T as might be found in a slightly enriched uranium fuel.

Basis: 16 tons Th irradiated to 25,000 Mwd/T, 6 tons stainless steel cladding.

Note: All figures are approximate.

process waste cannot be reduced to very small volumes, it was assumed that the storage cost for this material would be about the same as for Darex-Purex waste. Costs were also given for stainless steel storage tanks for Thorex waste. It may not be practical to store highly active Darex-Purex wastes in the neutralized condition because of heat dissipation problems resulting from large amounts of precipitated solids. Table 4 gives information regarding costs of permanent tank storage of wastes resulting from one kilogram of uranium clad in 0.333 kg of stainless steel. Cost of storage of waste from a total dissolution process are shown both for acidic and neutralized waste storage. Much higher concentrations of stainless steel were allowed for the nitrate system than for the sulfate system. While the nitrate system does allow higher stainless steel concentrations, the ratio used may be too great.

One can only conjecture concerning the cost of converting deacid solutions to solids. Chemical Development Section has been engaged in experimental work along this line and indications are that the volume might be increased by as much as a factor of two. If solidification costs \$100 per cubic yard and there is a volume increase of two, then the per-gallon cost will be ~ \$1.

Table 4. A Cost Comparison for Permanent Storage of Sulfex-Purex Wastes vs. Darex-Purex

	<u>Sulfex-Purex</u>	<u>Darex-Purex</u>
<u>Declad Solution</u>		
Stainless steel content, g/liter as sulfate	25	
Condition	Neutralized	
Volume, gal	3.5	
Cost storage, \$/gal	3	
Cost storage, \$/kg U	10.5	
<u>Core Solution</u>		
Stainless steel content, g/liter as nitrate	nil	100
Condition	Neutralized	Neutralized
Volume, gal	0.06	0.88
Cost storage, \$/gal	14	10
Cost storage, \$/kg U	0.84	8.80
Condition		Acid
Cost storage, \$/gal		25
Cost storage, \$/kg U		22
TOTAL COST WASTE STORAGE, \$/kg U	11.3	8.8 Neutralized 25 Acid

Note: Unit costs for storage based on unpublished report by Arnold, Blomeke, and Stockdale.

Basis: 1 kg U as UO<sub>2</sub> clad with 333 g stainless steel.

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