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SOLUBLE POISONS FOR CRITICALITY CONTROL

By

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ABSTRACT

Studies indicated that the use of soluble neutron poisons as a primary control offers economic and other advantages in that it permits the factors of vessel size and shape and solution concentrations to be dictated by considerations other than those of criticality. It is believed that soluble poison criticality control can be made as reliable as other methods of conditional control if the application is preceded by adequate development work and is monitored by multiple, independent safeguards.

The studies included multigroup machine calculations of the required content of poisons in solutions of fissile and fertile material, a compilation of data on the detection, stability, decontamination, and costs of soluble poisons, and an assessment of the possible effects of a nuclear excursion.

(A paper for oral presentation at the 147th National ACS Meeting, Atlantic City, New Jersey, September 9-14, 1962.)

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SOLUBLE POISONS FOR CRITICALITY CONTROL

Homogeneous solutions of fissile material may be rendered incapable of a sustained neutron chain reaction, criticality, through the inclusion of sufficient quantities of elements which absorb more neutrons than they produce. Some elements, such as B, Cd, and Gd, have very high efficiency for net neutron absorption and may be included in relatively small concentrations to "poison," i.e., to preclude criticality in, solutions of fissile material.

For several years, at ORNL, we have studied the applicability of soluble neutron poisons for criticality control in fuel processing plants. The results of these studies, which I will summarize today, are described in an ORNL report, ORNL 3309, which can be purchased from the Office of Technical Services. The studies indicated that the use of soluble poisons as a primary criticality control offers economic and other advantages in that it permits the factors of vessel size and shape and solution concentrations to be dictated by considerations other than those of criticality. It is believed that soluble poison criticality control can be made as reliable as other methods of conditional control if the application is preceded by adequate development work and is monitored by multiple, independent safeguards.

In the evolution of nuclear fuel processing it has been recognized that the use of nuclearly geometrically safe equipment, i.e., vessels of area to volume ratio such that neutron leakage prevents a sustained nuclear reaction, imposes a large penalty in cost and capacity to chemical processing plants, while experience has shown that the increased

expenditure per unit of capacity may not be justified in light of the relatively minimal effects of an accidental nuclear excursion in a remote, shielded area.

This cognition led to the use of non-geometrically safe equipment accompanied by administrative or procedural control which stated that at least two independent human or mechanical operating errors must be made before a nuclear accident can occur. This type of control allowed a finite probability of a nuclear accident but provided that this probability have a suitably low value. It permitted the use of batch size or concentration control provided that two or more independent methods of ensuring the batch size or concentration were in effect.

This type of control has not, in general, been extended to the use of soluble poisons since it has been argued that one error, i.e., forgetting to add the poison, would result in a nuclear excursion. It is possible, however, that even in the use of soluble neutron poisons the probability of an accidental excursion may be made as low as required. This low probability can be achieved by providing that two or more unrelated errors must be made before poisons are left out of a solution or before a physical or chemical process for removing the poison from solution can occur.

The use of soluble poisons is particularly applicable in moderate- or large-scale standard chemical processing equipment that is difficult or impractical to modify for inclusion of fixed poisons and is severely limited by the requirements of concentration or batch control. It is ordinarily possible to include sufficient poison that an infinite volume of the solution could not sustain a nuclear reaction; thus, one is not

concerned with neutron interaction or the use of geometry-safe catch basins, which are typical of geometry-safe or fixed-poison-safe installations.

Ordinarily, soluble poison control would be used in head end vessels such as the fuel element dissolver, feed adjustment tanks, accountability tanks and solvent extraction feed tanks. It is ordinarily not desirable or practical to use soluble poison control in the solvent extraction columns or in the final product purification system. These systems usually are operated conveniently with geometry, concentration, or fixed poison control.

At ORNL, we have managerial indorsement for use of soluble poisons as a primary control in a remotely operated, shielded, and contained facility in which due precautions are to be taken to ensure the addition of poison and the stability of poison in solution. We had incorporated this type of control in our interim power reactor fuel processing plant which was cancelled in the construction stage since private industry desired to process the power reactor fuels.

The only occasion in which we have used soluble poisons as a primary control in practice has been in the shipment of Homogeneous Reactor fuel solution inside the Laboratory. We have used it as a secondary control on numerous occasions in washing and decontaminating plant vessels which potentially contain fissile material.

Questions (Fig. 1) that are asked when soluble poison control is contemplated are:

(1) What concentrations are required?

(2) What safeguard techniques are available?

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FACTORS IN SOLUBLE POISON CONTROL

(1) REQUIRED CONCENTRATIONS?
(2) SAFEGUARD TECHNIQUES?
(3) SOLUBILITY AND STABILITY LIMITS?
(4) SEPARATION FROM FISSILE MATERIAL?
(5) COSTS?
(6) EFFECTS OF NUCLEAR EXCURSION?

Fig. 1

(3) What are the limits of solubility and stability?

(4) Can the poisons be separated from the fissile materials?

(5) What about costs? and

(6) What are the effects of a nuclear excursion?

I will describe some of the answers that have resulted from our studies.

Required Concentration of Soluble Poisons. Because of the extreme scarcity of experimental data we made multigroup machine calculations to determine the required concentration of soluble poisons. The concentrations of B, Cd, Sm, and Gd required to cause an infinite system multiplication factor of 1 were calculated for natural water solutions of U^{235}, U^{233}, Pu^{239}, 5% enriched uranium, and 10% U^{235} - 90% Th. All the calculations were made by the IBM-7090 MODRIC neutron diffusion code, an ORNL code similar to GNU. Thirty-four group cross sections, recently prepared at ORNL, were used.

An example of the type of results which were obtained is shown in Fig. 2. This figure shows the concentration of boron required to cause $k_\infty = 1$ as a function of the type of fissile and fertile material and the concentration of the fissile material. It is seen that U^{233} and Pu^{239} are considerably more reactive and require more poison than U^{235}. Five per cent enriched uranium and 10% U^{235}-90% Th appear to be about equally reactive, especially at low concentrations (high values of H/X).

The effectiveness of the various poisons on a weight basis, per unit weight of U^{235}, is illustrated in Fig. 3. In the normal range of solution concentrations, $H/X > 50$ (< 500 g U^{235}/liter), Gd is most effective and it is followed by B, Sm, and Cd, in that order. The required concentrations

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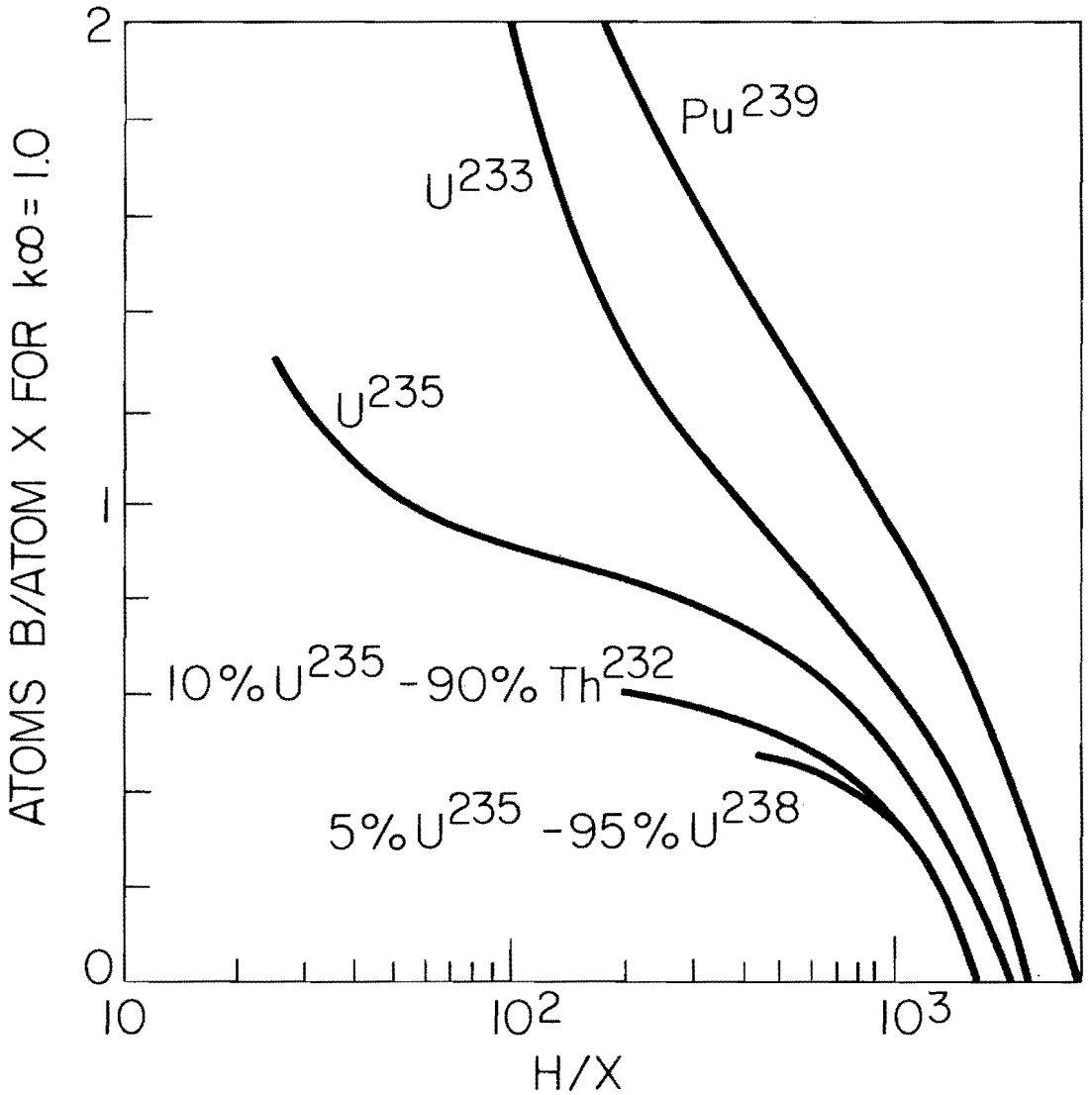
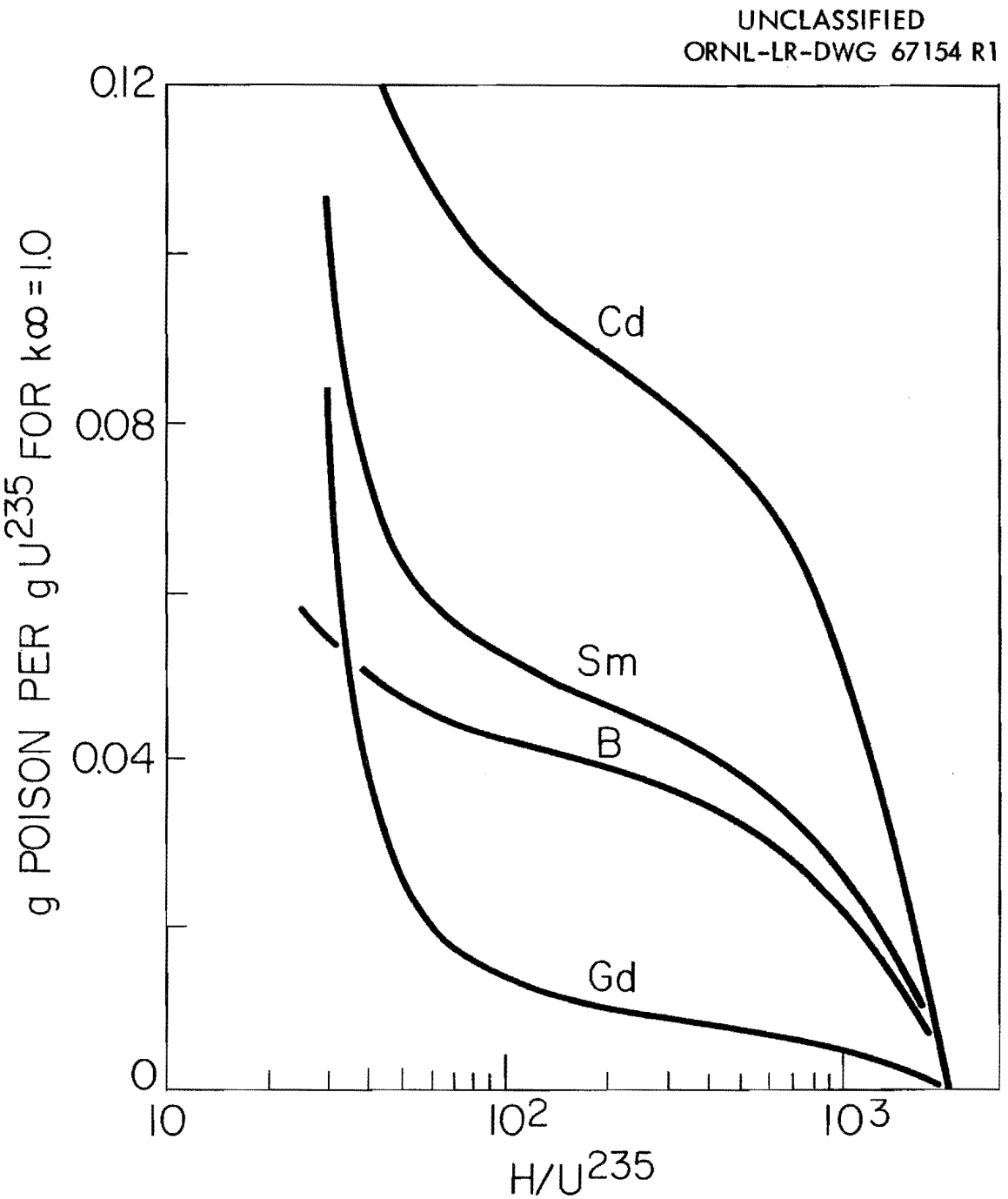


Fig. 2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0.12
0.08
0.04
0
g POISON PER g U235 FOR k∞ = 1.0
Cd
Sm
B
Gd
10
10^2
10^3
H/U235

Fig. 3

of Cd, Sm, and Gd increase very rapidly in comparison to boron as the concentration of the solution is increased and the neutron spectrum becomes harder. Cd, Sm, and Gd have relatively high cross sections for thermal neutrons but relatively low cross sections for neutrons of higher energy while the boron cross section decreases in a regular manner as the reciprocal of the neutron energy.

We attempted to verify the accuracy of these calculations by comparing them with the very few critical experiments that are applicable (Fig. 4). The calculations indicated limiting critical concentrations of U^{235}, U^{233}, and Pu^{239} in water of 12.3, 11.8, and 9.1 g/liter, respectively. These calculated numbers are all within 10% of the current best estimates for these values. Calculations of bare and reflected spheres of solutions of U^{235}, U^{233}, and Pu^{239} without poisons indicated critical fissile material concentrations which were within 10% of the experimentally determined values. The only directly applicable experimental data on the poison concentration required for $k_\infty = 1$ were obtained at the PCTR with boron and 3% enriched uranium. The calculations duplicated these experiments with a maximum error of 20%.

Although the calculations appear to be in reasonably good agreement with the few pieces of experimental data we recommend that in practice a safety factor of at least two should be applied to the poison concentration for a given fissile material concentration. It would be wise to perform a neutron multiplication measurement to verify the safety of proposed poison concentrations.

Calculations also were made to compare the effective multiplication factors of solutions in finite vessels with the infinite system

COMPARISONS OF CALCULATIONS WITH EXPERIMENTS

EXPERIMENT	MAXIMUM DEVIATION FROM EXPERIMENT
(1) LIMITING CRITICAL CONC. U^{235}, U^{233}, Pu^{239}	< 10%
(2) CRITICAL CONC. FINITE SPHERES U^{235}, U^{233}, Pu^{239}	< 10%
(3) PCTR EXPERIMENT B-3% ENRICHED URANIUM	< 20%

Fig. 4

multiplication factors. Effective multiplication factors in vessels larger than 5 ft dia were less than 5% lower than the infinite system multiplication factors, indicating that the finite vessel size of typical plant vessels will not ordinarily cause an appreciable safety factor.

Safeguard Techniques. Safeguard techniques (Fig. 5) for providing a high degree of assurance of the safe soluble poison concentration in solutions may be of the procedural and/or instrumentative types. The procedural type of safeguard would consist of independent batch additions of poisons perhaps backed up by an independent chemical analysis.

In the batch card system two persons independently add safe batches of poisons to a solution that subsequently is to contain fissile material. Each person then initials a batch card attached to the vessel or unlocks one of two valves which are in series. An additional safeguard is achieved by taking a sample of the solution for chemical analysis; once the analysis is verified, another initial would be placed on the batch card or another valve, or perhaps a pump, would be unlocked.

The best on-stream instrument for ensuring soluble poison content is probably the neutron absorptiometer. The instrument has been developed and used at most of the AEC installations and is now commercially available. It consists of an alpha-neutron source on one side of the stream and a neutron detector on the other side. The instrument can be made simple, reliable, and accurate and it furnishes a direct measurement of the macroscopic neutron absorption cross section of the solution. It can be used in a radiation background but would ordinarily be used to monitor nonradioactive solutions flowing into a process. A signal from the instrument could be used to shut off flow in the event of low poison concentration.

SAFEGUARD TECHNIQUES

(A) PROCEDURAL BATCH CARD - DUPLICATE, INDEPENDENT ADDITIONS TO SOLUTION MAKEUP TANK

INDEPENDENT OFF-STREAM ANALYSIS

(B) INSTRUMENTATIVE ON-STREAM ANALYSIS - NEUTRON ABSORPTIOMETER

Fig. 5

Solubility. We have made solubility studies of the neutron poisons in most of the fuel processes that are currently used. Other data are reported in the literature. It is always necessary to verify the solubility limits in specific processes but, in general, the limits are approximately those shown in Fig. 6.

Borates or perborates are usually soluble to the extent of 0.2-0.6 M in typical nitrate, sulfate, chloride, or fluoride solutions. These solubility limits are such that boron can ordinarily not be used to poison U^{235} solutions of concentration greater than 100-150 g/liter.

Cadmium is usually more soluble than boron, 0.2-1.5 M in typical nitrate, sulfate, or fluoride solutions, and it can be used to poison more concentrated fissile solutions.

Samarium and gadolinium ordinarily have sufficient solubility to poison essentially any fissile nitrate solution. Care must be exercised with these rare earth elements, however, since the oxides, hydroxides, and fluorides are generally insoluble.

Stability. In addition to solubility effects we have studied other mechanisms which might tend to cause loss of soluble poisons from fissile solutions. They are volatilization, deposition, and radiation effects (Fig. 7).

Loss of soluble poisons by volatilization in aqueous solutions does not appear to be a problem, even with boron, which is more susceptible to volatilization than Cd or the rare earths. We have evaporated nitrate solutions of B and U and Th until the temperature rose as high as 180°C without significant loss of boron to the distillate.

SOLUBILITY OF NEUTRON POISONS (25°C)

POISON	SOLUBILITY LIMITS
BO_3^{-3}, $B_4O_7^{-2}$	0.2 - 0.6 *M* IN TYPICAL NO_3^-, SO_4^{-2}, Cl^- OR F^- SOLUTIONS
Cd^{+2}	0.2 - 1.5 *M* IN TYPICAL NO_3^-, SO_4^{-2}, OR F^- SOLUTIONS
Sm^{+3}, Gd^{+3}	> 1 *M* IN TYPICAL NO_3^- SOLUTIONS - GENERALLY INSOLUBLE AS OXIDES, HYDROXIDES, AND FLUORIDES

Fig. 6

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MECHANISMS FOR LOSS OF POISONS

(1) VOLATILIZATION
(2) DEPOSITION
(3) RADIATION EFFECTS

Fig. 7

Solutions of poisons tend to deposit the poisons by an ion exchange mechanism on corrosion product films of metal vessels. This ordinarily constitutes a very insignificant source of loss of poison since the weight of corrosion products in process vessels is usually relatively low and poison will ordinarily not be deposited to an extent greater than 1% by weight in the corrosion product.

There appears to be no radiation effect in solutions which would preferentially separate the poisons from uranium.

Costs. Savings in capital plant and equipment investment can be realized through the use of soluble poison criticality control since the shape, size, spacing, and location of vessels can be dictated by process and operational requirements rather than by those of criticality. The operational costs in soluble poison control would be higher than in the use of strict geometry control but probably not significantly higher than in the use of mass or concentration conditional controls. All conditional control systems, which are believed to be the only systems feasible in future moderate-to large-scale plants, require accurate volume measurement and multiple determinations of solution composition.

The actual cost of the soluble poison, generally < 1$ per kilogram of fissionable material processed, assuming no recovery of poison, is ordinarily negligible compared with other operational costs, which are now of the order of $1000-3000 per kilogram of fissionable material for fuels of enrichment greater than a few per cent. In 100-lb lots the current cost of granulated technical grades of boric acid and borax is ~ $0.07 per lb; cadmium nitrate costs ~ $0.90 per lb; gadolinium oxide is ~ $44 per lb and samarium oxide is ~ $33 per lb. These costs and the

calculated concentrations of poisons for $k_\infty = 1$ were used to construct Fig. 8. This figure compares the relative costs of the poison per kilogram of U^{235} required to cause $k_\infty = 1$ as a function of solution concentration. The cost of B, Cd, Gd, and Sm per unit weight of U^{235} varies approximately as 1:10:25:100.

When criticality is not of primary consideration, it is usually desirable to operate fuel processing plants at fissile plus fertile material concentrations of the order of 300 g/liter. At these concentrations, solutions of fuels less than ~3% in enrichment ordinarily will be safe because of the low concentrations of fissile material. As enrichment increases above 3%, poison control permits significantly greater throughput for a given plant. Bernie Manowitz, in a recent article in Nucleonics, showed that there is an appreciable cost savings associated with the greater throughput in the use of soluble poisons. He estimated that, for a 1-ton/day central processing plant operating on fuel of enrichments greater than 3%, the separation cost with the use of concentration control will be 45-80% greater than for the same plant using predominantly soluble poison control.

Effects of a Nuclear Excursion. An ORNL study, which was described this morning by Eldon Arnold, has shown that the effects of a water-moderated nuclear excursion, as well as possible chemical explosions, in a facility which meets the ORNL containment criteria would result in tolerable personnel exposures and downwind ground contamination. In view of the tolerable effects of credible nuclear excursions in a "contained" facility, it appears that such accidents should not be avoided at all costs but should be minimized through the use of conditioned

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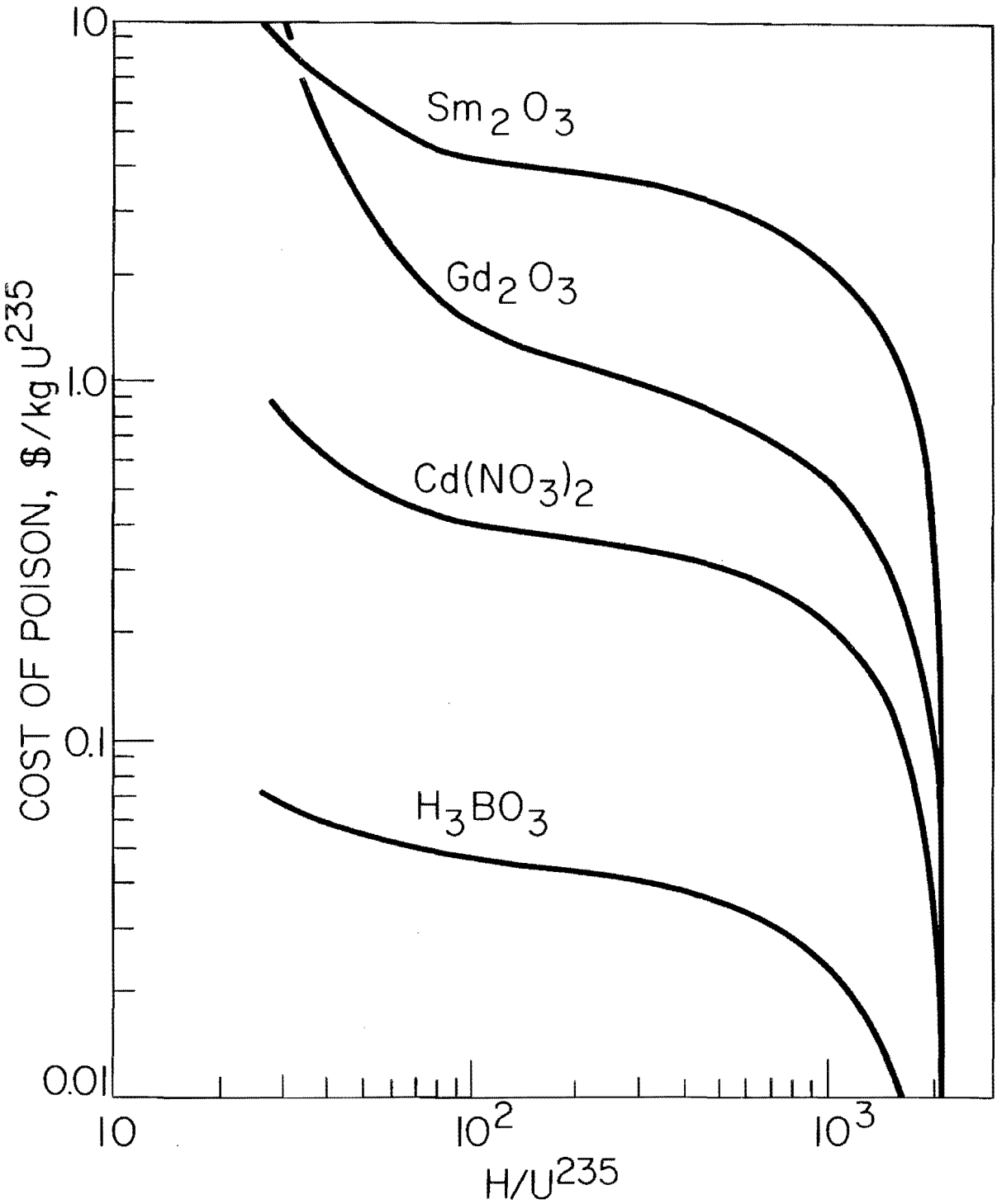

Fig. 8

control, to a level such that the cost of lost production time, decontamination, and bad publicity resulting from an accident is balanced by the cost savings and other benefits of the use of the conditional controls. Such an evaluation cannot be performed rigorously but must be in the form of an educated judgment. Perhaps it could be decided that the effects of a nuclear accident could be tolerated once per 100-1000 years of plant operation. Such a low probability could be ensured by providing two or three independent controls that are 99 to 99.9% reliable in each of the potentially hazardous operations in a plant.

Summary. In summary, our investigations indicate that soluble poison criticality control is a feasible, desirable, and logical extention of administrative controls which have been in use for some time. Because of its advantages in greater economy and use of vessels which are not limited by geometry or fixed poison lattices and because we believe the effects of criticality accidents to be tolerable we advocate use of soluble poisons as a primary criticality control in remotely operated, shielded, and contained facilities.

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