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BNWL-1807
UC-70

THE TECHNOLOGY OF TRITIUM FIXATION AND STORAGE

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JANUARY 18, 1974

Prepared for the U.S. Atomic Energy Commission under Contract AT(45-1):1830

BNWL-1807

NOTICE

PACIFIC NORTHWEST LABORATORY
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BATTELLE
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U.S. ATOMIC ENERGY COMMISSION
Under Contract AT(45-1)-1830

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $4.00; Microfiche $1.45

AEC-RL RICHLAND, WASH.

BNWL-1807
UC-70, Waste Management

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SUMMARY AND CONCLUSIONS

The technology of fixation of tritium in a solid form was examined. The principal emphasis was on the storage in solid form of tritium waste from the nuclear fuel cycle with the aim of preventing its significant entry into the biosphere.

Sources and routes of tritiated wastes in the fuel cycle were reviewed. It was concluded that the bulk of the tritium produced in the fuel cycle ends up in the fuels reprocessing plant, and with current reprocessing practice, ends up as a very large volume of low-level tritiated water. Alternative practice might produce much smaller volumes.

Criteria were established for narrowing the very wide possible choice of tritium fixation methods and the merits of various classes of tritium compounds are discussed. Current tritium fixation technology and fixation research was reviewed.

The basic chemical and technical aspects of known and potential fixation methods and the applicability of these methods to specific sources or types of tritiated waste with some estimate of economics are given. These fixation methods are compared briefly to some other tritium disposal methods. Recommendations for further studies are made. Clays, Portland cement, and hydrides all appear to have merit, depending on the nature (principally degree of dilution) of the tritium waste.

CONTENTS

THE TECHNOLOGY OF TRITIUM FIXATION AND STORAGE

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I. INTRODUCTION

Historically tritium has been considered one of the most innocuous of the fission products. A rough determination of the path of the tritium in a nuclear plant together with calculation of yields has usually been substituted for routine monitoring. Invariably the calculated discharges were well below set standards for either gaseous or liquid radioactive wastes. However, as the production rate from increased numbers of power reactors goes up, and downward evaluations of maximum permissible concentrations are contemplated, more attention is being given to both the production and the control of tritium in the nuclear fuel cycle.

Many estimates have been made of the world's tritium production and inventory.[1-9] Recent considerations[2] of both the natural level and the projected man-made contribution are not greatly different than Peterson's estimates.[4] Figure 1 shows the authors' evaluation of these data and are essentially Peterson's values. Uncertainties include:

- The reactor inventory is based on light water reactors. Extensive use of Pu recycle will raise the T yield since the fission yield from Pu is about twice that of U. (Estimates for LMFBR are about double those for PWR's). The molten salt reactor and heavy water reactor give a yield from 40 to 100 times higher.[8,9]
- The weapons residue curve assumes no additions since 1963 whereas there have been several atmospheric tests.
- The "natural" level is uncertain because accurate measurements were not made before the inventory was radically disturbed by man-made tritium.

- Fusion reactors will produce and consume about 5 x 10^4 times as much tritium per unit power as a fission reactor.[7] A power system based on fusion with a tritium loss of 0.01% per day would increase the man-made environmental tritium by a factor of 10.

On a global scale it can be argued that tritium production poses no problems. An inventory of 10^9 Ci (what appears now to be a maximum steady state value) could be dissolved in the top 75 m of the oceans (2.7 x 10^{19} liters[2]) to give a concentration of 3.7 x 10^{-10} μCi/ml. This is a comfortable distance from the present mpc of 3 x 10^{-3} μCi/ml. However, on a local scale the problems become real. A 10 ton/day reprocessing plant may have 6,000 Ci per day to dispose of requiring 2 x 10^9 liters of water per day to dilute to the mpc level. The atmosphere is more efficient in dispersing wastes and Barry[10] has suggested that 2,000 Ci/day could be released continuously through a 300-600 ft stack. Single discharge incidents of 6.8 x 10^4 Ci (Doury[11]) or 4 x 10^6 Ci (Barry[10]) are suggested as possible. Internal recycle of aqueous streams can build the concentration to levels such that such discharges could be made but this may be questionable operating philosophy. Storage of concentrated tritium wastes possibly preceded by isotopic concentration may be a necessary future operation in the nuclear fuel cycle.

The excellent review by Jacobs[2] includes a discussion of the impact of local releases of tritium and its movement in the environment. A report, "Tritium and Noble Gas Fission Products in the Nuclear Fuel Cycle," being issued by Argonne National Laboratories[12] discusses tritium production and behavior in present power reactors and in fuel reprocessing plants. This report also reviews tritium and Noble gas collection and retention methods currently used or considered. The current tritium control practices in use in the United States in laboratories, reactors and processing plants are surveyed in a state-of-the-art report being issued by Mound Laboratories.[13]

The present report is much narrower in scope and surveys the technology available for fixation and storage of tritiated wastes and suggests some research work to advance the technology.

II. HANDLING OF TRITIUM WASTES

Most of the man-made tritium will continue to be produced in power reactors. Table 1 lists typical production rates for different reactor types. The wide ranges listed indicate variation in design and operation. To a considerable extent the higher values show the effect of using boron in reactivity control, e.g., control rods for boiling water reactors and the LMFBR, and boric acid in the pressurized water reactor.

In the case of the heavy water reactor (HWR) neutron reactions with deuterium make a major contribution. In the molten salt reactor it is n-reactions with lithium. For the fusion reactor (CTR), tritium is a fuel and is also bred in the lithium blanket. The development of the CTR will place tritium control in a completely different perspective. This topic will not be considered in this report. However, the CTR will have a number of tritium problems in common with fission reactors, e.g., monitoring, waste treatment and tritium storage.

The fraction of fission tritium that escapes from the fuel into the cooling system depends on the cladding and the operating temperature. Stainless steel is quite permeable while zirconium blocks the escape. In the LMFBR a considerable fraction of the tritium will diffuse through the stainless cladding to the sodium and be removed in cold traps. EBR-II measurements[17] showed that 65% of the tritium appeared in the primary system trap, 25-30% was returned in the fuel and less than 1% escaped to the steam system.

Our principal concern will be the light water reactors (LWR) which will comprise the bulk of the power reactors for the next few decades. A few of the existing loadings are stainless clad. Most are zirconium clad, zircalloy-2 or zircalloy-4, and of the tritium that diffuses from the fuel matrix nearly all will be held by the zirconium as the hydride. The fraction of fission tritium that escapes to the coolant then is somewhat uncertain. Smith and Gilbert[18] assume a leakage rate about twice the rate of formation from deuterium activation or about 3×10^{-4} μCi/MW(th)-sec.

This is less than 1% of the fission production rate. Other leakage rates estimates are similarly low.[8]

Table 1

Production of Tritium in Power Reactors

Reactor Type	Production Rate (Ci/MW_{th}-yr)	Reference
LWR	5 - 10	(8)
HWR	200 - 1000	(8) (9)
LMFBR	5 - 50	(8) (9) (12)
HTGR	7	(8)
MSBR	300	(3) (15) (14)
CTR	4-5 x 10^5	(9) (16)

With stainless cladding losses may be highly variable depending on the temperature reached.[8,9] Tritium losses into the reactor coolant have been reviewed by Steindler, et. al.,[12] and by Rhinehammer and Lamberger.[13]

Cladding defects are another variable and in addition to affecting the reactor coolant levels they will be largely responsible for any tritium buildup in storage basins for discharged fuel. In each case released tritium will be rapidly converted to HTO.

Most of the fission produced tritium will follow the fuel to the reprocessing plant. Here part will go to burial with the cladding. Of the remaining, part will be released in the "head end" steps, i.e., chopping, head end treatments such as "voloxidation," etc., and finally the remainder will equilibrate with the aqueous phase on dissolution. Most off-gas systems will employ an oxidant such as CuO or $CuO-MnO_2$ to convert tritium to tritiated water. If chopping is followed by voloxidation then more than 99% of the tritium in the fuel will be removed and converted to water.[19] Heating of the chopped fuel in an inert atmosphere is also being considered as a tritium removal process.

If such pretreatment is not employed, then the bulk of the fission tritium will end up as HTO in the dissolver and virtually all will pass into the first cycle waste. Measurements by Henry at Idaho Falls[20] have shown that only about 0.1% follows the organic phase in the first solvent extraction column, and nearly all remains in the waste stream. This first cycle waste is concentrated and nitric acid is recovered. The water and acid recovered must then be recycled, discharged or stored.

It is seen that a wide variety of tritium-containing aqueous streams is produced in the fuel cycle. These include:

Reactor coolant water
Rad waste from reactors
Storage basin water
Condensates from head-end treatments
Recovered acid
Recovered water
Condensates from other off-gas systems
and other low-level wastes.

The volumes and tritium concentrations in these streams are highly variable. Reactor coolant of LWR's may range from a few nanocuries/ml to a few microcuries/ml.[11][12][21] The secondary coolant of the PWR has been reported to be lower by a factor of 10-1000.[13] Lin[21] estimates waste streams from the reactors to be 1×10^{-3} μCi/ml for the BWR and 1×10^{-2} μCi/ml for the PWR. However, at a tritium loss rate of 1% or about 100 Ci this represents a large volume.

Waste water can be cleaned up and recycled to the reactor thus permitting the tritium level to build up to higher concentrations. It has been suggested that the coolant in a PWR could be maintained at 5 μCi/ml[13] or greater. In the long run, extensive recycle simply raises the tritium concentration and lowers the volume of the waste streams. Thus, it is seen that tritiated water from power reactors may cover the concentration range from 10^{-6} μCi/ml in secondary coolant to 10 μCi/ml in primary coolant with waste volumes ranging from hundreds of liters to hundreds of thousands of liters per day.

In the reprocessing plant, volumes and concentrations cover an equally wide range. Off-gas condensates may be very small in volume, liters/day, but very high in tritium concentration. Storage basin water is high in volume and will normally build up to low levels of concentration only after relatively long periods of time.

The major concern is the first cycle waste, under the condition of no head-end tritium removal. A 10 ton per day reprocessing plant will produce about 50,000 ℓ/day of first cycle waste.[22] At 40,000 MW days/ton exposure and a T production rate of 5 Ci/MW-yr, the concentration of this waste would be 100 μCi/ml.

Very little tritium will follow the organic phase to subsequent extraction cycles.[20] However, restriction of the tritium to this first cycle means that recovered acid and water can only be used in preparing first cycle feed, i.e., in fuel dissolving operations and feed make-up. Some use in the first cycle scrub stream may be possible depending on phase separation efficiency. In the purex process the total water condensate volume is at least an order of magnitude greater than the above and, depending on how the condensates from acid recovery are combined, much lower concentrations--and higher volumes may be produced. For effective tritium control it would appear prudent to isolate first cycle recovered acid and condensate from the rest of the plant. However, since this cannot all be used in the first extraction cycle, a large waste stream containing greater than 100 μCi/ml tritium would be produced.

It is seen that tritium wastes in the fuel cycle are varied. Volumes can be reduced by recycling in both reactors and reprocessing plants. This, of course, raises the concentration of the wastes. The tritium waste in each case can probably be effectively channeled into a "pure" water form, i.e., free of solutes.

III. GENERAL CONSIDERATIONS

An almost infinite number of compounds of hydrogen can be prepared which are capable of producing a solid storage form for tritium. These include most organic compounds, hydrates (including hydroxides), hydrides, adsorbents, etc. Because the number of compounds is so large, it is important to start by listing some of the criteria that are important in narrowing the extremely large field of possibilities. These include cost of raw materials, ease of preparation of the tritium containing product and costs related thereto, capacity for binding tritium, stability and safety of handling of the tritium containing product for long term storage, compatibility of the product with any possible storage container, and degree of tritium loss as measured by vapor pressures, solubilities, and exchange rate with water. These are obviously all interrelated and together determine the overall costs of storing tritium in a solid form with minimum release rates.

It is highly unlikely that any one compound, or for that matter any given type of compound, will best satisfy all of these criteria, and it is quite possible that the optimum compound (or class of compound) for fixation might depend on the particular application such as the volume of tritiated water involved and its tritium concentration. Thus for fixation of large volumes of tritiated water, the cost of preparing a tritiated compound is a much more important criterion than it is for the fixation of a small volume of very high level tritiated water.

The carbon-hydrogen bond in organic compounds is usually highly covalent and nonlabile and thus very low hydrogen exchange rates can be expected compared to other hydrogen compounds (including even the much more expensive boron-hydrogen and silicon-hydrogen compounds). A major objection to organic compounds is that the cost of preparing hydrocarbons (or their derivatives) from tritiated water will almost certainly be quite high if large volumes of water are involved. Starting with tritiated water, the lowest cost method of preparing a tritiated organic compound having low hydrogen

exchange or leach rates is probably through the reaction of water with calcium carbide to form acetylene followed by the conversion of this to a polymeric hydrocarbon.

There is perhaps no clear-cut line that divides adsorbents from hydrates and the binding of water by adsorbents may range from that very loosely held in large pores strictly by capillary action and by swelling of hydrophilic polymers (mechanical adsorbents) to a much smaller amount of water strongly chemisorbed on surfaces by what is more truly a surface hydration mechanism. Many mechanical adsorbents such as sawdust, etc., are very inexpensive and are capable of very easily absorbing large amounts of water. Unfortunately these materials bind water extremely weakly resulting in water vapor pressures little different from that of liquid water, and the water exchange rate of material exposed to atmospheric humidity or liquid water can be expected to be quite high. Storage of tritiated water on such materials would therefore require some type of outer container (tank, etc.) as a primary containment. For most purposes, it must be concluded that for long term storage there is not a great deal of difference between storage as liquid water or as water in a mechanical adsorbent. Thus corrosion of tanks, etc., by water on a mechanical adsorbent would probably be as severe or worse than corrosion by liquid water. This type of material might find use in minimizing short term leakage rates from containers such as barrels, etc., since for a leaky container not immersed in water, the loss from the container or exchange with external water vapor would be by vapor diffusion instead of by liquid flow as in the case of liquid water.

Several adsorbents have extremely large surface areas and adsorb water moderately strongly. Some of these, such as activated alumina and silica gel, have reasonably high capacities and are moderately inexpensive. These have been used to a considerable extent as drying agents and their properties are well known. Their principal drawbacks for tritium fixation would be that, although the vapor pressure is low at low water loading, it becomes rather high as loading increases so that the effective capacity for the more tightly bound water is low, and they will isotopically exchange very rapidly with water vapor or liquid water.

An extremely large number of hydrates (including hydroxides) exists but a relative few of these warrant consideration. Many hydrates are water soluble, many are expensive, and many of those which are not soluble or only slightly so can be expected to exchange water rapidly because of large, readily accessible surface areas. Relatively low cost compounds which form hydrates of low water vapor pressure and which bind or exchange water rapidly have been studied and used as drying agents. The most notable of these is anhydrous calcium sulfate which is very low in cost and is of relatively low solubility but which has rather low water capacity and rapid water exchange. The hydrated silicates constitute the group most likely to contain the best candidate compounds having a combination of low solubility, low cost, high water capacity, low vapor pressure, and (compared to other hydrates) in some cases low exchange rates. These include materials such as Portland cement and similar materials, zeolites (molecular sieves), and clays.

The cement materials are of particular interest because the hydrated forms are massive solids which can be expected to have much lower practical exchange rates than other hydrates which are typically in powdered, granular, or pelletized form.

It is instructive to consider the radiolysis problem associated with tritium waste storage. One mg of tritium will produce hydrogen by radiolysis of water at the rate of 4.44×10^{-11} (G = 1.0) moles/second based on complete absorption of the (0.4) (0.018×10^{6} ev) β particle. A maximum G value is 1.7 molecules per 100 ev absorbed.[23] This value might be approached in water. In solid hydrates it is probably an order of magnitude less. Thus the total tritium waste per day from our reference 10 ton/day plant would produce hydrogen at a rate of from 4×10^{-4} to 4×10^{-3} moles per day. In one year the corresponding range would be 0.15 - 1.5 moles and for complete decay extrapolates to 3.6 - 36 moles.

This will produce appreciable pressures only if the tritium is stored in concentrated form. One day's production in a 55-gallon drum with 25% void space would produce a maximum of 0.007 atm./day or 2.44 atm. per year.

Although G values for recombination are much higher, ~ 10,[24] the radiation level (low T content) of the vapor phase is small enough that the reaction is negligible. HT formed will equilibriate rapidly with water. Hence the radiolysis system is equivalent to a normal water system with a radiation source in the liquid phase. For solid hydrates, the gas production rate is certain to be smaller--perhaps by as much as a factor of ten. Thus it appears that except for very highly enriched HTO, H_2 production is not a problem. In the latter case, explosive concentrations of hydrogen and oxygen may be produced and would need to be provided for.

The production of ^3He is also generally insignificant. The 6000 Ci, 624 mg daily output of our reference 10 ton/day plant would produce helium at a rate of about 0.1 mg/day, or 4.8 ℓ of ^3He after total decay.

The hydrides differ from the other groups of materials considered here in binding elemental hydrogen rather than water. This is a distinct advantage, particularly for temporary storage, when the starting form is elemental hydrogen, but is by itself a very strong disadvantage for the problem of tritiated water storage. Additionally hydrides (or the starting materials to prepare them) are quite expensive. The main advantage and potential use of hydrides would appear to be the temporary storage or shipment of tritium where it is desired to again release the tritium as elemental gas. Many hydrides are very reactive materials, and all (but particularly the more chemically stable transition metal hydrides such as hydrides of titanium, zirconium, yttrium, etc.) are rather expensive. For this reason it is not likely that hydrides would be considered for storage of low level tritiated hydrogen wastes. Hydrides will undoubtedly be of considerable importance for the temporary storage of tritium gas in the operation of fusion reactors.

IV. CURRENT PRACTICES AND STUDIES IN TRITIUM FIXATION

Current tritium control technology has recently been rather thoroughly reviewed by Rinehammer and Lamberger.[13] This review covers current control and disposal practices for tritium wastes generated by laboratories and processing facilities, reactors (government and private), and reprocessing plants. Several methods for the solidification of these tritium wastes are discussed, as is current research on tritium solidification and waste storage methods.

It is very important to note that currently these solidification methods are being applied almost entirely to relatively small volume laboratory and tritium processing wastes. Since much of this solidification is with mechanical adsorbents, such as pelletized corn cobs or vermiculite, its principal function can be considered to be the prevention of leakage from a watertight container (usually a metal drum, sometimes polyethylene lined) during packaging, temporary storage, shipment, and burial and minimizing of leakage after burial until gross failure of the drum occurs because of corrosion. Since these drums are usually presently buried directly in burial trenches, the current solidification and containment in the drums can be considered only a temporary safe fixation for shipment and burial operations and for some unknown time thereafter, since it must be assumed that after burial the drums will corrode away before essentially total decay of the tritium. After such drum failure, tritiated water on such adsorbents must be considered to be completely free in the soil of the burial trench. Some of the current water wastes are mixed with materials such as Portland cement in the drums, and this will leach at a slower but still appreciable rate[25] after drum failure. Under present thinking no credit for control by the solidification medium or the containment is assumed after burial.[26]

The amount of tritium waste from projected nuclear fuels reprocessing plants is quite large and, with current fuels reprocessing methods, the volume of water in which it is diluted very much exceeds that of current liquid tritium wastes which are being solidified and buried in steel drums

or other containers. With current reprocessing methods the volume of this water may be as large as several million gallons per year, and it is thus apparent that if a decision is made not to release this tritium to the environment that either the extent to which it is diluted in the reprocessing plants or the manner of disposal or both must be significantly changed.

Current solidification methods can be divided into several categories. These are: the temporary fixation of tritium gas as hydrides, the fixation of water vapor by drying agents, fixation of liquids by adsorbents, fixation of water by materials such as cement with limited leach rates, and studies of fixation methods having very low leach rates. These are treated in this order below:

a. Hydrides

Because they are expensive, hydrides have not been used to fix large amounts of tritiated waste. They have, however, been used for the temporary storage of rather concentrated tritium and are also quite suited to the removal of hydrogen and tritium from inert gas systems where absence of oxygen eliminates conversion to water by catalytic recombiners. The use of uranium beds for the storage of tritium gas as UH_3 and for its purification, including decomposition of water, is well known.[27] Uranium beds for purification have been generally limited to gases having >1% tritium and have been used for storage of large amounts of tritium.[28] Titanium sponge has been proposed as a getter and possible storage medium for hydrogen and tritium removal from the helium coolant of a high-temperature gas-cooled reactor.[29]

b. Drying Agents

Molecular sieves have been very widely used to remove tritiated water vapor from gas streams and to provide temporary storage of such water.[13] Silica gel beds have been reported to be equally effective[30] but have been less widely used. Molecular sieve and silica gel beds have been used in conjunction with catalytic (Pd) recombiner beds or with CuO beds to remove elemental hydrogen and tritium from gas streams. In

some cases where relatively small amounts of tritiated hydrogen or water vapor are involved, the molecular sieve or silica gel beds have been used for extended periods before appreciable tritium breakthrough has occurred, and it has been found most convenient to discard the loaded beds as solid waste rather than to regenerate them.

c. Adsorbents

A variety of physical or mechanical adsorbents have been used to convert tritiated liquids (principally water and oils) to solid or semisolid materials. These include vermiculite, pelletized corn cobs, clay base materials, colloidol silica (a thickener), and similar materials.[13] These materials are generally very inexpensive but can only be considered a means of preventing liquid leaks from waste containers prior to burial. Indeed liquid can be forced from them by simple pressure, and the amount of water which can be absorbed on several of these materials without "weeping" at the bottom of 55 gal. drums has been noted.[31]

d. Fixation as Solids with Limited Leach Rates

This category includes principally the fixation of tritiated water as hydrates. Portland cement has been the principal material in this category used to fix tritiated water[32], and in addition to its direct use, it has also been used in mixtures with Plaster of Paris and with vermiculite.[33] Generally, it has been used to fix tritiated water in metal drums, and these are considered as the primary containment. Some burial of tritiated cement not in steel containers has occurred in the past.[34] Unlike the adsorbents and drying agents, however, hardened cement does have a moderately slow[25] tritium leach rate when immersed in normal water. This difference between cement and molecular sieves and other drying agents is no doubt due much more to the physical nature of hardened cement than it is to any chemical difference in the nature of the water bonding.

Urea-formaldehyde resin has also been used to solidify tritiated water, but details are lacking.[35]

e. Current Fixation Research Aimed at Low Tritium Loss Rates

Some studies[25] have been made to decrease tritium loss from cement blocks by use of various coating materials. Coatings of organic materials in which hydrogen is strongly bound and which are relatively impervious to water were studied. Asphalt, beeswax, and paraffin were all found to be quite effective. Because of its lower cost, asphalt was studied most extensively and, as a result of this work, asphalt coating of containers or of tritiated solids is currently being used in some burial operations.[36] This work is continuing at a slow pace, and the study of coating such as epoxies which can be applied cold to the cement is planned.[37] The cold applied coating should eliminate the vaporization of water from the cement surface into the coating which no doubt occurs on application of hot asphalt.

Another method of tritium fixation which is being examined[38] is the incorporation of tritium waste into acetylene through the reaction of tritiated water with a calcium carbide. The acetylene is then converted to a crosslinked, high-molecular-weight polymer by gamma irradiation. This insoluble material containing strongly covalently bound hydrogen would be expected to have low exchange and leach rates and can be incorporated into concrete in several ways. Leach and diffusion studies are being carried out.

V. TECHNOLOGY OF POSSIBLE FIXATION METHODS

It is the aim of this section to treat the basic chemical and technical aspects of various known and potential fixation methods. The applicability of the methods to various specific sources of tritiated waste are discussed with particular emphasis on tritium produced in the nuclear fuel cycle. Very rough estimates of relative costs are made. The various fixation methods are treated according to the nature of the chemical binding of the tritium and only compounds binding tritium rather strongly are considered.

Weak adsorbents are not considered, but adsorbents which bind water strongly are treated as hydrates.

a. Hydrides

Metal hydrides include a widely divergent group of materials that range from extremely unstable compounds to quite stable alloy-like materials. Three types, covalent, saline, and metallic hydrides, are known. Of these only saline and metallic hydrides are of interest here since covalent metal hydrides are very reactive materials. Even these hydrides are rather reactive and most of them will react readily with either air or moisture or both if moderately finely divided. The most stable of the hydrides, those of Ti, Zr, Hf, Y, Nb, and Ta, are quite expensive because of the cost of the metals from which they are formed and thus are not candidates for fixation of large amounts of dilute tritium wastes for disposal. Cheaper (although still expensive) hydrides such as calcium hydride are certainly too reactive with water to be considered for large volume waste disposal.

By far the most certain application of hydride formation is in temporary storage of elemental hydrogen-tritium mixtures. This is of considerable importance in laboratory and tritium processing applications and will be very important if and when fusion reactors are developed. As noted in Section IV, uranium has been widely used for storage of and purification of tritium gas. Although UH_3 is pyrophoric, whereas some other hydrides such as those of Zr, Ht, Ti, Nb, and Ta are much less reactive, it has other marked advantages for this application. Its stability is such that it can be formed readily at low temperatures (using finely divided U metal produced by decomposing hydride) and yet can be decomposed again to give moderately high tritium pressures at reasonable temperatures (one atmosphere at 408°C).[39] Even more importantly, the decomposition pressure is virtually constant at any given temperature over essentially the entire composition range UH_3 to U metal. On the other hand, the hydrides of Zr, Hf, Ti, Nb, and Ta exhibit very steep isotherms[39] and would require much higher temperature to recover a major fraction of the tritium on the beds. Several of

the less expensive saline hydrides also have reasonably flat isotherms, but the decomposition pressures are either rather low (Ca and Li), requiring high decomposition temperatures, or the low melting points of the metals cause kinetic problems in hydride formation.[39] It is conceivable that some alloys might possess some advantage over uranium for this purpose, but it does not appear likely that the advantage over uranium would be large.

Another promising potential use of hydrides for tritium fixation is in the removal of small amounts (on a mole basis) of hydrogen and tritium from inert gas streams. A fuel cycle application of this usage would be the removal of hydrogen and tritium from the inert gas of a gas-cooled reactor mentioned in Section IV. This usage would probably require one of the more stable hydrides. Titanium (as sponge) is probably the least expensive of the metals which produce the more stable hydrides and is a likely candidate for such application, but other metals (including alloys) might possibly have characteristics that would offset the cost differential.

The only way in which hydrides could conceivably be of interest in fixation of tritium produced in water-cooled power reactors would be for this tritium to be recovered from the irradiated fuels in a very small volume. This could not be the case if the fuels are simply dissolved in nitric acid as is currently the practice. It might be the case, though, if tritium were removed in a head-end process such as voloxidation and was kept in a quite small volume. The cost of a metal such as titanium or zirconium required to fix and store such tritiated waste would certainly markedly limit the acceptable dilution of the tritium. About 2.5 to 5.0 kg. of Ti and about 5 to 10 kg. of Zr would be required to fix the hydrogen contained in one liter of water. One possible approach in handling water produced by a voloxidation process might be to convert the tritiated water to hydrogen (using a magnesium bed or electrolysis) followed by hydriding of zircalloy cladding hulls which must be stored as radioactive waste anyway. The loss of tritium from massive zirconium hydride is very low,

even at 760°C in air, because of formation of an oxide surface film.[40] Studies to determine tritium release rate as a function of degree of hydriding of the Zr or Ti and of surface treatment (intentional oxide film formation) would be needed. The feasibility, both technical and economic, of using cladding hulls which already have considerable oxide film on parts of the surface would have to be determined.

b. Organic Compounds

The advantage of tritium fixation through conversion to organic compounds is the low tritium exchange rate that can be expected to occur for hydrogen attached to carbon by a strong covalent bond. Of particular interest are low volatility, hydrophobic compounds such as polymeric hydrocarbons.

Undoubtedly the simplest (and probably cheapest) approach to preparation of such polymeric materials starting with tritiated water is to produce acetylene through the reaction of water with calcium carbide:

$$2H_2O + CaC_2 \rightarrow C_2H_2 + Ca(OH)_2.$$

The acetylene produced can then be converted to a high molecular weight polymeric material. This fixation method is currently being studied[38] as noted in Section IV. A very rough order-of-magnitude estimate can be made of the cost of such a tritium fixation method. Based on published 1962-1963 costs of calcium carbide and of acetylene made from it using ordinary water[41], the cost of calcium carbide for making tritiated acetylene from tritiated water would be $1.50 to $1.70 per gallon of water. Considering the probable increase in calcium carbide cost since 1962, the costs involved in handling tritiated water and acetylene relative to the costs with ordinary water and acetylene, and the fact that half of the water ends up as $Ca(OH)_2$ which must be calcined and the water recycled, the cost of preparing tritiated acetylene will surely be well over $2.00 per gallon of water. To this will be added the cost of converting the acetylene to a polymeric material. It seems likely that the end result would be that fixation in this

manner could not be accomplished for less than about $3.00 per gallon of tritiated water and might likely be considerably more. By conversion of the acetylene to ethylene, the amount of hydrogen fixed per carbon atom would be doubled but the added complexity of producing hydrogen from the tritiated water and hydrogenating the acetylene would probably actually be more expensive.

From the above it is quite apparent that this method of fixation would not be economically acceptable for 10 ton/day fuels reprocessing plant waste amounting to 10-20,000 gal/day (first cycle waste, HAW, isolated, once through basis) or the even larger volumes produced by current methods in which the HAW is not isolated and recovered acid is used throughout the plant. Even with isolation of the first solvent extraction cycle wastes and recycle of recovered acid to the dissolver, the volume of tritiated water waste probably could not be decreased more than about a factor of five because of the necessity of using nontritiated scrub streams to keep the first extraction cycle isolated. At the other extreme, a head-end process such as voloxidation may produce a very small volume of tritiated water, and the cost of making tritiated polymers would be much less significant. It must be remembered, however, that whereas tritium losses due to radiation damage would not be significant for polymer made from low level tritiated water, they might be for the much higher tritium level polymer produced if tritiated water output of a 10 ton/day plant were say a few liters/day. Thus with small volumes of higher level wastes, it seems unlikely that this moderately complex route would be competitive with a simpler solidification method (such as cement) coupled with confinement in high integrity and long-life containers (probably welded metal).

c. Hydrates

As noted in Section III many hydrates exist. It appears, however, that some commercial drying agents and the hydrated silicates (some of which are also drying agents) have characteristics most desirable for tritium fixation.

1. Drying Agents

Of the commonly used commercial drying agents[42], four can be considered at least briefly. These are activated alumina, silica gel, calcium sulfate, and molecular sieves. Since all of these drying agents absorb or exchange water rapidly, they are of great value for the removal of water vapor from air or other gases and for its temporary storage. They are usable for long-term storage of tritium waste only if they are fully contained and protected from contact with environmental water and water vapor. All four of these drying agents are stable solids even when water loaded. All of them have been widely used and their properties have been thoroughly studied. All of them, with the exception of calcium sulfate, would be more expensive for permanent disposal of tritiated water than Portland cement.

Calcium sulfate has the advantage of being low in cost but has the disadvantage of having a low capacity for water. It forms a hemihydrate containing 6.2% water and up to this composition binds water strongly, giving a dew point of -62°C[42] or about 6 ppm water vapor in air. Higher water loading can be obtained only at the expense of much higher water vapor pressures. This material is also more difficult to regenerate and has a shorter useful life than many other regenerative drying agents.

Silica gel has the advantage of a very high capacity, taking up 40% by weight water on the dry basis and remaining a physically "dry" material.[42] Unfortunately such high capacities can be achieved at 25°C only with high water vapor pressures and silica gel binds water strongly and exhibits a low water vapor pressure only at quite low loadings. Water vapor pressures over silica gel at 25°C are approximately 0.4, 2.0, 5.0, 9, and 18 mm. at water loading of 1, 5, 10, 20, and 40 gms H_2O per 100 gms silica gel, respectively.[42] Adsorption of water by activated alumina is very similar to that by silica gel except that the capacity is about 50% of that of silica gel.

Molecular sieves have the advantage of having very high affinity for water and much flatter isotherms than does silica gel.[43,44] As a result, at 25°C, they have a higher capacity at all except the highest water vapor pressures than silica gel does.[43,44] They are quite stable to regeneration by heat, are stable to multiple cycling, and are physically stable to liquid water. Their capacities are typically about 20% based on dry weight. They have been widely used for removal of tritiated water vapor from air and gas streams and for its temporary storage.[13] In some cases tritiated water loaded columns of molecular sieves have been sealed and buried rather than regenerated. Various schemes have been used to remove tritiated water from gas streams. They have been used as two beds in series to maintain water vapor levels at <1 ppm, and have been used as a two-bed system with the first bed regenerated and the second saturated with normal water.[43] In the latter case, isotopic exchange is very rapid and very low tritium levels result.

2. Portland Cement

Portland cement is probably the cheapest material available which will bind water strongly and have a moderately low practical exchange rate. The fairly low exchange rate is no doubt due much more to the massive nature of hardened cement than to its chemical exchange rate, and pulverized hardened cement might be expected to exchange water rather rapidly as do other hydrates including drying agents.

The chemistry of Portland cement and its hydration is quite complex but has been the subject of a considerable amount of study and is reasonably well understood.[46,47,48,49] A "typical" cement has the approximate composition:[46]

54.1%	$3CaO \cdot SiO_2$
16.6%	$2CaO \cdot SiO_2$
10.8%	$3CaO \cdot Al_2O_3$
9.1%	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

Hydration reactions of these compounds are thought to be:

$$2(CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$$

$$2(CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$$

$$3CaO \cdot Al_2O_3 + 6H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O$$

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 2Ca(OH)_2 + 10H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaO \cdot Fe_2O_3 \cdot 6H_2O$$

Although the two letter reactions fix more water, it is the $3CaO \cdot 2SiO_2 \cdot 3H_2O$ (tobermorite gel) that accounts for essentially all of the strength of the hardened cement. These different hydration reactions proceed at different rates. The hydration of calcium aluminate is the fastest and gypsum is added in carefully controlled amount (too much weakens the product) to form $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ and prevent fast set. Some of the hydration reactions proceed quite slowly so complete hydration requires several months. Much faster hydration is obtained by steam curing.

The net result of the hydration of Portland cement is the binding of a theoretical value of 28 $\pm$1% water (within the normal range of variation in composition) and a measured experimental value of 26%.[46] Hardened cement is quite porous and the tobermorite gel has a very large surface area. The result is that even though the solubility of the cement hydrates is low,[50] a gradual leaching of tritium occurs when cement blocks made with tritiated water are immersed in water.[25] Various methods of waterproofing cement have been studied, and studies of cement coatings to prevent tritium loss from cement blocks were mentioned in Section IV, part e. Further studies of methods of waterproofing of cement or combinations of these methods would be of value. Studies of loss from larger blocks, steam cured, and longer aged blocks than those used[25] would also be valuable.

Fixation of tritiated water with cement has the very marked advantage of being a very simple process and most of the cost can be expected

to be the cost of cement, plus whatever coating or containment is necessary to prevent tritium loss, plus storage of the hardened cement. The 1962 average U. S. cost of Portland cement was $3.24 per 376 lb. barrel.[48] Assuming a binding of 25% H_2O relative to dry cement, the cost of the cement (1962 basis) would be $0.29/gal. of water ($0.075/ℓ). Assuming a fuels reprocessing plant in which first cycle waste was isolated but not recycled, the cement cost would be about $400-500 per ton of fuel. In addition a very large volume of tritiated cement would be generated. If tritium were recovered as a very small volume of tritiated water by a head-end process (such as voloxidation), cement would still be an attractive compound for fixation because of the simplicity of preparing it. Under these conditions of small volume, containment of the cement in high integrity metal containers becomes economically attractive.

3. Clays

Water held by clays is basically of three types.[51] The first type is the water in pores, on the surfaces, and around the edge of discrete particles of the minerals composing the clay material (mechanically adsorbed by capillary action, etc.). The second type is, in the case of clays such as montmorillonite, vermiculite, and similar materials, the interlayer water between the unit-cell layers and, in the case of attapulgite and similar minerals, the water which occurs within the tubular openings between the elongate structural units. The third type is the OH lattice water. The first type of water requires very little energy for removal and drying slightly above ambient temperatures will remove it. The second type requires definite energy for removal, and in most clays, temperatures at least approaching 100°C are required for essentially complete removal. Removal is slow at 100°C but is rapid at somewhat higher temperatures. This water is replaced very readily in most (but not all) clay minerals if dehydration is not absolutely complete and only a trace of the original water is left. The third type, hydroxyl water, is strongly bound and is

not removed until temperatures in excess of 300°C are reached. This water loss is not readily completely reversible. A small portion of it is taken up again by some of the clay minerals at 25°, but rapid complete rehydration requires (in the cases of kaolinite and illites which have been studied) steam pressures of 1000 to 10,000 p.s.i.

The strongly bound hydroxyl water in various clay minerals typically runs about 15% (dry basis) or less. It does not appear that the binding of tritiated water in this manner would be practical for a waste fixation method because of the difficulty of rehydrating fully dehydrated clays. Although the interlayer water is held weakly, some clays, particularly montmorillonites, have quite high capacities for this type of water. Water capacities of up to 46 percent (dry weight basis) at 90% relative humidity at 30°C have been reported for montmorillonites in the Ca^{2+} form.[51] Even larger amounts of water can be mixed with clays before they become fluid. The plastic range for montmorillonite is reported to be 83 to 250% water (dry weight basis).[52] Through this range the clay-water mixture is a plastic gel. Even though this water is bound very loosely and would be expected to exchange readily, the permeability of masses of such clay-water mixtures is very low. Clays, particularly the Wyoming type bentonites (principally montmorillonite in calcium form) have been used to impede or virtually stop the movement of water through earthen structures, to waterproof basement walls, to seal ponds and lakes, etc.[52] These same bentonite clays are widely used in drilling fluids because of their outstanding ability even at only 5% clay concentration, to produce an impervious seal on the wall of the drill hole and thus to prevent leakage of fluid from the drilling mud into porous structures.[52]

The low permeability of natural clay layers is well known in soils science and use has been made of this property of natural clay beds in low level radioactive waste disposal by burial. It seems likely that this property could also be used in disposal of relatively

large volumes of tritiated water. If tritiated water were mixed with a dried clay of high water capacity and then buried completely in a natural clay of low permeability or if it were buried enclosed completely by an outer layer of an impermeable clay, such as montmorillonite wet with ordinary water, very low tritium loss rates should occur. In this way the nontritiated clay in the outer layer of the natural clay bed would act as an impermeable container for the tritiated clay. Even if the outer layer were broken, exchange and tritium leaching would only occur near the surface of the exposed tritiated clay. It seems reasonable that in such an application, a dry montmorillonite could be loaded with tritiated water up to at least the lower plastic limit.

It is difficult to estimate the cost of such a disposal method because of uncertainties with regard to the amount of water which can be fixed per unit of clay. Clays of a grade usable with foundry molding sands sold for $15-20/ton in 1962-1963. At a capacity of 80% water and $20/ton of clay, the cost of clay for this purpose would be about $0.10/gal. of tritiated water. Higher water-clay ratios would lower the cost accordingly. Some costs would, of course, be incurred in drying the clay prior to loading with tritiated water, etc.

Another fixation route in which the low permeability of clay might be used would be to use clays to seal tritiated cement. In this application tritiated cement blocks might be buried in a very impermeable clay mass to prevent exchange and leaching of tritium from the cement blocks.

VI. COMPARISON OF FIXATION TO OTHER DISPOSAL METHODS

It is important, at least for applications involving large volumes of tritiated water such as that expected from a fuels reprocessing plant not using a head-end tritium removal step, to compare the economics of tritium fixation methods to other alternatives. Lin[21] has made estimates of isotope separation for a 100-fold concentration of the tritium

and a decontamination factor of 5,000 on the 99% of the water released. His lowest estimate is for dual temperature H_2S-H_2O exchange and is $0.10 to $0.20/gal. water. His estimate for other processes is higher by at least a factor of two. Arnold, et al,[53] have estimated costs of long term tank storage of tritiated water at $0.10/gal. Their estimate for costs for deep well injections range from less than $0.01/gal. to $0.10/gal. depending on the geological nature of the injection site. Any required transportation (tank car, tank truck, pipeline, etc.) to a distant site for deepwell injection would be in addition to this.

From the above, it would appear that of the fixation methods discussed here, only the clay route offers much chance of being significantly cheaper than either enrichment or deep well injection as a primary disposal means of handling large volumes of low level tritiated water. It is also apparent that unless high transportation costs are involved, deep well disposal offers by far the most economical alternative for disposal outside of the biosphere. The costs for cement fixation are such that it becomes attractive if the volume of tritiated water waste is significantly smaller (perhaps by a factor of ten or more) than that expected from fuels reprocessing plants with isolation only of the first cycle solvent extraction wastes (HAW) on a once-through basis. At very large volume reductions, as might be possible with head-end removal from fuels, metal hydrides may become competitive, but cement in high integrity containers would be a strong contender.

VII. RECOMMENDATIONS

It has been pointed out that for large water volumes or for low tritium concentrations of tritiated water, alternatives to fixation are attractive. Disposal by dilution into the environment remains feasible in some locations. Eventually of course this path may be arbitrarily blocked. Other methods of direct disposal of water, such as deep well storage, remain economically attractive. However, it has also been noted that portions of the nuclear fuel cycle may produce small volume streams of moderately high concentrations of tritium. Certain waste streams may lend themselves to isotopic enrichment. In still other cases, deliberate storage of tritium in

recoverable form may be desirable. Thus tritium fixation will still be employed in numerous locations in the nuclear fuel cycle and further studies should be made.

In view of the efficacy, low cost and availability of Portland cement, studies of this material should continue. Coatings need to be improved. Possibilities here include other silicates and low-temperature curing organics such as epoxy resins. Portland cement is a well studied material but the emphasis is usually on strength and curing time, neither of which is tremendously important for the present problem. Chemical binding (low vapor pressure) and low porosity (low diffusion rates) are much more significant and possibly experiments involving pure constituents or simple combinations of the pure constituents of Portland cement might be instructive.

The clays are well characterized, and although diffusion (permeability) data were not seen, undoubtedly adequate data exist. Little appears to have been done on isotopic equilibration rates with the different forms of water held in clays. Stewart[54] has examined kaolinite, montmorillonite, and illite and noted that the isotopic effects are quite complex. Isotopic fractionation studies of pure clay materials would be interesting.

The metal hydrides are interesting compounds, especially for recoverable storage of tritium. Further study is also warranted for purification processes and for possible isotope separation methods. Except for the recoverable storage application, it is not likely that they will be competitive for tritiated waste fixation. Thus even though many gaps exist in vapor pressure data, reactivity data, etc., a detailed study for low level waste fixation is probably not warranted. Some effort might be addressed to the complex hydrides, e.g., metal-carbon (or nitrogen) -hydrogen compounds and the ternary metal hydrides. Data appear much less complete for these systems. Specific applications will always exist. An example is the use of titanium sponge as a tritium getter. The use of zircalloy cladding hulls as a tritium scavenger is a possibility. This leads to an area of study that is very important in practical hydride chemistry --the effect of oxide films on the uptake and release of tritium. This would require some study.

Finally, other methods of binding hydrogen should be further examined. The most obvious candidates are probably carbon compounds. Reference was made to work with acetylene. Another method that should be examined is direct hydrogenation of unsaturated and aromatic compounds. Although producing a lower tritium loading, this approach avoids the recycling problem of the acetylene synthesis.

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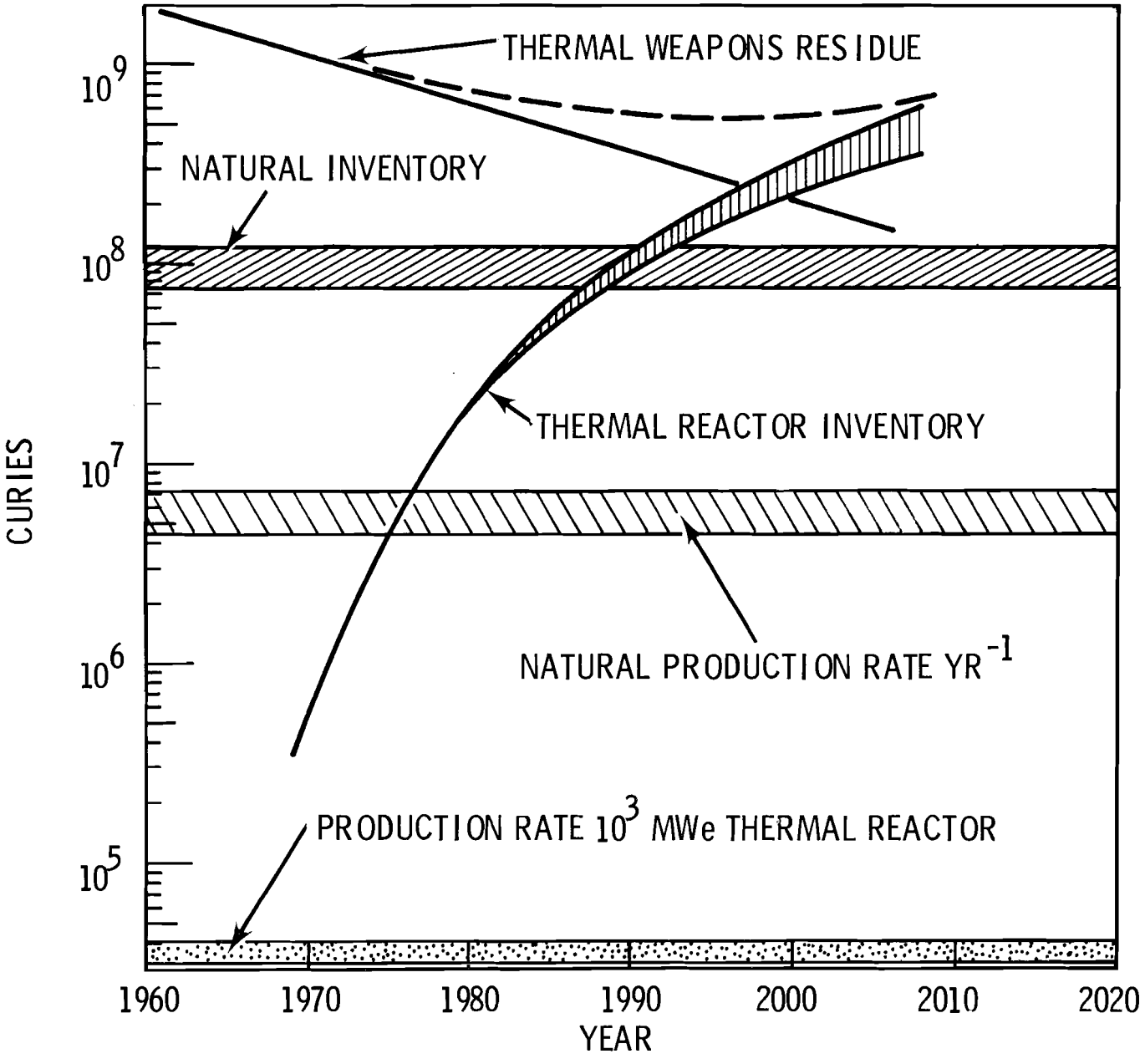

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