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A LOW TRITIUM HYDRIDE BED INVENTORY ESTIMATION TECHNIQUE

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A nominal 1500 STP-L Passively Cooled, Electrically heated hydride (PACE) Bed was developed and deployed into tritium service in Savannah River Site (SRS) Tritium Facilities. Process beds to be used for low concentration tritium gas were not fitted with instrumentation to perform the steady-state, flowing gas calorimetric inventory measurement method: In-Bed Accountability (IBA). In some instances, two physical beds, or canisters, were joined together with one process line connection, creating a bed with a total capacity of nominally 3000 STP-L or up to 815 grams of tritium. The IBA detection limit for these beds was estimated to be 9.75 grams tritium.

After deployment of these low tritium beds, the need arose to estimate tritium inventories of these beds without installation of IBA instrumentation. Two methods have been developed to estimate the tritium inventory of these low tritium content beds. The first approach assumes the bed is half-full and uses a gas composition measurement to estimate the tritium inventory and uncertainty. The second approach utilizes the bed's hydride material pressure-composition-temperature (PCT) properties and a gas composition measurement to reduce the uncertainty in the calculated bed inventory.

I. INTRODUCTION

At the United States Department of Energy (US DOE) Savannah River Site (SRS) Tritium Facilities, nuclear material control and accountability (NMC&A) programs were established to maintain control of nuclear materials. Periodically, a physical inventory (PI) is performed in which the nuclear material in a facility is measured.

For process vessels and components such as tritium hydride storage beds, significant effort is expended in developing tritium measurement techniques to obtain inventory and uncertainty measurements for the beds[1,2]. For Passively Cooled, Electrically heated hydride (PACE) Beds[3] used in the facilities for tritium storage, the tritium In-Bed Accountability (IBA) measurement error of a bed is expressed as the Student's t-factor multiplied by the inverse regression uncertainty, σ_{INV}, for the bed. The measurement errors for these beds range from 4.98 to 7.85 grams of tritium[2]. Averaging the squares of the uncertainties (variances) for these beds gives an average uncertainty of 2.48 g, and multiplying the average by a 2.776 t-value (α=0.05/2, 4 degrees of freedom) produces a nominal IBA detection limit 6.90 g.

Numerous PACE beds filled with $LaNi_{4.25}Al_{0.75}$ (LANA0.75) are used in the facilities to process low tritium content gas. In some instances, two physical beds, or canisters, are joined together with one process line to create a larger process bed, increasing the nominal gas capacity from 1500 STP-L to 3000 STP-L. The IBA uncertainty for the two canister bed is assumed to be additive so the IBA detection limit would be the square root of two times the uncertainty for a single bed: a detection limit of 9.75 g.

These low tritium beds contain less than the detection limit of the IBA technique and were not fitted with IBA instrumentation. The facility's NMC&A program requires an inventory value and statistical uncertainty (σ) of tritium for these low tritium beds. This paper describes two techniques for estimating tritium content and uncertainty for low tritium content beds to be used in the facility's physical inventory (PI).

II. BACKGROUND

Between the time periodic PIs are performed, materials transferred in and out of defined Material Balance Areas, or MBAs, must be tracked or measured to demonstrate control of nuclear materials. Material transferred into an MBA is a "Receipt" and material leaving the MBA is a "Shipment." As part of NMC&A programs, an inventory difference (ID) is used to determine the difference in nuclear materials inventories between two discrete inventory periods. The definition of ID is

$$ID = SI + R - S - EI \quad (1)$$

where SI is the previous book physical inventory (i.e., Starting Inventory), R is the sum of Receipts after the previous book inventory, S is the sum of Shipments after the previous book inventory, and EI is the current Ending physical Inventory.

Since the ID is based on physical measurements, errors in these physical measurements will typically cause a non-zero ID. To determine if the ID found during a PI exceeds established control limits, a statistical uncertainty of the ID is determined. The Limit of Error on Inventory Difference (LEID) is the statistical uncertainty in the calculated ID and is determined by propagating measurement system uncertainties. For random measurement errors, the variance (σ^2) of the ID is the sum of the variances of the terms in Eqn. 1 and is given by

$$\sigma_{ID}^2 = \sigma_{SI}^2 + \sigma_R^2 + \sigma_S^2 + \sigma_{EI}^2 \qquad (2)$$

The σ_{EI}^2 term is the summation of all variances for all physical inventory measurements in the facility. Each hydride bed in the facility contributes to the EI (gram) quantity in Eqn. 1 and the variance term in Eqn. 2. This paper described methods to estimate these values for low tritium hydride beds.

III. HYDRIDE BED TRITIUM CONTENT

The tritium content of a metal hydride bed (g_{bed}) can be expressed by

$$g_{bed} = \left(\frac{Q}{M}\right) \cdot x_T \cdot MR \cdot \frac{M_H}{MW_H} \cdot \frac{MW_T}{2} \qquad (3)$$

where Q/M, the hydride loading value, is the ratio of the moles of hydrogen isotope atoms (Q, the sum of protium (H), deuterium (D), and tritium (T) atoms) to the moles of metal atoms (M); x_T, tritium composition, is the mole fraction of tritium in the solid; MR is the molar ratio of metal atoms per mole of hydride atoms; M_H is the mass of the hydride; MW_H is the molecular weight of the hydride; and MW_T is the molecular weight of tritium gas. For calculation purposes, a dual canister $LaNi_{4.25}Al_{0.75}$ (LANA0.75) storage bed has a MR value of 6, a M_H of 25.22 kg, a MW_H of 408.62 g per mole, and a MW_T of 6.032 g per mole. For capacity calculations, 0.725 Q/M produces the bed's 3000 STP-L process capacity. x_T is the unknown.

It is proposed to estimate the tritium composition in the bed, x_T, by measurement of the tritium composition of the gas phase above the bed: y_T. To simplify the discussion and presentation, assume the bed contains only tritium and protium. The separation factor for the hydride, $\alpha_{T,H}$, is defined as the ratio of tritium-to-protium mole fractions in the gas phase divided by those of the solid phase. For a separation factor of 1.0, x_T equals y_T and x_H equals y_H. The relationship between x_T and y_T has been derived[4] and using that result in Eqn. 3 yields

$$g_{bed} = \left(\frac{Q}{M}\right) \cdot \frac{y_T}{\alpha+(1-\alpha)y_T} \cdot MR \cdot \frac{M_H}{MW_H} \cdot \frac{MW_T}{2} \qquad (4)$$

It is assumed in Eqn. 4 that the tritium composition is uniform in the hydride material. For the methods proposed, the uncertainty in the parameters MR, M_H, MW_H, and MW_T do not contribute significantly to the error in calculating g_{bed} so variances for these terms will not be derived or calculated.

Although the equation can be derived to include uncertainties in the separation factor value for a hydride, for this discussion it will be assumed $\alpha_{T,H}$ equals one so the discussion can focus on Q/M and gas measurement uncertainties. For this case, Eqn. 4 becomes

$$g_{bed} = \left(\frac{Q}{M}\right) \cdot y_T \cdot MR \cdot \frac{M_H}{MW_H} \cdot \frac{MW_T}{2} \qquad (5)$$

and the random error variance is given by

$$\sigma_{g_{bed}}^2 = (g_{bed})^2 \left[\left(\frac{\sigma_{Q/M}}{Q/M}\right)^2 + \left(\frac{\sigma_{y_T}}{y_T}\right)^2\right] \qquad (6)$$

Within the brackets in Eqn. 6, the first term is the relative error in estimating the bed hydride loading while the second term is the relative error in the gas composition measurement. In most instances, relative errors for gas composition measurements can be on the order of several percent. The uncertainty in the hydride bed loading value will now be established, and its impact will be compared to that for the gas composition uncertainty for two estimation methods.

IV. THE MID-POINT APPROXIMATION (MPA) METHOD

Metal hydride beds, like tanks or other physical containers, have limits on the maximum amount of gas that can be contained within the vessel. There are theoretical limits for the hydride material and also process limitations such as lowest temperature and highest pressure that can be applied to a bed. A bed will not be instrumented for IBA measurements if the bed's maximum tritium inventory will be below the IBA detection limit, based on the bed's expected tritium composition.

Process limitations and material selection create a maximum loading value, Q/M_{max}, that can be used in Eqn. 5. Without focused operational tracking, the amount of gas stored in the bed is typically unknown. The Mid-Point Approximation (MPA) method will be used to estimate this amount. If a hydride bed inventory is assumed to be one-half of its maximum value, all possible bed loadings are within 50% of the bed's capacity from this mid-point value, Q/M_{mid}. This span of 50% of bed

capacity can be treated as a tolerance for bed inventories since all measured values will fall within that range. For statistical analysis, a value of two times the uncertainty (σ) is typically taken as equal to the tolerance, so the uncertainty of a hydride bed being loaded at it mid-point value is one-fourth of its maximum value [$\sigma_{Q/Mmid} = ¼ \cdot Q/M_{max}$].

Under the assumption that the bed is at its mid-point and is at least 25% of the full-bed inventory, Eqn. 6 shows that σ_{gBed} will increase with an increase in composition measurement uncertainty. A dual canister bed filled to 0.725 Q/M with 1.204% tritium gas will contain the 9.75 g: the estimated IBA detection limit. The mid-point loading value will be 0.3625 Q/M, corresponding to 4.875 g of tritium. The contribution to the uncertainty just from the estimate of Q/M is 2.437 g, which is one-half of the bed's mid-point inventory (as expected). Adding in a relative tritium composition measurement uncertainty of 10% increases σ_{gBed} to only 2.486 g, showing the results are truly driven by the bed gas inventory uncertainty. The mid-point inventory result for this example is thus 4.875 ± 2.486 g of tritium. As the gas composition value decreases, the inventory and uncertainty values will also decrease.

V. TECHNOLOGY AND PROCESS KNOWLEDGE UNCERTAINTY REDUCTIONS

Eqn. 6 shows that much smaller measurement uncertainties can be obtained if the uncertainty of the bed gas inventory loading, expressed as Q/M, can be reduced. The pressure-composition-temperature (PCT) properties will be utilized to decrease the uncertainty in a bed's Q/M value.

Most metal hydrides used for process tritium storage consist of a mixture of two hydride phases: typically an alpha-phase and a beta-phase. The alpha-phase is the initial solubility of gas into the hydride. There is a steep increase in the PCT isotherm plots for the hydride, typically plotted as the logarithm of pressure versus Q/M. At some Q/M value characteristic of the hydride, additional gas absorption produces some beta-phase hydride. As more gas is absorbed by the hydride, less alpha-phase material is present and more beta-phase material is formed. The mixture of alpha- and beta-phase hydrides typically produces a relatively horizontal line on the isotherm plot of logarithmic pressure versus Q/M values. As gas absorption by the hydride increases, the hydride becomes essentially pure beta-phase material and additional gas absorption into the hydride is beta-phase solubility of the gas. Gas solubility in the beta-phase also exhibits a steep increase in the slope of the PCT isotherm.

Hydrides like depleted uranium show a transition from the alpha plus beta-phase to the alpha-phase nominally at loadings (Q/M values) around 0.15 Q/M and from the alpha plus beta-phase to the beta-phase nominally at loadings around 2.90 Q/M. These transition points vary with temperature; the plateau region transition to pure beta-phase occurs at values less than 2.90 Q/M as temperature increases. The PCT properties change relatively little with tritium exposure for such hydrides.

In contrast, significant changes occur in the PCT properties due to tritium exposure for LANA0.75 alloys [5]. As tritium exposure duration increases, alterations of the alpha-phase and plateau region properties change drastically, but there is relatively less variation in the location of the pure beta-phase. The beta-phase PCT properties of LANA0.75 can be used to obtain reduced uncertainties estimates of LANA0.75 bed tritium inventories.

The low tritium inventory PACE beds can be filled with tritium containing gases at a temperature and pressure that indicate the bed is "full," that is the hydride is in the beta-phase of the material. Based on this technique, an estimate can be made of the bed Q/M inventory based on bench scale PCT properties. For example, Fig. 5 of Ref. 5 shows a tolerance of approximately ± 0.060 Q/M for a 0.61 Q/M value corresponding to a temperature of 80°C and a pressure of 100 kPa. This tolerance produces an uncertainty of 0.030 Q/M, which can be used in Eqn. 6.

A sample calculation will be performed to compare the results of using hydride beta-phase information to estimate Q/M to the results of using the MPA method. Assume a gas composition measurement uncertainty of 10% as was done for the MPA sample calculation and use 0.03 Q/M for the bed loading uncertainty. Even though it was stated that the maximum bed loading is 0.725 Q/M, assume the bed is loaded to produce the 0.030 Q/M uncertainty to be used in Eqn. 6. The bed gas composition of 1.204% tritium will have the bed filled with 9.75 g tritium, but the bed uncertainty is now reduced to 1.055 g. It is worth noting that the relative contribution from the uncertainty from the Q/M term in Eqn. 6 is (0.030/0.725) or about 4% relative uncertainty compared to the assumed relative composition measurement uncertainty of 10% that now drives the uncertainty.

VI. DISCUSSION

On a facility-wide PI basis, the contributions to the σ_{EI}^2 term in Eqn. 2 from these low tritium inventory beds are typically much smaller than the variance contributions of the higher tritium content beds instrumented for IBA

measurements. However, not including an estimate of the inventory uncertainty from these beds could lead to a systematic error in the ID calculation, depending on the amount of tritium in the beds.

The MPA method produces the terms needed for Eqn. 1 and Eqn. 2. Use of the MPA method requires little time and effort, other than obtaining a gas composition measurement, to produce PI values and uncertainties that typically contribute little to the facility LEID.

The power of the MPA method is that it establishes an upper bound on tritium uncertainty in a hydride bed not instrumented for IBA measurements. As the gas composition stored on the beds decreases, so do the inventory value and uncertainty. The gas composition value for the bed is typically available from process operations measurements and is not required to be of low uncertainty.

The MPA method could also be applied in other similar accounting applications, such as tanks of low tritium content water that are large enough to contain accountable quantities of tritium. The MPA method could easily be employed for deuterium hydride beds used in fusion applications that may contain accountable quantities of tritium rather than installing IBA instrumentation for the beds and requiring the gas be desorbed to a tank for inventory purposes.

Better gram inventory estimates and uncertainties are obtained when process knowledge can be combined with physical property data of the hydride material within the bed. Extra effort is needed to prepare the bed for PI, but significant reductions in measurement uncertainties can be obtained for the bed.

There are a number of factors that can affect the estimated value of Q/M for a "process-full" bed. The PCT properties for hydrides can vary by lot or manufacture so this can produce additional variations in the Q/M uncertainty value selected for beta-phase inventory calculations. Production scale beds will also have relatively large temperature variations compared to bench scale test results, and bed temperature measurement points may not be representative of the hydride temperature within the bed. The easiest measurement to make under these conditions is pressure, though the pressure will vary based on thermal equilibration of the bed and the ability to maintain the bed temperature within some temperature control band. The measured pressure may also be a function of the mixture of H, D, or T isotopes stored in the bed. Despite these limitations, a representative Q/M value can be selected for the bed for PI and the uncertainty value used in Eqn. 6 increased to accommodate for these additional variations in the selection of the Q/M value.

VII. CONCLUSIONS

Two methods have been proposed to calculate tritium inventories in low tritium feed beds. The MPA method uses only maximum bed capacity information along with a bed gas composition measurement and uncertainty to supply the necessary information for the PI process. Improved statistical parameters for bed inventory and uncertainty can be obtained if PCT data for the bed hydride material is available and the bed is placed in a process configuration that narrows down the range for the bed's Q/M value. The uncertainty in the MPA method is driven by the magnitude of the uncertainty in the Q/M value, but the uncertainty in Q/M can be drastically reduced when PCT properties of the material are combined with process knowledge during bed PI measurements.

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