

JAERI-M
85-174

BRIEF REVIEW ON TRITIUM RECOVERY FROM
INERT GASES BY URANIUM GETTER BEDS

November 1985

Toshihiko YAMANISHI, Masahiro KINOSHITA,
Kenji OKUNO and Hiroshi YOSHIDA

JAERI-Mレポートは、日本原子力研究所が不定期に公刊している研究報告書です。
入手の問合わせは、日本原子力研究所技術情報部情報資料課（〒319-11 茨城県那珂郡東海村）あて、
お申しこしてください。なお、このほかに財団法人原子力弘済会資料センター（〒319-11 茨城県那珂郡
東海村日本原子力研究所内）で複写による実費領布をおこなっております。

JAERI-M reports are issued irregularly.
Inquiries about availability of the reports should be addressed to Information Division Department
of Technical Information, Japan Atomic Energy Research Institute, Tokaimura, Naka-gun, Ibaraki-
ken 319-11, Japan.

© Japan Atomic Energy Research Institute, 1985

編集兼発行 日本原子力研究所
印刷 日青工業株式会社

BRIEF REVIEW ON TRITIUM RECOVERY FROM INERT GASES
BY URANIUM GETTER BEDS

Toshihiko YAMANISHI, Masahiro KINOSHITA, Kenji OKUNO and
Hiroshi YOSHIDA

Department of Thermonuclear Fusion Research,
Naka Fusion Research Establishment, JAERI

(Recieved October 14, 1985)

The present report gives a brief, critical review of the previously published works on tritium recovery from inert gases by uranium getter beds. The attention of the review is focused on chemical engineering aspects. There is general agreement in the fusion research community that the design model proposed by Maienschein for metal getter beds gives good description to the experimentally observed breakthrough curve. The authors question this agreement in the review, and raise some problems to be solved. An improved design model is then proposed, and subjects to be treated in future experimental studies are clarified.

KEYWORDS : Tritium Recovery, Uranium Getter Bed, Design Model,
Breakthrough Curve, Gas Film Resistance, Fixed Bed
Reactor, Uranium Hydride, Unreacted Core Model,
Mass Transfer Zone

ウランゲッターによる不活性ガス中のトリチウム回収に関する研究のレビュー

日本原子力研究所那珂研究所核融合研究部
山西 敏彦・木下 正弘・奥野 健二・吉田 浩

(1985年10月14日受理)

本報は、ウランゲッターによる不活性ガス中のトリチウム回収について、現在までに報告されている研究を化学工学的観点から調査、検討し、その結果を要約したものである。核融合研究の分野では、Maienscheinが報告したウランベッドの設計モデルは、破過実験の結果と良く一致するとされている。著者らは、この結論を疑問視し、解決すべき問題点を列挙した。加えて、改良した設計モデルを提示するとともに今後必要な実験研究課題を明らかにした。

CONTENTS

1.	INTRODUCTION	1
2.	DESIGN MODEL PROPOSED BY MAIENSCHIN FOR URANIUM GETTER BED	3
2.1	Model Basis and Assumptions	3
2.2	Comments on Maienschin's Model	6
3.	EXPERIMENTAL STUDIES ON URANIUM GETTER BEDS FOR EXAMINATION OF MAIENSCHIN'S MODEL	7
4.	PROPOSAL OF ANOTHER DESIGN MODEL	11
4.1	Derivation of Basic Equations	11
4.2	Subjects to be Treated in Future Experimental Studies	13
5.	CONCLUSION	17
	ACKNOWLEDGEMENT	18
	APPENDIX I Equilibrium of Uranium-Hydrogen System	19
	APPENDIX II Solution Method of Equation (2-2)	20
	NOMENCLATURE	23
	REFERENCES	25
	FIGURES	26

目 次

1. 緒 言	1
2. Maienscheinによるウランベッドの設計モデル	3
2.1 モデルの論拠と仮定	3
2.2 Maienscheinのモデルの検討	6
3. Maienscheinのモデルの妥当性に関するウランゲッターの実験研究	7
4. 改良設計モデルの提示	11
4.1 基礎方程式の導出	11
4.2 今後必要な実験研究課題	13
5. 結 言	17
謝辞	18
付記 I ウラン-水素系の平衡	19
付記 II (2-2)式の解法	20
記号表	23
参考文献	25
図	26

1. INTRODUCTION

In the fusion fuel cycle, there are some situations where tritium must be removed from inert gases such as helium and argon. For instance, tritium leaking to the inert gas atmosphere of a glove-box must be recovered for the removal and reuse. Although there could be several methods applicable to the tritium recovery (e.g. catalytic oxidization of tritium followed by adsorption of tritiated water on molecular sieve, and some metal getter beds), the present report deals with the uranium getter bed which is most widely used. The following are several advantages of the uranium getter bed :

1. The plateau pressure (see APPENDIX I) of its hydride at room temperature is 0.3mPa ($\sim 2 \times 10^{-6}$ torr) ; so it is possible to remove tritium in inert gases to levels of $\sim 10\text{mCi/m}^3$ (Ref. 1).
2. Tritium can be collected from the hydride by dehydriding it at comparatively low temperature (c.a. 400°C) (Ref. 2).
3. Reactive uranium powder can be made by simply hydriding and dehydriding massive metal (Refs. 1 and 3).
4. Tritium recovered as the T_2 gas is much less hazardous to handle than as T_2O recovered from an oxidation/adsorption recovery process (Ref. 4).

For achieving the continuous gas/solid contact required for getting of tritium, it is necessary to use the reactors of fixed, moving or fluidized bed types. The fixed bed reactor is

chosen in the present report because of its simple design and operation. The design study for the metal getter of fixed bed type recovering tritium has been conducted by Maienschein⁽⁴⁾; and the design model proposed by Maienschein is, to our best knowledge, the only one that has ever been reported for fusion application. Folkers et al.⁽¹⁾ and Tanabe et al.⁽³⁾ have performed experimental studies for recovery of hydrogen isotopes using uranium fixed beds, and reported that Maienschein's model well described the dynamic behavior experimentally observed. Thus, it is recognized in the fusion research community that the uranium getter bed recovering tritium can be designed by using Maienschein's model. However, Folkers et al. and Tanabe et al. did not perform reasonable examinations of Maienschein's model. Additionally, the assumptions used by Maienschein have not yet been justified by any experimental studies.

The present paper gives a brief review of the design and experimental studies previously published for uranium getter beds recovering tritium. In the review, the authors point out that the above-mentioned recognition should be reconsidered, thus raising some problems to be solved. Also, the paper proposes another design model which could overcome some of the drawbacks of Maienschein's model, pending further experimental studies.

2. DESIGN MODEL PROPOSED BY MAIENSCHN FOR URANIUM GETTER BED

Maienschein⁽⁴⁾ proposed a design model of the metal getter bed using cerium. Since the mechanism of the hydriding reaction of cerium is essentially the same as that of uranium, his model can be applied to beds using uranium.

2.1 Model Basis and Assumptions

Maienschein assumed that the hydrogen (or deuterium or tritium) gettering process comprised the following steps : 1) Diffusion of hydrogen molecules through the gas film to the uranium surface ; 2) diffusion of hydrogen molecules through a layer of hydride to the unhydrided uranium surface ; 3) dissociation of hydrogen molecules to atoms on the uranium surface ; and 4) reaction of hydrogen with unhydrided uranium. It is known that uranium hydride tends to flake and spall because of the volume change induced by the hydriding (Ref. 5). Fresh surface of uranium powder can continually be exposed by this phenomena against the hydrogen gas. Based on that, Maienschein assumed that step 2 was not the controlling step. He also assumed that both the metal/hydrogen reaction and the dissociation of the hydrogen molecules to atoms were rapid, and step 1 was therefore the controlling step in the gettering process.

Under the assumptions made by Maienschein, one can write

$$(4\pi R^3/3)(\partial \bar{C}/\partial t)_z = 4\pi R^2 k_x (C - C_p) , \quad (2-1)$$

where \bar{C} is the average concentration of hydrogen in the uranium phase and C_p is the concentration of hydrogen in the gas phase at the uranium surface in equilibrium with uranium hydride ; R and k_x are the mass transfer coefficient and the radius of a uranium particle, respectively. Here, the following assumptions are further made : 1) The inert gas containing hydrogen flows downward through the bed of metal powder under isothermal and isobaric conditions ; 2) the concentration gradient in the radial direction in the gas phase is negligible ; and 3) the axial diffusion in the bed is negligible. By using Eq. (2-1), the total material balance for hydrogen in the fixed bed reactor can be written by

$$u(\partial C/\partial z)_t + \epsilon(\partial C/\partial t)_z + (1-\epsilon)(\partial \bar{C}/\partial t)_z = u(\partial C/\partial z)_t + \epsilon(\partial C/\partial t)_z + (1-\epsilon)k_x 3(C - C_p)/R = 0 , \quad (2-2)$$

where u , z , t and ϵ are the superficial velocity, space variable of the bed length, time and void fraction of the bed, respectively. Initial and boundary conditions are given by

$$\left. \begin{array}{l} \bar{C} = C = 0 \text{ at } t = 0 \text{ and } z_0 \geq z \geq 0 \\ C = C_0 \text{ at } z = 0 \text{ and } t \geq 0 \end{array} \right\} , \quad (2-3)$$

where C_0 is the concentration of hydrogen in the inlet stream and z_0 is the total bed length.

Maienschein gave the solution of Eq. (2-2) by using the approximation of constant pattern of the breakthrough curve, but did not describe its solution procedure. The rigorous solution procedure using the constant pattern approximation is therefore described by the authors in APPENDIX II : A key equation thus obtained is

$$L_{MTZ} = (uR) \ln\{(C_E - C_p)/(C_B - C_p)\} / \{3(1-\epsilon)k_x\} , \quad (2-4)$$

where L_{MTZ} is the length of the mass transfer zone, and C_B and C_E are the concentrations of hydrogen in the gas phase at break and end points of the breakthrough curve, respectively. By using the j-factor analogy and empirical correlations, the mass transfer coefficient for a fixed bed reactor can be estimated from

$$(k_x/u)(Sc)^{2/3} = 0.91Re^{-0.51} , \quad (2-5)$$

where Sc and Re are Schmidt and Reynolds Numbers, respectively. Substituting Eq. (2-5) into (2-4) gives

$$L_{MTZ} = A_3 u^{0.51} \ln\{(C_E - C_p)/(C_B - C_p)\} , \quad (2-6)$$

where A_3 is a combined coefficient of the constant terms.

2.2 Comments on Maienschein's model

Although there could be some problems of Maienschein's model, the authors point out the three problems :

1. Maienschein assumed that the fresh surface of metal powder was continually exposed against the hydrogen gas owing to the spalling and flaking effects. Nevertheless, effects of the variation of the uranium particle radius on the gas film coefficient are not accounted for in his model.

2. There is no guarantee that the mass transfer through the gas film is the controlling step. The degree of significance of the gas film resistance must depend on the gas velocity. Especially in the high gas velocity range, the uranium/hydrogen reaction rate can possibly be a major factor affecting the hydrogen gettering process.

3. Maienschein applied the constant pattern approximation in the solution of Eq. (2-2). This approximation can be applied only to the case where $\partial^2 \bar{C} / \partial C^2$ is negative and the getter bed is adequately longer than the mass transfer zone.

3. EXPERIMENTAL STUDIES ON URANIUM GETTER BEDS FOR EXAMINATION OF MAIENSCHHEIN'S MODEL

Folkers et al.⁽¹⁾ and Tanabe et al.⁽³⁾ have performed experimental studies for uranium getters by using fixed bed reactors, and examined the applicability of Maienschein's model.

Folkers et al. rearranged the experimental data of deuterium recovery by a purification factor (P.F.) and an atomic ratio (D/U) :

$$u^{1/2} \ln(\text{P.F.}) = - 0.048(D/U) + 0.144 , \quad (3-1)$$

where

$$\text{P.F.} = (\text{concentration of } D_2 \text{ in, } C_{in}) / (\text{concentration of } D_2 \text{ out, } C_{out}) . \quad (3-2)$$

The atomic ratio was calculated from the total amount of deuterium introduced into the uranium bed ; therefore, it was the variable which was proportional to time. A plot of P.F. vs. D/U is shown in Fig. 3-1. Since P.F. and D/U can be considered a dimensionless concentration and a modified dimensionless time, respectively, it can be understood that Fig. 3-1 represents the breakthrough curves. Replacing L_{MTZ} and C_B in Eq. (2-6) by z' and C , respectively, and regarding 0.51 as $1/2$, we obtain

$$z' = A_3 u^{1/2} \ln\{(C_0 - C_p)/(C - C_p)\} , \quad (3-3)$$

where z' is the coordinate along the bed length whose origin is the front of the mass transfer zone. In the case where C_p is very small compared to C and C_0 , Eq. (3-3) can be reduced to

$$z' = A_3 u^{1/2} \ln(C_0/C) . \quad (3-4)$$

A typical hydrogen concentration profile for the fixed getter bed is shown in Fig. 3-2 ; the hydrogen concentration in the gas phase is equal to C_0 where z' is zero. This equation can present the concentration gradient of hydrogen in the gas phase within the mass transfer zone. Because of the constant pattern approximation used in the model, Eq. (3-4) also gives the breakthrough curve. Folkers et al. therefore used Eq. (3-1) instead of Eq. (3-4). However, as revealed in Fig. 3-1, the time during which the deuterium concentration in the outlet gas increases from C_p to C_0 accounts for about 70% of the breakthrough time. Accordingly, it can be understood that the bed length of the getter is not adequately longer than the mass transfer zone : the approximation of constant pattern and therefore Maienschein's model cannot be applied to this case.

Tanabe et al. measured the breakthrough curve of a uranium bed, regarding the operating temperature, flow rate of gas mixture and hydrogen concentration in the inlet gas as parameters.

Figure 3-3 shows the effect of the operating temperature on the breakthrough curves. The uranium powder used as getter material is generally activated through several hydriding/dehydriding processes, and a slight amount of hydrogen remains in the powder. At comparatively low temperature, the solid solution and the uranium hydride are formed even in the extremely small hydrogen content range, and the equilibrium partial pressure of hydrogen in the gas phase is equal to the plateau pressure (see APPENDIX I). For the above reason, the concentration of hydrogen in the outlet gas before the break point is equal to the plateau pressure and depends on the operating temperature alone ; and these characteristics were verified by Tanabe et al. Figure 3-4 shows the breakthrough curves measured at three different gas flow rates. The plot of $\ln\{(C_0 - C_p)/(C - C_p)\}$ versus z' given in Fig. 3-5 exhibits a linear relationship. Tanabe et al. then concluded that the uranium getter process was well described by Maienschein's model.

Applying the approximate solution using the over-all mass transfer coefficient, we can derive the design equation similar to that of Maienschein's model in accordance with the procedure described in APPENDIX II :

$$z' = (uR) \ln\{(C_0 - C_p)/(C - C_p)\} / \{3(1 - \epsilon)K_{ox}\} , \quad (3-6)$$

where K_{ox} is the over-all mass transfer coefficient. The over-all mass transfer coefficient includes the hydriding reaction rate

and the mass transfer rate through the gas film. A significant result obtained by Tanabe et al. was that $\ln\{(C_0 - C_p)/(C - C_p)\}$ was proportional to z' . For this reason, they concluded that the validity of Maienschein's model was verified. However, their paper discussed neither the value of the slope nor the dependency of the slope on temperature, gas flow rate and hydrogen concentration. We can never make a reasonable examination of Maienschein's model only by verifying the proportional relation between $\ln\{(C_0 - C_p)/(C - C_p)\}$ and z' . The value of the slope and its dependency on the above-mentioned parameters are even more significant.

From Eqs. (A-11) and (2-5), we obtain

$$t^+ = A_3' u^{-0.51} , \quad (3-5)$$

where A_3' is a combined coefficient of the constant terms. Accordingly, if the uranium getter bed can be simulated by Maienschein's model, t^+ must be at least proportional to $u^{-0.51}$. As observed from Fig. 3-3, however, the proportional relationship is not obtained, and t^+ remains almost unchanged for the three breakthrough curves shown: The gas film resistance is not significant under the conditions in the figure.

Thus, the validity of Maienschein's model has been verified neither by Folkers et al. nor by Tanabe et al.

4. PROPOSAL OF ANOTHER DESIGN MODEL

4.1 Derivation of Basic Equations

The authors propose another design model which could overcome some of the previously mentioned drawbacks of Maienschein's model. The proposed model contrasts with Maienschein's model in that the effects of the variation of the uranium particle radius and the uranium/hydrogen reaction rate are taken into account. In addition, the approximation of constant pattern of the breakthrough curve is not used in the model. For the derivation of the basic equations, we apply the following assumption: Since the hydriding reaction is rapid in comparison with the diffusion of hydrogen atoms through uranium, the hydrogen/uranium reaction occurs at the surface of uranium alone; and the unreacted core model can therefore be applied.

We now apply the pseudo-steady state approximation for a uranium particle:

$$W_H = 4\pi r^2 k_X (C - C_S) = 4\pi r^2 k_S (C_S)^{1/2} = \text{const.}, \quad (4-1)$$

where k_S is the reaction rate constant per unit area and W_H is the mass transfer rate of hydrogen through the gas film. The kinetic order is assumed to be 1/2 with respect to hydrogen pressure⁽⁵⁾. From Eq. (4-1), we obtain

$$C_S = (1/2)(2C + k_S^2/k_X^2 - \{4Ck_S^2/k_X^2 + (k_S^2/k_X^2)^2\}^{1/2}) . \quad (4-2)$$

Accordingly, Eq. (4-1) can be rewritten by

$$W_H = (1/2)(\{4Ck_S^2 + (k_S^4/k_X^2)\}^{1/2} - k_S^2/k_X)4\pi r^2 . \quad (4-3)$$

Since the hydriding reaction is expressed by $H_2 + (2/3)U \rightarrow (2/3)UH_3$, the material balance for uranium is given by

$$- \partial(4\pi r^3 \rho_S / 3) / \partial t = (2/3)W_H , \quad (4-4)$$

where ρ_S is the density of solid. Since the radius of the uranium particle is very small, we assume that the variation of k_X can be expressed by

$$k_X = k_{XO} R / r , \quad (4-5)$$

where k_{XO} and R are the mass transfer coefficient and radius of the uranium particle before the reaction proceeds, respectively. Substituting Eqs. (4-3) and (4-5) into (4-4) gives

$$\partial r / \partial t = - \{1/(3\rho_S)\} \{ \{4Ck_S^2 + k_S^4 r^2 / (k_{XO} R)^2\}^{1/2} - k_S^2 r / (k_{XO} R) \} . \quad (4-6)$$

Equation (2-2) can be written by

$$u(\partial C/\partial z)_t + \varepsilon(\partial C/\partial t)_z - \{9r^2\rho_s(1-\varepsilon)/(2R^3)\}(\partial r/\partial t) = 0 \quad (4-7)$$

By solving Eqs. (4-7) and (4-6) in accordance with the Method of Characteristics Technique described by Acrivos (Ref.6), we can calculate the breakthrough curve. When r becomes zero, the reaction is considered terminated for the uranium particle.

Thus, the proposed model is not rigorous yet, but presents significant improvements of Maienschein's model.

4.2 Subjects to be Treated in Future Experimental Studies

In the preceding section, we derived a set of design equations by considering both the external diffusion and the hydriding reaction steps. To estimate the major parameters in the model such as k_s and k_{xO} , the kinetics of the gettering process must be studied with the thermal balance under the condition that either the external diffusion or the hydriding reaction is the rate-controlling step. For instance, the former can be the rate-controlling step in the case where the flow rate of the gas mixture is very small and the latter can be the rate-controlling step in the high gas flow rate range. In this section, the relation between the conversion ratio and reaction time is derived for the single-resistance cases (Ref. 7). The concentration of hydrogen in the gas phase is assumed to be constant and is denoted by C_0 .

(i) Hydridding reaction is rate-controlling step

For this case, one can write

$$- dr/dt = 2k_s(C_0)^{1/2}/(3\rho_s) . \quad (4-8)$$

Relation between x_B and r is described by

$$(1-x_B) = (r/R)^3 \quad (4-9)$$

and

$$- dx_B/dt = (3r^2/R^3)(dr/dt) . \quad (4-10)$$

Substituting Eqs. (4-8) and (4-9) into (4-10) gives

$$dx_B/dt = (1-x_B)^{2/3} 2k_s(C_0)^{1/2}/(R\rho_s) . \quad (4-11)$$

Integrating Eq. (4-11) gives

$$t = 3R\rho_s \{1 - (1-x_B)^{1/3}\} / \{2k_s(C_0)^{1/2}\} . \quad (4-12)$$

The plot of t vs. $\{1 - (1-x_B)^{1/3}\}$ gives a straight line whose slope is $3R\rho_s / \{2k_s(C_0)^{1/2}\}$.

(ii) External diffusion is rate-controlling step

For this case, we obtain

$$-r^2 dr/dt = 2k_{xO} Rr(C_0 - C_p)/(3R\rho_s) . \quad (4-13)$$

Substituting Eqs. (4-13) into (4-10) gives

$$dx_B/dt = (1-x_B)^{1/3} 2k_{xO} (C_0 - C_p)/(R\rho_s) . \quad (4-14)$$

Integrating Eq. (4-14) gives

$$t = 3R\rho_s \{1 - (1-x_B)^{2/3}\} / \{4k_{xO} (C_0 - C_p)\} . \quad (4-15)$$

In the case where C_p is very small in comparison with C_0 , Eq. (4-15) can be rewritten by

$$t = 3R\rho_s \{1 - (1-x_B)^{2/3}\} / (4k_{xO} C_0) . \quad (4-16)$$

The plot of t vs. $\{1 - (1-x_B)^{2/3}\}$ gives a straight line whose slope is $3R\rho_s / (4k_{xO} C_0)$.

From Eqs. (4-12) and (4-16), k_s and k_{xO} can be calculated. If neither Eq. (4-12) nor Eq. (4-16) can describe the experimental result, we must derive design equations by using another

model such as the volume reaction model (Ref. 8). If it has been verified that the proposed model can well describe the experimental result, we can proceed with the next step : It is necessary to perform hydrogen recovery experiments and compare the experimentally observed breakthrough curve with the curve predicted by the design model for examination of the validity of the model.

5. CONCLUSION

The design study for the uranium getter bed performed by Maienschein and the experimental studies where Maienschein's model was examined, have critically been reviewed in the present report. Some of the major conclusions are recapitulated here.

(1) There is general agreement in the fusion research community that the breakthrough curve is well described by Maienschein's model. In our opinion, however, no reasonable examination of Maienschein's model has been performed yet. For example, the workers in the experimental studies verified only the linear relationship between z' and $\ln(C_0/C)$, and did not discuss the value of the slope and the dependence of the slope on operating parameters.

(2) The authors do not claim that Maienschein's model fails to describe the actual breakthrough curve, but can point out three major drawbacks of the model : The effect of variation of the particle radius on the gas film coefficient is not taken into consideration ; the model does not account for the hydrogen/uranium reaction step ; and it uses the approximation of constant pattern of the breakthrough curve.

(3) The authors propose another design model that differs from Maienschein's model in that the above three drawbacks are eliminated.

(4) Some discussion is made on experimental studies needed to

verify the applicability of the proposed model and determine the key parameters used in the model.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Dr. M. Tanaka and Mr. Y. Naruse for their encouragement and guidance.

verify the applicability of the proposed model and determine the key parameters used in the model.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Dr. M. Tanaka and Mr. Y. Naruse for their encouragement and guidance.

APPENDIX I Equilibrium of Uranium-Hydrogen System

Figure A-1 shows the pressure-concentration-temperature (P-C-T) relation for the hydrogen-uranium system. As shown in the figure, each equilibrium isotherm consists of three parts. Two phases of the uranium hydride and solid solution coexist in the plateau region. In accordance with Gibbs' phase rule,

$$\begin{aligned} (\text{degrees of freedom}) = (\text{number of components}) - (\text{number of} \\ \text{phases}) + 2 . \end{aligned} \quad (\text{A-1})$$

The number of components is two and that of phases is three in this case, and the degree of freedom is unity. Accordingly, the equilibrium hydrogen pressure depends on temperature alone and remains constant without being affected by the hydrogen content. This equilibrium pressure is known as the plateau (or dissociation) pressure.

APPENDIX II Solution Method of Equation (2-2)

The moving rate of the mass transfer zone, v_a , is given by

$$v_a = (\partial z / \partial t)_C . \quad (A-1)$$

Since the hydrogen concentration in the gas phase is a function of z and t ,

$$dC = (\partial C / \partial z)_t dz + (\partial C / \partial t)_z dt . \quad (A-2)$$

Hence,

$$(\partial C / \partial z)_t (\partial z / \partial t)_C + (\partial C / \partial t)_z = 0 . \quad (A-3)$$

From Eqs. (A-1) and (A-3),

$$v_a = - (\partial C / \partial t)_z / (\partial C / \partial z)_t . \quad (A-4)$$

Since \bar{C} can be considered a function of C ,

$$(\partial \bar{C} / \partial t)_z = (\partial \bar{C} / \partial C)_z (\partial C / \partial t)_z . \quad (A-5)$$

From Eqs. (A-4), (A-5), (2-1) and (2-2), we obtain

$$v_a = u / \{ \varepsilon + (1-\varepsilon)(\partial \bar{C} / \partial C)_z \} . \quad (\text{A-6})$$

The moving rate of the mass transfer zone is assumed to be constant :

$$(\partial \bar{C} / \partial C)_z = A_1 \text{ (constant)} . \quad (\text{A-7})$$

Accordingly,

$$\bar{C} = A_1 C + A_2 . \quad (\text{A-8})$$

Equation (2-7) is to be solved under following boundary conditions :

$$\left. \begin{array}{l} C = 0 \text{ at } \bar{C} = 0 \\ C = C_0 \text{ at } \bar{C} = \bar{C}_0 \end{array} \right\} . \quad (\text{A-9})$$

From Eqs. (A-8) and (A-9), the relation between \bar{C} and C is expressed by

$$\bar{C} = (\bar{C}_0 / C_0) C . \quad (\text{A-10})$$

Substituting Eq. (A-10) into Eq. (2-1) and integrating the resultant equation give

$$t^+ = R\bar{C}_0/3K_x C_0 \int_{C_B}^{C_E} dC/(C-C_p) , \quad (A-11)$$

where t^+ is the time during which the hydrogen concentration in the gas phase leaving the bed increases from C_B to C_E , and C_B and C_E are the concentrations of hydrogen in the gas phase at break and end points of the breakthrough curve, respectively. The moving rate of the mass transfer zone can be calculated from Eqs. (A-6) and (A-10) :

$$v_a = u/\{\varepsilon + (1-\varepsilon)(\bar{C}_0/C_0)\} . \quad (A-12)$$

Generally, ε is very small in comparison with $(1-\varepsilon)\bar{C}_0/C_0$:

$$v_a = uC_0/\{\bar{C}_0(1-\varepsilon)\} . \quad (A-13)$$

From Eqs. (A-11) and (A-13), L_{MTZ} is expressed by

$$\begin{aligned} L_{MTZ} &= v_a t^+ \\ &= uR/\{3(1-\varepsilon)k_x\} \int_{C_B}^{C_E} dC/(C-C_p) = uR/\{3(1-\varepsilon)k_x\} \ln\{(C_E - \\ & C_p)/(C_B - C_p)\} . \end{aligned} \quad (A-14)$$

NOMENCLATURE

- A_1 = constant in Eq. (A-7) (-)
 A_2 = integration constant in Eq. (A-8) (-)
 A_3 = combined coefficient of constant terms in Eq. (2-6)
 $(m^{0.49} \cdot s^{0.51})$
 A_3' = combined coefficient of constant terms in Eq. (3-5)
 $(m^{0.51} \cdot s^{0.49})$
 C = concentration of hydrogen (or deuterium or tritium) in
gas phase (mol/m^3)
 C_B = concentration of hydrogen in gas phase at break point of
breakthrough curve (mol/m^3)
 C_E = concentration of hydrogen in gas phase at end point of
breakthrough curve (mol/m^3)
 C_0 = concentration of hydrogen in inlet stream (mol/m^3)
 C_p = concentration of hydrogen in gas phase at surface of
uranium particle in equilibrium with uranium hydride
(mol/m^3)
 C_s = concentration of hydrogen in gas phase at surface of
uranium particle (mol/m^3)
 \bar{C} = average concentration of hydrogen in uranium phase (mol/m^3)
 D_H = diffusion coefficient of hydrogen in inert gas (m^2/s)
 D/U = atomic deuterium-to-uranium ratio in Eq. (3-1) (-)
 K_{ox} = over-all mass transfer coefficient (m/s)
 k_s = reaction rate constant per unit area ($\text{mol}^{1/2}/(\text{m}^{1/2} \cdot \text{s})$)

- k_x = mass transfer coefficient (m/s)
 k_{x0} = mass transfer coefficient before reaction (m/s)
 L_{MTZ} = length of mass transfer zone (m)
P.F. = purification factor defined by Eq. (3-2) (-)
 r = radius of uranium particle (m)
 R = radius of uranium particle before reaction (m)
 Re = Reynolds Number = $2Ru\rho/\mu$ (-)
 Sc = Schmidt Number = $\mu/(\rho D_H)$ (-)
 t = time (s)
 t^+ = time during which hydrogen concentration in gas phase
leaving bed increases from C_B to C_E (s)
 u = superficial velocity (m/s)
 v_a = moving rate of mass transfer zone (m/s)
 W_H = mass transfer rate of hydrogen through gas film (mol/s)
 x_B = conversion ratio of uranium particle (-)
 z = space variable of bed length (m)
 z_0 = total bed length (m)
 z' = coordinate along length of bed, origin at front of unused
portion of bed (m)
 ϵ = void fraction of bed (-)
 μ = viscosity of gas (kg/(m.s))
 ρ = density of gas (kg/m³)
 ρ_s = density of solid (kg/m³)

REFERENCES

- 1) Folkers, C. L. and M. F. Singleton : "Collection of Deuterium on a Uranium Getter during Dynamic Flow Conditions," UCRL-76734, Lawrence Livermore National Laboratory (1975).
- 2) "Gmelins Handbuch der anorganischen Chemie," Kohlenstoff, Teil C1 (1970).
- 3) Tanabe, T., T. Yamamoto and S. Imoto : "Recovery of Hydrogen Isotopes Using a Uranium Bed," J. Less-Common Metals, 89, 393 (1983).
- 4) Maienschein, J. L. : "Feasibility of Chemical Getter Beds in Scavenging Tritium from Inert Gases," Nucl. Technol., 38, 387 (1978).
- 5) Condon, J.B. and E.A. Larson : "Kinetics of the Uranium-Hydrogen System," J. Chem. Phys., 59, 855 (1973).
- 6) Acrivos, A. : "Method of Characteristics Technique," Ind. Eng. Chem., 48, 703 (1956).
- 7) Hashimoto, K. : "Chemical Reaction Engineering," Baifūkan, Tokyo (1979) (in Japanese).
- 8) Ramachandran, P. A. and L. K. Doraiswamy : "Modeling of Noncatalytic Gas-solid Reactions," AIChE J., 28, 881 (1982).

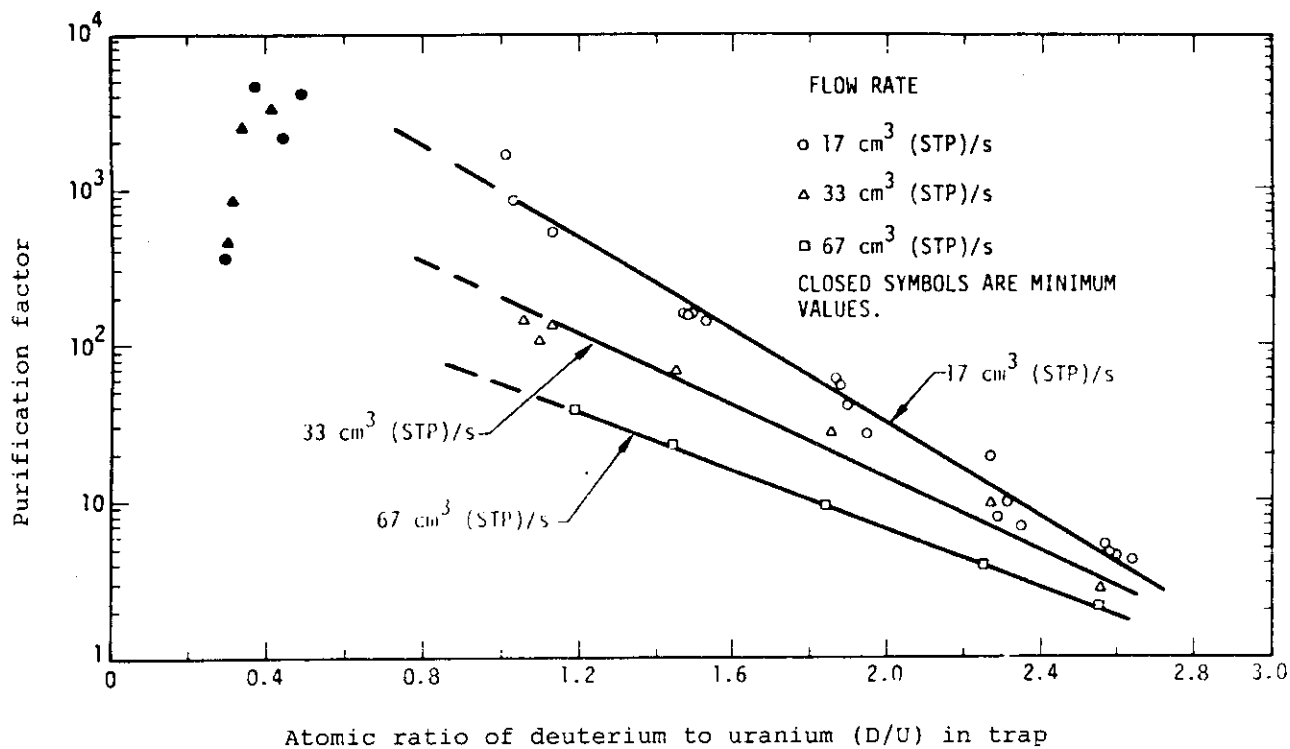


Fig. 3-1 Purification factor (C_{in}/C_{out}) vs. atomic ratio of deuterium to uranium (D/U) in getter.

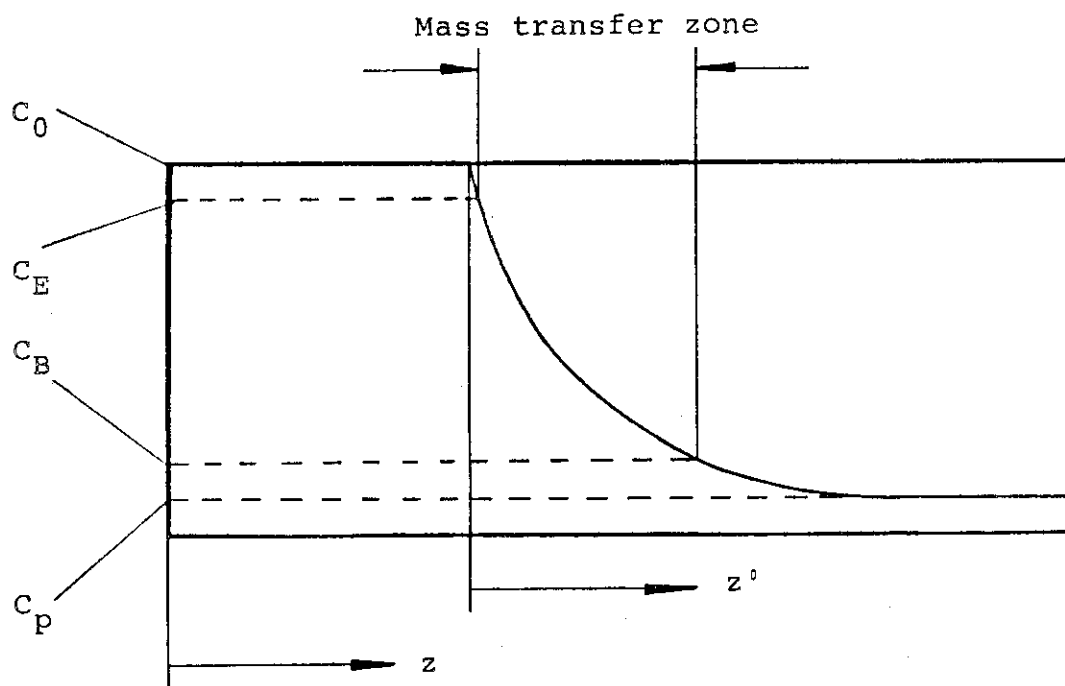


Fig. 3-2 Typical hydrogen concentration profile for fixed getter bed.

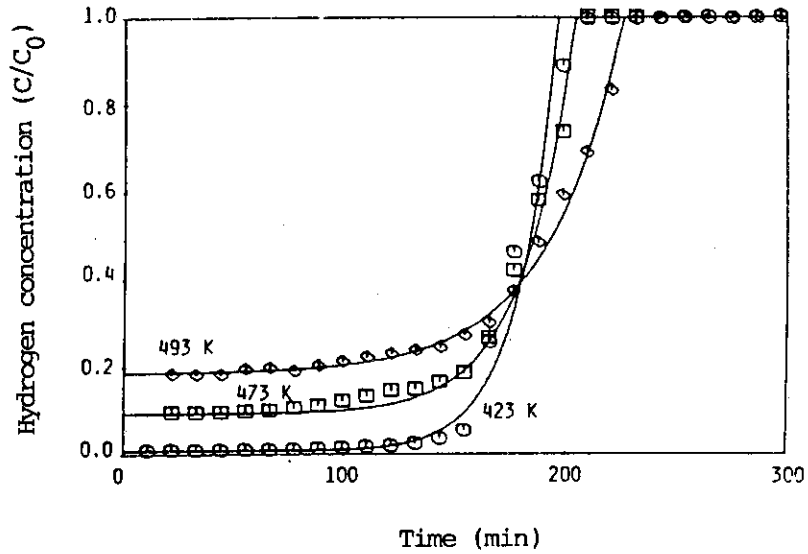


Fig. 3-3 Breakthrough curves for an inlet gas mixture consisting of vol % H₂ in argon at three different temperatures.

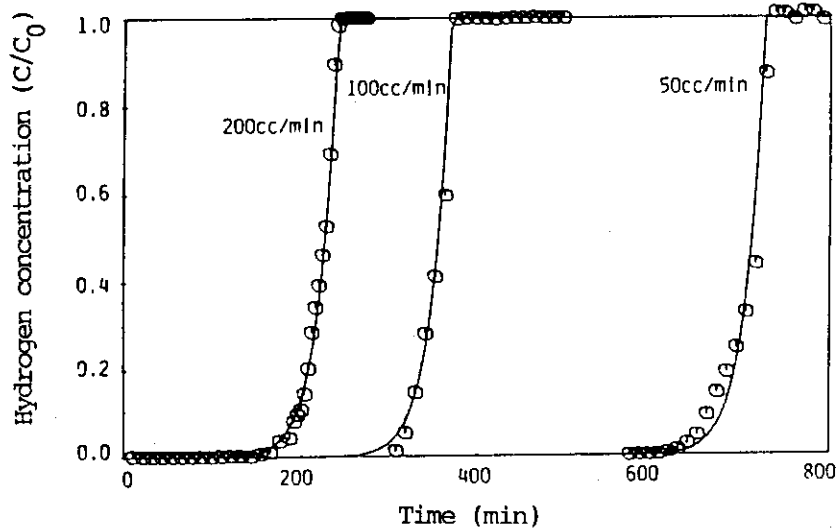


Fig. 3-4 Breakthrough curves at 273 K for an inlet gas mixture consisting of 1 vol % H₂ in argon at three different flow rates.

The value of t^+ in the cases of 50, 100 and 200 cm³/min are about 115, 100 and 100 min, respectively.

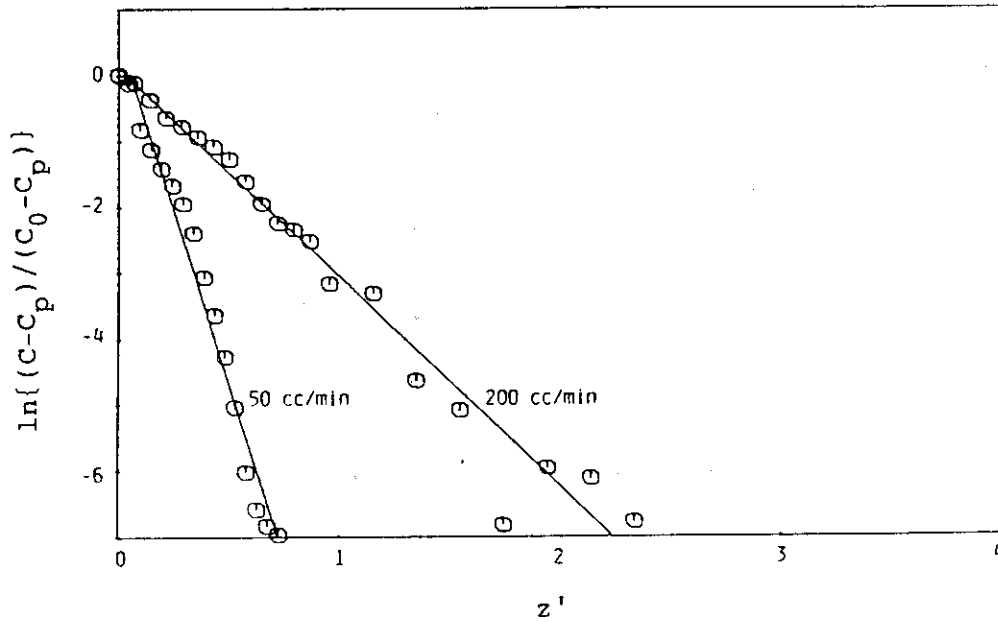


Fig. 3-5 Plot of $\ln\{(C-C_p)/(C_0-C_p)\}$ vs. z' for inlet gas mixture consisting of 1 vol % H_2 in argon for flow rates of 50 and 200 cm^3/min at 273 K.

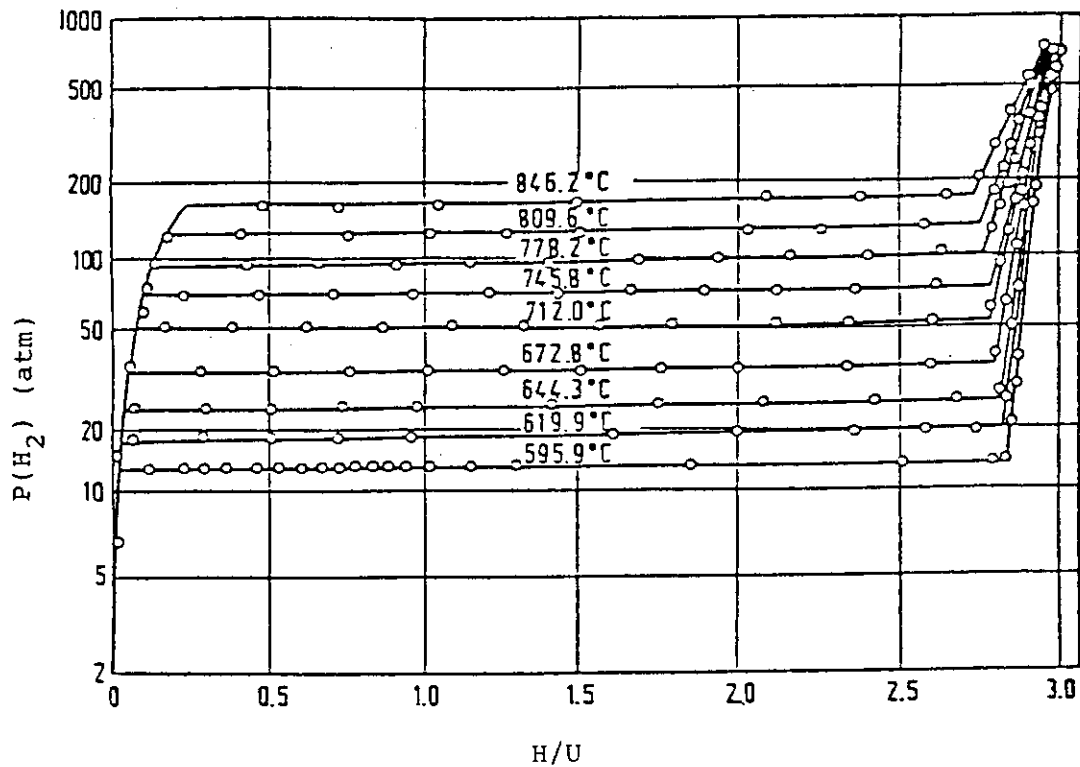


Fig. A-1 Pressure-concentration-temperature relation for uranium-hydrogen system⁽²⁾.