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ELIMINATION OF CO₂ AND H₂O AS OXYGEN TRANSPORT SPECIES IN MIXED OXIDE FUEL PINS

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IN MIXED OXIDE FUEL PINS

J. M. Leitnaker and K. E. Spear

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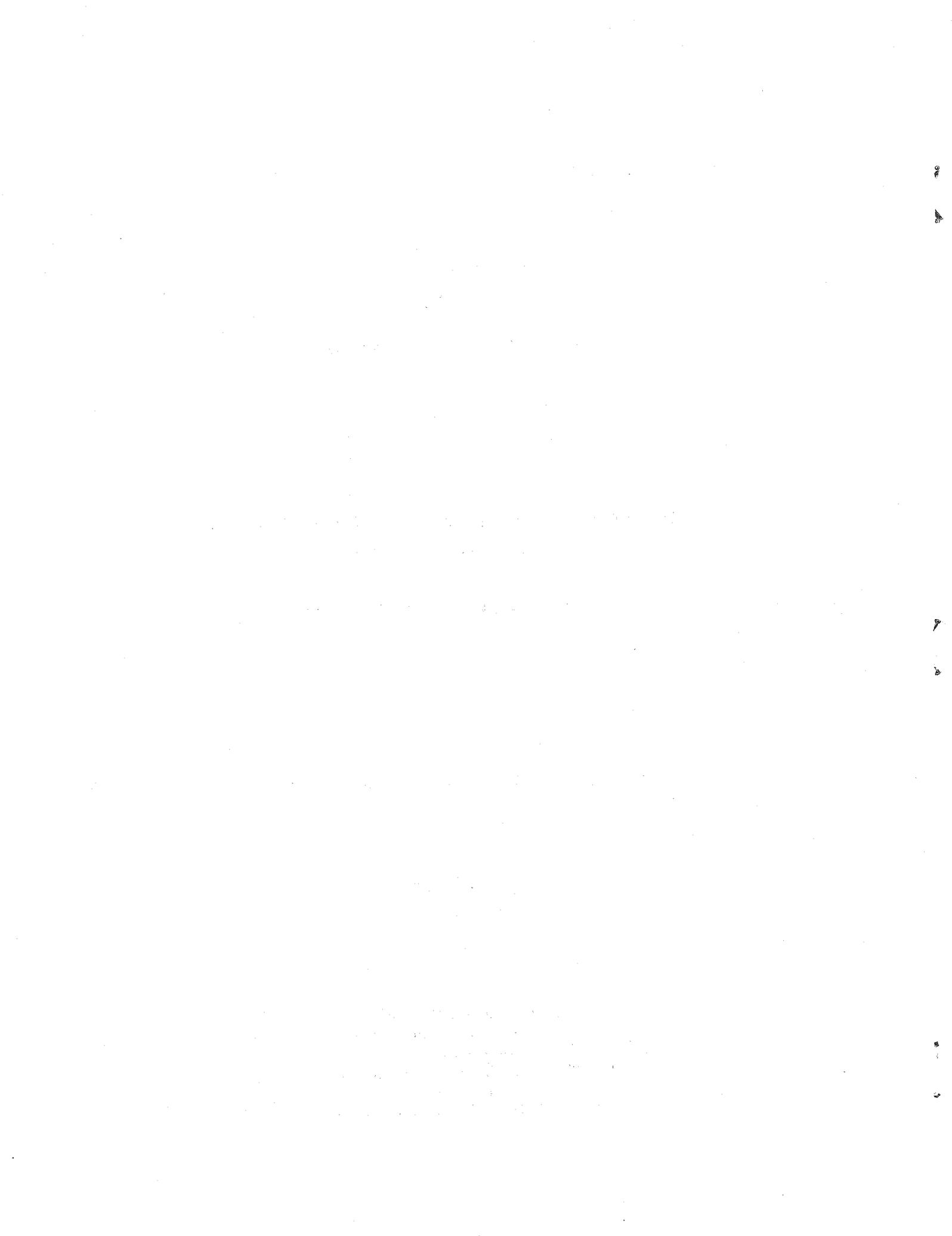
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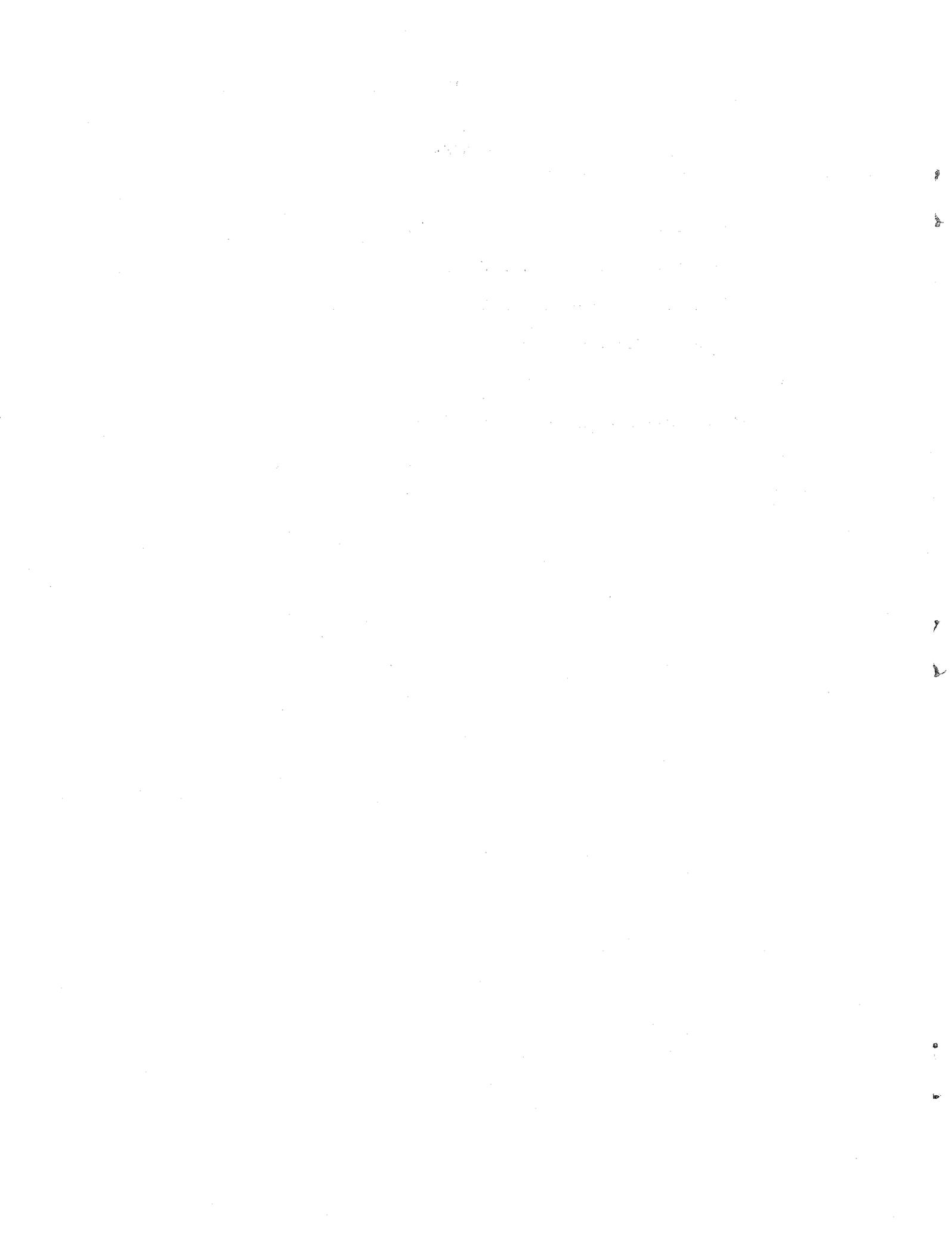


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CONTENTS

	<u>Page</u>
Abstract	1
Introduction	2
Elimination of CO ₂ from the Fuel	3
Elimination of H ₂ O from the Fuel	6
Discussion	8
Method of Measuring Oxygen Potential Gradient	10
References	12



ELIMINATION OF CO₂ AND H₂O AS OXYGEN TRANSPORT SPECIES
IN MIXED OXIDE FUEL PINS

J. M. Leitnaker and K. E. Spear*

ABSTRACT

Thermodynamic and kinetic calculations show that both CO₂ and H₂O are eliminated as oxygen transporting species in typical, near-stoichiometric LMFBR mixed oxide fuel. Thus, current gas phase transport theories do not correctly describe the oxygen distribution in such a pin. A method for measurement of the oxygen potential across an oxide fuel pin is presented.

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INTRODUCTION

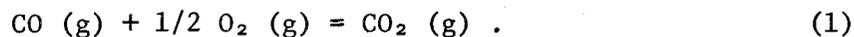
Because oxidation seems to be the principal fuel-cladding chemical interaction in stainless steel-clad oxide fuel, considerable interest has been aroused in the behavior of the oxygen within the fuel. Rand and Roberts¹⁾ recognized that the strong temperature gradient in a (U,Pu)O₂ fuel element operated at high temperatures would influence the distribution of oxygen in the fuel. In a later paper Rand and Markin²⁾ made more explicit the earlier suggestion¹⁾ that a CO₂:CO gas mixture will fix the oxygen potential, and hence the observed radial variation in oxygen-to-metal ratio in the fuel. An alternative possibility suggested was that an H₂O:H₂ gas mixture would serve as the transport mechanism, although it was recognized that "it is likely that most of the hydrogen will diffuse through the can wall during irradiation."²⁾ This theory has gained wide acceptance because it fit, at least qualitatively, the experimental observations concerning oxygen redistribution, and many experiments have been interpreted in light of its predictions.

Aitken³⁾ has shown that in hypostoichiometric (U,Pu)O₂ fuel, where the H₂O:H₂ ratio and/or CO₂:CO ratios would be reduced to a very small value, insufficient H₂O or CO₂ is present to effect the transport proposed by the Rand-Roberts-Markin theory even though the total pressure is large.

It is the purpose of this paper to present evidence that the carbon would, in fact, be removed from the system by reaction with the cladding and that the H₂ is removed from the system by diffusion through the cladding. As a result, the Rand-Roberts-Markin mechanism is not operative even for stoichiometric fuels.

ELIMINATION OF CO₂ FROM THE FUEL

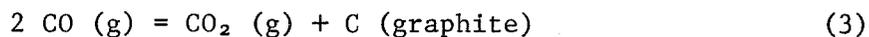
The thermodynamic basis for the Rand-Roberts-Markin theory is the equilibria which would be imposed by the existence of a constant ratio of CO₂ and CO gas across a fuel pin. The important equation to be considered is:



The standard free energy for Reaction (1), $\Delta G^\circ(1)$, is well known⁴⁾ and the oxygen potential at each point in the fuel is assumed by the theory to be determined by the relationship:

$$RT \ln P_{\text{O}_2} = 2\Delta G^\circ(1) + 2RT \ln \frac{P_{\text{CO}_2}}{P_{\text{CO}}} . \quad (2)$$

Another reaction is important within the system, however. This is:



for which $\Delta G^\circ(3)$ is given by:

$$\Delta G^\circ(3) = -40,800 + 41.7 T \text{ (calories)} , \quad (4)$$

from appropriate data in Kubaschewski et al.⁴⁾ Equation (4) reveals that at equilibrium Reaction (3) tends to proceed to the right at low temperatures and to the left at high temperatures. At 978 K, $\Delta G^\circ(3)$ is zero; thus with a fuel in equilibrium with graphite whose overall oxygen potential would correspond to a $P_{\text{CO}_2}/P_{\text{CO}}$ ratio of unity, the P_{CO} would also be unity, and sufficient gas could be assumed to be present to transport oxygen within the fuel.

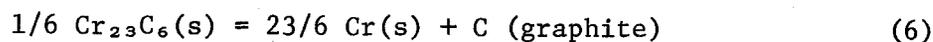
Because of the arrangement of a typical sodium-cooled reactor, a significant axial temperature gradient exists along the fuel rod. Thus, the end of the rod at which sodium enters the core will be more than 200° colder than the hottest portion of the rod. With current design criteria, significant portions of cladding interior surfaces could be 750 K or colder. At 750 K, $\Delta G^\circ(3) = -9,525$ cal, or $\log K = 2.775$. Since for Reaction (3) the equilibrium constant, K, is:

$$K = \frac{P_{\text{CO}_2} \alpha_{\text{C}}}{P_{\text{CO}}^2}, \quad (5)$$

with an oxygen potential fixed at that of the fuel surface, the equilibrium pressure of CO₂ and CO is fixed by the activity of carbon.

The activity of carbon in type 316 stainless steel is reduced, relative to graphite, by formation of the M₂₃C₆ phase. We approximate this reduction in carbon activity as follows. The solubility limit of carbon in stainless steel, in equilibrium with M₂₃C₆, is given by Weiss and Stickler⁵⁾ as 0.029 wt % at 1650°F (1172 K) and 0.015 wt % at 1500°F (1089 K). A plot of log (wt % C) versus 1/T yields the solubility limit of 2.24×10^{-4} wt % C at 750 K. The activity of carbon in austenite at this composition can be obtained by extrapolating the data of Smith⁶⁾ on the activity of carbon in pure austenite. An activity of carbon relative to graphite of 1.82×10^{-3} at 750 K is obtained.

The carbon activity can also be computed from consideration of the equation



for which the standard free energy change ΔG° (6) is given by⁴⁾

$$\Delta G^\circ = 16,380 + 1.54 \cdot T . \quad (7)$$

By assuming the activity of chromium is 0.2 and that of Cr_{23}C_6 is 0.7, which is the mole fraction of Cr_{23}C_6 in M_{23}C_6 ,⁵⁾ we obtain an equilibrium carbon activity of 3.5×10^{-3} . The agreement within a factor of two between the two independent calculations reinforces the confidence in value of the carbon activity. Thus, at 750 K equilibrium with type 316 stainless steel containing the M_{23}C_6 phase should be established when:

$$\log \frac{P_{\text{CO}_2}}{P_{\text{CO}}} - \log P_{\text{CO}} = 5.515 . \quad (8)$$

If $P_{\text{CO}_2}/P_{\text{CO}}$ is taken as fixed at unity by the fuel near the cladding, which corresponds to a stoichiometric $(\text{U},\text{Pu})\text{O}_2$ fuel and an oxygen potential greater than that required to oxidize Mo to MoO_2 , then P_{CO} is 3.0×10^{-6} atm, which also equals P_{CO_2} for this case.

Tuma et al.⁷⁾ have recently determined carbon activities on a steel containing 18% Cr and 9% Ni (versus 18% Cr, 13% Ni, and 2% Mo for type 316 stainless steel now proposed for LMFBR). The carbon activity calculated from their equations was 2×10^{-5} in the austenite-carbide phase region. The reason for this large a discrepancy is not apparent, but we choose to use the higher activity calculated above as a more conservative number.

This calculation is important for the following reason: Transport of oxygen within a fuel might take place either by gas phase movement or by solid state diffusion, or a combination of both. Rand and Markin²⁾ believed 10 ppm C from the fuel converted to a CO:CO₂ mixture would provide enough pressure of CO and CO₂ to transport the oxygen by a gas phase mechanism. If one assumes an 85% smear density for the fuel, an effective temperature of 1200°C, 10 ppm C could produce a pressure of about 6 atm, or 6 orders of magnitude greater than that in equilibrium with M₂₃C₆ in the cladding at 750 K. However, the fact that carbides of the M₂₃C₆ type are seen concentrated near the inner cladding surface of stainless steel-clad oxide fuel rods⁸⁾ indicates that P_{CO} and P_{CO₂} will be reduced, in time, by several orders of magnitude.

ELIMINATION OF H₂O FROM THE FUEL

One can also show that the pressure of H₂ and H₂O diminishes to a very low value shortly after startup of a typical LMFBR. For calculational purposes a 0.25-in.-diam (0.635 cm) fuel rod, clad in 0.015-in. (0.0381 cm) type 316 stainless steel, of 85% smear density (U,Pu)O₂, and a fractional gas release of 0.09 cm³ (STP) per gram of fuel, all assumed to be H₂, was considered. The calculation considers a centimeter length of rod. The free volume is thus 0.0368 cm³ and the gas release is 0.204 cm³ (STP). We have used results of the study by Randall and Salmon⁹⁾ on type 347 stainless steel to approximate type 316 stainless steel. The rate of H₂ diffusion from the fuel pin, R_o, in cm³ (STP)/hr is given by:

$$R_o = \alpha \sqrt{P} \frac{A}{d} \left[\frac{\beta d \sqrt{P}}{1 + \beta d \sqrt{P}} \right], \quad (9)$$

in which P is the pressure in cm of Hg; A is the area in cm², 1.755; d is the thickness in mm, 0.381; α is given by:

$$\alpha = \alpha^{\circ} \exp(-E/2 RT) \text{ (cm}^2 \text{ torr}^{-1/2} \text{ hr}^{-1}) \quad (10)$$

β is γ/α , where γ is given by

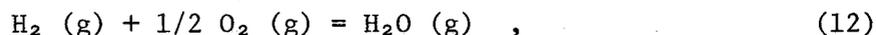
$$\gamma = \gamma^{\circ} \exp(-E'/RT) \text{ (cm/hr)} \quad (11)$$

Units of E and E' are cal/mole; those of R are cal mole⁻¹ K⁻¹, and T in K. Values of the constants are: $\alpha^{\circ} = 105.6$, $E = 33.01 \times 10^3$, $\gamma = 616.0$, and $E' = 16.86 \times 10^3$. The pressure, P, of Eq. (9) was always calculated via the ideal gas law assuming an effective gas temperature of 1073 K. At a given pressure, the amount of H₂ lost by diffusion through the cladding in incremental time was calculated. Then the amount of gas present was adjusted and the calculation repeated for a second increment, and the two results were averaged to yield a better approximation for the first increment. The calculation was repeated until the pressure of H₂ was reduced below 7.6×10^{-8} torr. The time increment size was reduced by a factor of 10 during calculation if the calculated loss was greater than the amount of H₂ present. Initial increments of 0.01 and 0.001 hr gave the same results within 0.6%. The time required to reduce the H₂ pressure to 1×10^{-10} atm was 0.33 hr at 873 K, and was 1.56 hr at 750 K, where the temperature is that of the cladding.

The above calculation indicates that any H_2 initially present will rapidly be eliminated from the fuel-cladding system by diffusion through the cladding. Since P_{H_2O} near the fuel will be fixed by the oxygen potential of the fuel surface and P_{H_2} , the value of P_{H_2O} can be calculated and must also be of this order of magnitude for stoichiometric fuel.

DISCUSSION

Aitken et al.^{10,11)} have performed transport experiments in a temperature gradient out-of-reactor which relate to this problem. They show that for $(U_{0.8}, Pu_{0.2})O_{1.94}$ heated 15 hr in a gradient between 2000 and 1250°C, the heat of transport, Q^* , is -7.1 kcal/mole down to about 1500 K. This value was interpreted by Aitken as indicating that oxygen transport does not take place via an $H_2:H_2O$ mechanism. Since the molybdenum capsule used for the experiments was surrounded with N_2 -6% H_2 , one should expect that the inside of the tube also contained H_2 at approximately 0.06 atm pressure. For the reaction



the standard free-energy change is given by:⁴⁾

$$\Delta G^\circ = -58,900 + 13.1 T = RT \ln \frac{P_{H_2}}{P_{H_2O}} + 1/2 RT \ln P_{O_2} \quad . \quad (13)$$

For $(U_{0.8}, Pu_{0.2})O_{1.94}$, from Rand and Markin,²⁾ at 1500 K, $RT \ln P_{O_2} = -142,000$ cal. Using 0.06 atm as P_{H_2} , we compute P_{H_2O} as 1.4×10^{-6} atm.

Hence, at 1500 K with the material used for the experiment, transport by H_2O at 1.4×10^{-6} atm is slower than some other as yet unspecified mechanism.

The 15-hr experiment¹¹⁾ described above used short pellets which were observed to be bonded together in the high temperature region. Another experiment used long pellets of $(\text{U}_{0.75}, \text{Pu}_{0.25})\text{O}_{1.956}$ over the range 1445 to 1005°C for 2000 hr.¹⁰⁾ Two ranges of behavior were observed: 1445 to 1070°C in which a heat of transport, Q^* , of -10.2 kcal/mole was observed, and 1070 to 1005°C in which Q^* was -26 kcal/mole. The lower temperature region has a Q^* which is significantly different than that corresponding to transport by $\text{H}_2:\text{H}_2\text{O}$ (approx -45 kcal/mole). But even if they were the same, one can assume that at approximately 1400 K, $\text{H}_2:\text{H}_2\text{O}$ transport no longer dominates because of the greatly reduced Q^* above this point. Using the same data sources as before, we calculate $P_{\text{H}_2\text{O}} = 3.1 \times 10^{-6}$ atm at $P_{\text{H}_2} = 0.06$ atm and $T = 1400$ K.

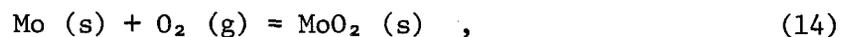
The present calculations for nearly stoichiometric fuel show that the pressure of the oxygen-carrying species in a typical fuel pin will be approximately 3×10^{-6} atm in the case of CO_2 , when equilibrium is established with the cladding, and will be much less than this in the case of H_2O because of loss of H_2 through the cladding. Oxygen transport must therefore occur by another mechanism, such as solid state diffusion. Moreover, under irradiation bulk diffusion would surely be faster than in out-of-reactor tests because of the large number of irradiation-produced defects.

Equation (8) reveals that as the $\text{CO}_2:\text{CO}$ ratio increases by a factor of 10, P_{CO_2} increases by a factor of 100; Eq. (2) reveals that a corresponding increase then occurs in the oxygen potential. If such a high oxygen potential could be maintained within a fuel pin, it would seem that at some point the oxygen distribution might indeed be controlled by a $\text{CO}_2:\text{CO}$ mechanism. At present it seems more likely that oxidation of the cladding itself will buffer any oxygen buildup above that corresponding to a $\text{CO}_2:\text{CO}$ ratio of unity and that the $\text{CO}_2:\text{CO}$ control mechanism will not be observed in reactor operation except for relatively short times at the beginning of the irradiation.

From the above discussion it seems clear that after carbon is removed from the fuel the in-reactor transport of oxygen in the bulk of a $(\text{U},\text{Pu})\text{O}_2$ fuel in-reactor must take place by some process(es) other than the $\text{CO}:\text{CO}_2$ transport process postulated by the Rand-Roberts-Markin theory. Measurement of the oxygen potential across a fuel pin would not only help establish the oxygen transport mechanism but would also help elucidate the fuel-cladding interaction.

METHOD OF MEASURING OXYGEN POTENTIAL GRADIENT

In principle, the oxygen activity could be measured indirectly by making use of fission products in a fuel element. Experiments have already been carried out at Argonne National Laboratory demonstrating that such a measurement is practical,^{12,13)} although the actual application has not been made. The method involves measuring the distribution of molybdenum and MoO_2 across an irradiated fuel element. From the equation



one sees that the oxygen potential can be obtained from the relationship:

$$RT \ln P_{O_2} = \Delta G^\circ(14) + RT \ln k \frac{[MoO_2]}{[Mo]}, \quad (15)$$

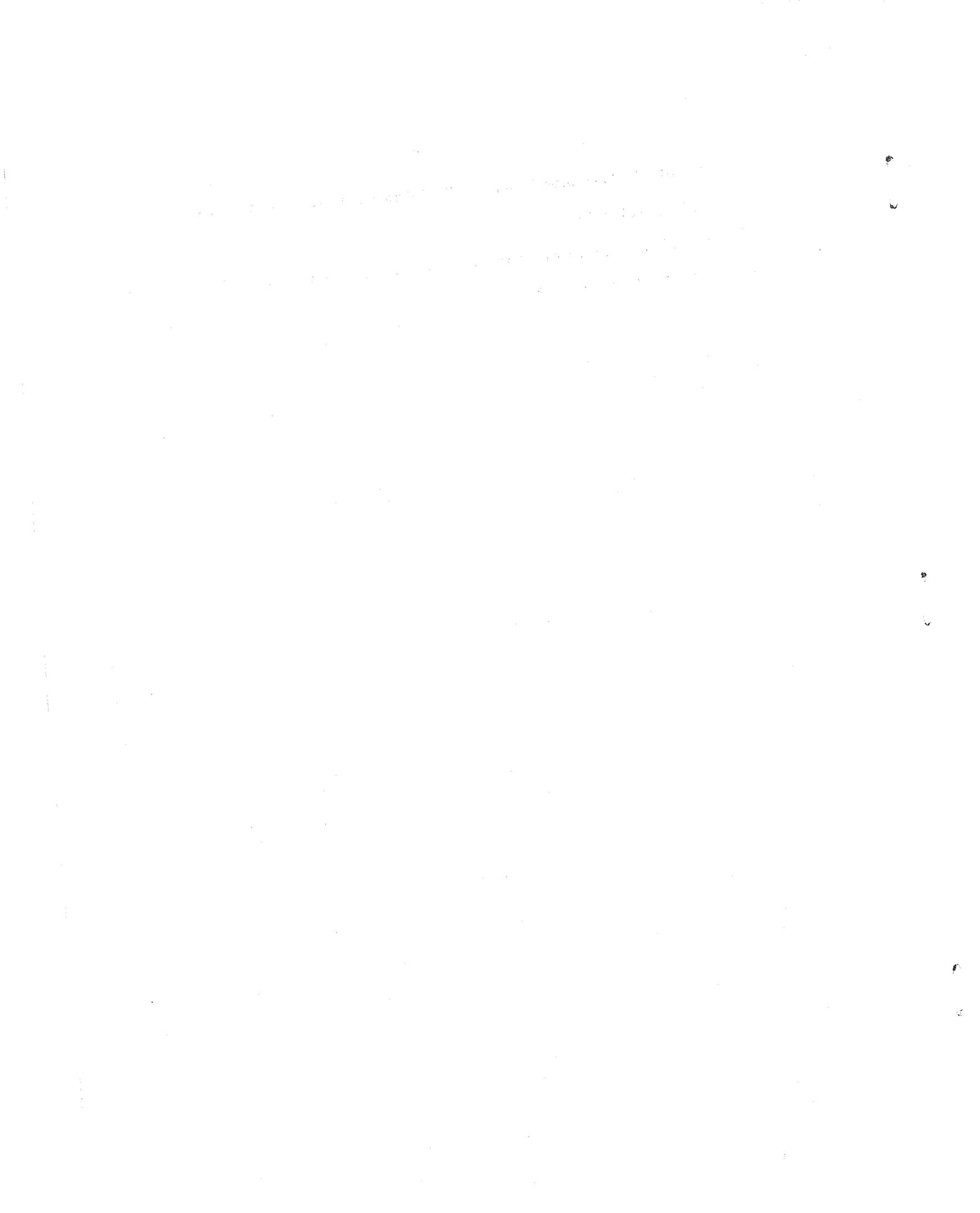
where k is the ratio of the activity coefficients of MoO_2 in the oxide phase and molybdenum in the metallic inclusion phase. Crouthamel and Johnson¹²⁾ have measured the concentration of Mo, Tc, Ru, Rh, Pd, and Fe in the metallic inclusions across several fuel sections with an electron microprobe and have also measured¹³⁾ the MoO_2 concentration in the oxide matrix, unfortunately on different pins. All that is lacking is the auxiliary thermodynamic data for Eq. (15) to be able to give a measurement of the oxygen potential.

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