ELSEVIER

Journal of Nuclear Materials 299 (2001) 181–198

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Review

A review of the thermophysical properties of MOX and UO_2 fuels

Juan J. Carbajo [a,*], Gradyon L. Yoder [a], Sergey G. Popov [b], Victor K. Ivanov [b]

[a] *Oak Ridge National Laboratory, P.O. Box 2009, Oak Ridge, TN 37831-8057, USA*
[b] *Institute of Nuclear Reactors, Russian Research Center, Kurchatov Institute, Kurchatov Square 1, 123182 Moscow, Russian Federation*

Received 29 January 2001; accepted 28 August 2001

Abstract

A critical review of the thermophysical properties of UO_2 and MOX fuels has been completed, and the best correlations for thermophysical properties have been selected. The properties reviewed are solidus and liquidus temperatures of the uranium/plutonium dioxide system (melting and solidification temperatures), thermal expansion and density, enthalpy and specific heat, enthalpy (or heat) of fusion, and thermal conductivity. Only fuel properties have been reviewed. The selected set of property correlations was compiled to be used in thermal-hydraulic codes to perform safety calculations.

PACS: 44.50.+f, 28.41.Bm

1. Introduction

The excess weapon-grade plutonium available in the Russian Federation (RF) and the United States from the reduction in strategic nuclear weapons will be mainly disposed of by burning it as mixed-oxide (MOX) fuel in existing reactors. These reactors will be primarily VVER-1000s in the Russian Federation and pressurized-water reactors (PWRs) in the United States.

Safety analyses are required by the respective national regulatory bodies to prove that MOX fuel can be burned safely in these reactors. These safety analyses require calculations with safety codes that need the appropriate thermophysical properties of the MOX fuel.

The MOX fuel contains between 3% and 5% PuO_2 blended with natural or depleted uranium dioxide (in the proportion of 95–97%). The PuO_2 replaces the enriched fraction of ^{235}U oxide in the regular UO_2 fuel. Uranium and plutonium dioxides are isostructural, and they form solid solutions. The small fraction of PuO_2 in the MOX fuel will change the thermophysical properties of MOX fuel slightly when compared to regular UO_2 fuel. Nevertheless, appropriate thermal properties for the MOX fuel need to be selected.

There is a considerable body of data and correlations in the open literature covering thermal properties of UO_2. An excellent review by Fink in 2000 presents the best correlations for UO_2 fuel [1]. The work of Fink is also available at the International Nuclear Safety Center (INSC) database of Argonne National Laboratory on the World-Wide Web [2].

However, for MOX and PuO_2 fuels the available data are not extensive, and no recent reviews are available. An open-literature review of MOX and PuO_2 properties was completed in 1982, also by Fink [3]. There is a report on thermophysical properties [4] prepared in 1997 by an International Working Group for the International Atomic Energy Agency (IAEA) compiling available data and correlations for materials of water-cooled reactors (both light and heavy water). It considers UO_2, MOX, and other fuels (e.g., uranium metal and uranium–aluminum alloys) and also cladding, absorbers, and structural materials. The report lists available correlations and data without evaluating their accuracy or merits and without making recommendations. The data covered in

* Corresponding author. Tel.: +1-865 574 5856; fax: +1-865 574 8216.
E-mail addresses: carbajojj@ornl.gov (J.J. Carbajo), yodergljr@ornl.gov (G.L. Yoder), ivanov@vver.kiae.ru (V.K. Ivanov).

0022-3115/01/$ - see front matter
PII: S0022-3115(01)00692-4

Nomenclature

A	coefficient of Eq. (33) (mK/W)
B	burnup (MWd/kgHM or at.%)
C	coefficient of Eq. (33) (m/W)
c_i	constants used in Eqs. (22) and (23) (various units)
C_i	constants used in Eqs. (20) and (21) (various units)
C_P	heat capacity at constant pressure (J/mol/K or J/kg/K)
E_a	electron activation energy divided by the Boltzmann constant (Eqs. (20) and (21)) (K)
FD	factor for effect of dissolved fission products, Eq. (34)
FM	factor for fuel porosity, Eq. (36)
FP	factor for effect of precipitated fission products, Eq. (35)
FR	factor for effect of radiation damage, Eq. (37)
H	enthalpy (J/mol or J/kg)
HM	heavy metal (U or Pu)
L	length for expansion (m)
O/M	oxygen-to-metal (ratio)
p	porosity $(\rho_{TD} - \rho)/\rho_{TD}$
TLTEC	true linear thermal expansion coefficient (1/K)
t	modified temperature T/1000 (K)
T	temperature (K)
V	volume (m^3)
x	deviation from stoichiometry (2 − O/M)
y	mole fraction of PuO_2 in MOX
$\alpha(T)$	coefficient of expansion (1/K)
θ	Einstein temperature (Eqs. (20) and (21)) (K)
ω	variable used in Eq. (34)
ρ	density (kg/m^3)
Δ	increment (various units)
λ	thermal conductivity (W/m/K)
Subscripts	
a	activation
L	liquidus
ℓ	liquid
m	melting
P	pressure
o	unirradiated, fully dense fuel
s	solid
S	solidus
TD	theoretical density (for fully dense fuel with zero porosity)
v	volume

the report have been compiled and stored in a computer database named THERSYST, developed by the Institute for Nuclear Technology and Energy Systems (IKE) at the University of Stuttgart, Germany.

PuO_2 or MOX properties are not available on the INSC database [2] except for the solidus and liquidus temperatures of the uranium/plutonium dioxide system. Therefore, there is a need to search for the available MOX thermophysical properties, to complete a critical review of the properties and compare them with UO_2 properties, and to select the best sets of properties/correlations to be used by codes to perform safety calculations.

In this paper, a comprehensive review of the open literature on fuel properties has been completed with emphasis on MOX fuel. The PuO_2 and UO_2 fuel properties were also reviewed and compared to MOX properties. The PuO_2 properties were studied when they were required to calculate MOX properties. This is the case for most properties that follow the law of mixtures. Finally, the best correlations for both MOX and UO_2 fuel have been selected.

The properties reviewed are:

1. solidus and liquidus temperatures of the uranium/plutonium dioxide system (melting and solidification temperatures),
2. thermal expansion and density,
3. enthalpy and specific heat,
4. enthalpy (or heat) of fusion,
5. thermal conductivity.

Only fuel properties are covered in this work.

For each property, a review of the available data and correlations is presented followed by recommendations for the best values of the property and/or the best correlations. Also, the variables that influence the property are described. Variables considered are: fuel composition (if UO_2 or MOX, and in the case of MOX, PuO_2 mole fraction, y), temperature (T), porosity (p) or fraction of the theoretical density (% TD), burnup (B), and oxygen-to-metal (O/M) ratio or deviation from stoichiometry ($x = 2 - O/M$). Gadolinium in the fuel has not been considered, but some correlations consider it as part of the fuel composition. It is anticipated that these variables can accommodate fuel property variations caused by different fuel manufacturing processes, including different grain sizes and fuel microstructures.

2. Solidus and liquidus temperatures of uranium/plutonium dioxide system

2.1. Review of available data and correlations

There is a large amount of data on the melting temperature of fuels. Table 1 presents values in chro-

Table 1
Available data and formulas on melting temperatures of UO_2 and PuO_2

Reference	UO_2 (K)	PuO_2 (K)	Comments
Pijanowski [5] 1960	3033 ± 30	2596 ± 30	
Chikalla [6] 1961	3003 ± 30	2553 ± 30	
Lyon and Baily [7] 1964	3046 ± 20	2511 ± 135	
Latta and Fryxell [8] 1965	3149 ± 7		
Hausner [9] 1965	3078 ± 15		
Lyon and Baily [10] 1967	3113 ± 20	2663 ± 20	
Aitken and Evans [11] 1968	3128 ± 15	2718 ± 15	O/M ratio effect
Brassfield [12] 1968	3113		Burnup effect = −3 K/MWd/kg, O/M ratio effect
Hein et al. [13] 1968	3115 ± 25		
Latta and Fryxell [14] 1970	3138 ± 15		
Rand [15] 1978	3120 ± 30		
Adamson et al. [16] 1985	3120 ± 30	2701 ± 35	Burnup effect = −0.4 K/MWd/kg
Komatsu [17] 1988	3138	2718	Burnup effect = −0.7 K/MWd/kg, O/M ratio effect
MATPRO [18] 1997	3113	2647	Burnup effect = −3.2 K/MWd/kg

nological order reported since 1960. The UO_2 fuel melts at a higher temperature than PuO_2, with values for UO_2 ranging from 3003 K [6] to 3149 K [8]. Melting temperatures for PuO_2 range from 2511 K [7] to 2718 K [11,17]. The UO_2–PuO_2 system follows the solid–liquid phase diagram of Fig. 1. MOX fuel melts at a temperature between that of pure UO_2 and PuO_2.

The data also show that burnup and/or deviation from stoichiometry lowers the melting temperature. The burnup usually changes the stoichiometry of the fuel. Fresh stoichiometric fuel may get converted into non-stoichiometric (with an O/M ratio $\neq 2$) fuel after burnup. Aitken and Evans [11], Brassfield [12] and Komatsu [17] have studied the O/M ratio or deviation from stiochiometry dependence. The MATPRO [18] correlations are based on the melting temperature of Brassfield [12] and the Lyon and Baily phase diagram [10], and they yield the largest temperature reductions from burnup effects. Adamson's melting temperatures and equations [16] provide the best fit to the experimental data. They agree also with the recommended melting temperature of Rand [15].

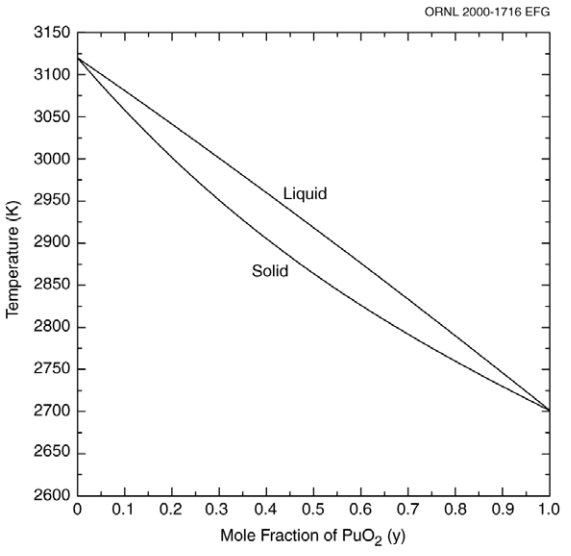

Fig. 1. Phase diagram of the UO_2–PuO_2 system.

2.2. Recommendation

Adamson's melting temperatures and correlations [16] are the best fit to the experimental data and are, therefore, recommended. This recommendation is identical with that of the INSC database [2].

The recommended values for the melting temperatures of $UO_{2.00}$ and $PuO_{2.00}$ are Adamson's:

$$T_m(UO_{2.00}) = 3120 \pm 30 \text{ K}, \quad (1)$$

$$T_m(PuO_{2.00}) = 2701 \pm 35 \text{ K}. \quad (2)$$

The recommended liquidus $[T_L(y)]$ and solidus $[T_S(y)]$ temperatures (in K) are given by Adamson's

$$T_L(y) = 3120.0 - 388.1y - 30.4y^2, \quad (3)$$

$$T_S(y) = 3120.0 - 655.3y + 336.4y^2 - 99.9y^3, \quad (4)$$

where y is the mole fraction of PuO_2. The solid–liquid phase diagram for the UO_2–PuO_2 system is shown in Fig. 1. The enlarged portion of this figure for y less than 0.1 (for most MOX compositions) is shown in Fig. 2.

For mole fractions of PuO_2 in fuel from 0 to 0.6, the two-standard-deviation estimated uncertainties are ±35 K for the solidus temperature and ±55 K for the liqui-

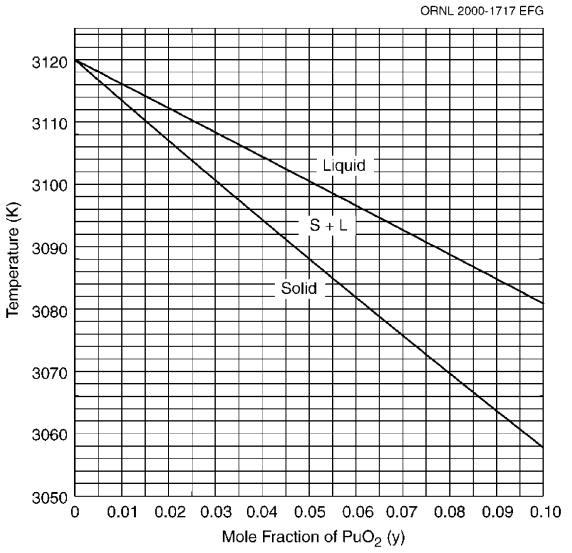

Fig. 2. Phase diagram of the UO_2–PuO_2 system for PuO_2 mole fraction under 0.1.

dus temperature. For mole fractions of PuO_2 above 0.6, the two-standard-deviation uncertainties increase to ±50 K for the solidus and to ±75 K for the liquidus temperatures.

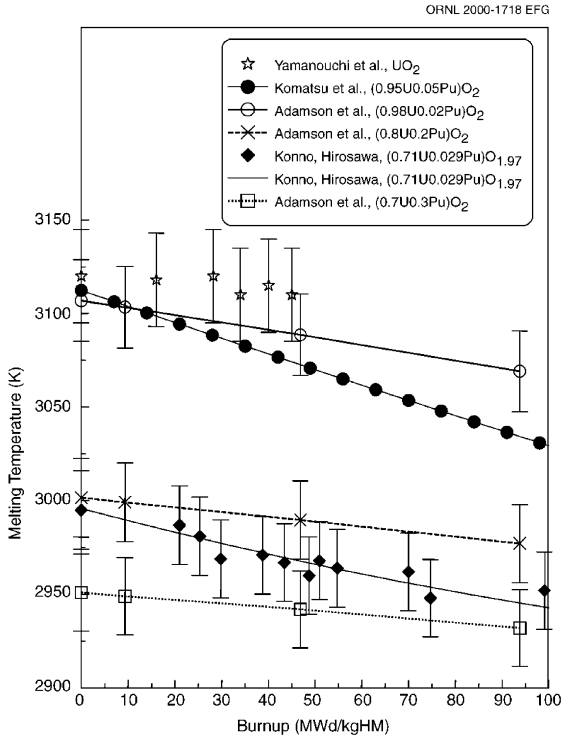

Fig. 3. Influence of burnup on the melting temperature of UO_2–PuO_2 fuel for various contents of PuO_2.

The effect of burnup on the melting temperatures of MOX fuel and UO_2 was investigated in [12,16,17,19,20]. Data from these references are shown in Fig. 3 as a function of burnup. From this figure, we recommend a correction for burnup by decreasing the melting temperature by 0.5 K/MWd/kgHM (heavy metal) for both MOX and UO_2 fuels. We do not recommend a correction for deviations from stoichiometry.

2.3. Variable dependence and concluding remarks

The melting temperature of the fuel is a function of the fuel composition (PuO_2 and UO_2 fractions), O/M ratio or deviation from stoichiometry, and burnup. The melting temperature decreases with increasing PuO_2 content, with increasing burnup, and with deviations from stoichiometry. The MOX fuel will melt at a lower temperature than UO_2 fuel. Fuel with burnup or non-stoichiometric fuel will also melt at a lower temperature than fuel without burnup or of stoichiometric composition.

3. Thermal expansion and density of fuel

3.1. Review of available data and correlations

Table 2 shows the relevant references and data for thermal expansion and density of fuel. The UO_2, PuO_2, and MOX fuels have very similar thermal expansions [21,22] as shown in Fig. 4. MATPRO [18] employs a different linear thermal expansion coefficient for UO_2 than [21,22], as shown in Fig. 5. The density of PuO_2 is higher than the density of UO_2. Density values in Table 2 are for fully dense fuel with zero porosity or 100% theoretical density (TD) at 273 K.

3.2. Recommendation

The UO_2, PuO_2, and MOX fuels have very similar thermal expansions. Martin [21] developed equations to be used for UO_2 and MOX, with the corresponding basic property at 273 K. The relative thermal expansion

$$[(L(T) - L(273)]/L(273) = \Delta L(T)/L(273), \tag{5}$$

the true linear thermal expansion coefficient (TLTEC)

$$\alpha_s(T) = \frac{1}{L(273)}\left(\frac{dL}{dT}\right)_p \quad (1/K), \tag{6}$$

and density $[\rho_s(T)]$ of solid stoichiometric UO_2 or MOX fuel are recommended to be calculated by Martin's correlations [21]:

Table 2
Thermal expansion and density of solid UO_2 and MOX fuels

Reference	UO_2 thermal expansion	MOX/PuO_2 thermal expansion	$\rho(UO_2)$ at 273 K (kg/m^3)	$\rho(PuO_2)$ at 273 K (kg/m^3)
Martin [21]	Equations	Equations		
Tokar [22]		Equation		
MATPRO [18]	Equation	Equation	10980 ± 20	
Fink [1]	Equation		10963 ± 70	
Benedict [23]			10970 ± 70	11460 ± 80

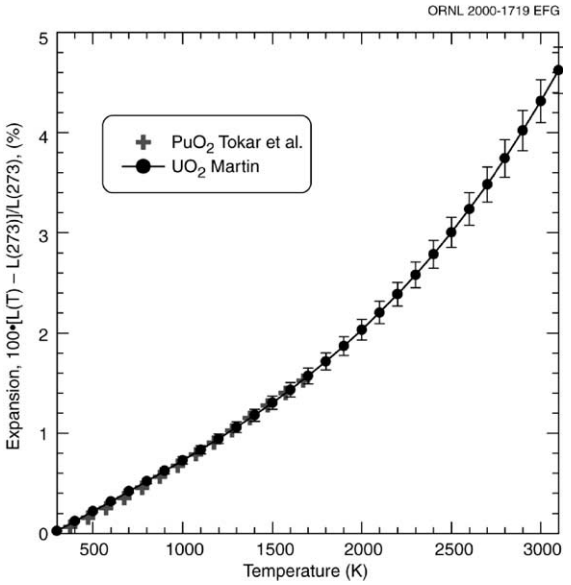

Fig. 4. Relative thermal expansion of UO_2 and PuO_2 fuels.

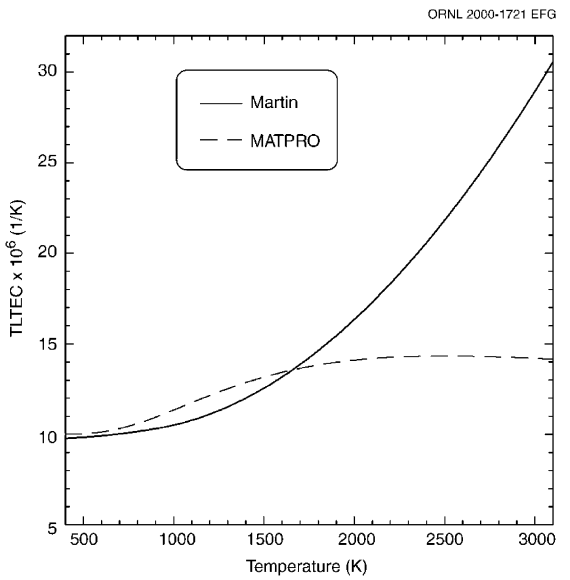

Fig. 5. Comparison of Martin and MATPRO TLTEC for UO_2.

$$\Delta L(T)/L(273) = -2.66 \times 10^{-3} + 9.802 \times 10^{-6} T - 2.705 \times 10^{-10} T^2 + 4.391 \times 10^{-13} T^3, \quad (7)$$

$$L(T) = L(273)(9.9734 \times 10^{-1} + 9.802 \times 10^{-6} T - 2.705 \times 10^{-10} T^2 + 4.391 \times 10^{-13} T^3) \quad \text{(m)}, \quad (8)$$

$$\alpha_s(T) = 9.828 \times 10^{-6} - 6.39 \times 10^{-10} T + 1.33 \times 10^{-12} T^2 - 1.757 \times 10^{-17} T^3 \quad (1/\text{K}), \quad (9)$$

$$\rho_s(T) = \rho_s(273)(9.9734 \times 10^{-1} + 9.802 \times 10^{-6} T - 2.705 \times 10^{-10} T^2 + 4.391 \times 10^{-13} T^3)^{-3} \quad (\text{kg/m}^3), \quad (10)$$

for temperatures from 273 to 923 K. For temperatures from 923 K to the UO_2 or MOX fuel melting temperature, the following equations are recommended:

$$\Delta L(T)/L(273) = -3.28 \times 10^{-3} + 1.179 \times 10^{-5} T - 2.429 \times 10^{-9} T^2 + 1.219 \times 10^{-12} T^3, \quad (11)$$

$$L(T) = L(273)(9.9672 \times 10^{-1} + 1.179 \times 10^{-5} T - 2.429 \times 10^{-9} T^2 + 1.219 \times 10^{-12} T^3) \quad \text{(m)}, \quad (12)$$

$$\alpha_s(T) = 1.1833 \times 10^{-5} - 5.013 \times 10^{-9} T + 3.756 \times 10^{-12} T^2 - 6.125 \times 10^{-17} T^3 \quad (1/\text{K}), \quad (13)$$

$$\rho_s(T) = \rho_s(273)(9.9672 \times 10^{-1} + 1.179 \times 10^{-5} T - 2.429 \times 10^{-9} T^2 + 1.219 \times 10^{-12} T^3)^{-3} \quad (\text{kg/m}^3). \quad (14)$$

Densities $\rho_s(273)$ at 273 K of uranium and plutonium dioxides are 10 970 and 11 460 kg/m^3, respectively. The density of the solid solution of uranium and plutonium

dioxides $(U_{1-y}Pu_y)O_2$ changes according to the linear law

$$\rho_s(273) = 10970 + 490y \quad (\mathrm{kg/m^3}), \tag{15}$$

for $(0 \leqslant y \leqslant 1)$ with y, mole fraction of PuO_2.

Errors in the values of the relative expansion are given by Martin [21] as $\pm 2.6 \times 10^{-4}$, $\pm 4.4 \times 10^{-4}$, and $\pm 7 \times 10^{-4}$ in the temperature regions of 293–1273, 1273–2273, and 2273–2929 K, respectively. The corresponding errors in the values of the TLTEC are $\pm 0.11 \times 10^{-6}$, $\pm 0.22 \times 10^{-6}$, and $\pm 1.1 \times 10^{-6}$ 1/K. The recommended uncertainty in the density of UO_2 and MOX fuels is 1% for the entire temperature range.

The parameters of thermal expansion of hypostoichiometric, $(U_{1-y}Pu_y)O_{2-x}$, solid MOX fuel are recommended to be calculated by the corresponding parameters of the stoichiometric fuel, multiplying them by a factor of $[1 + 3.9(\pm 0.9)x]$ with x being the deviation from stoichiometry. This factor was developed by Martin [21]. Analysis of the experimental data showed that this recommendation is valid up to 1800 K [21]; however, in the absence of high-temperature data, it can be used up to the melting temperature.

These density correlations are for fully dense fuel with zero porosity. Generally, commercial fuel density ranges from 94% to 96% of fully dense fuel prior to irradiation. During the early phases of irradiation, commercial fuel will densify by approximately 1–2% with maximum densification occurring by 5–15 MWd/kg burnup [24]. Fuel also swells, due to progressive buildup of fission products, at a rate of 0.7–1.0% $\Delta V/V$ per 10 MWd/kg [25]. Maximum fuel density occurs between 5 and 15 GWd/MT burnup; thereafter, the fuel density decreases proportionally with increasing burnup.

Porosity is defined as

$$p = \frac{\rho_{TD} - \rho}{\rho_{TD}} \tag{16}$$

with ρ_{TD} the density of fully dense fuel (fuel TD). From Eq. (16) the actual density of the fuel can be calculated from the ρ_{TD} and the porosity or the percent TD:

$$\rho = \rho_{TD}(1 - p) = \rho_{TD}\frac{(\%\ \mathrm{TD})}{100} \quad (\mathrm{kg/m^3}). \tag{17}$$

The recommended correlations for the coefficient of volume expansion and density of liquid UO_2 and MOX fuels as functions of temperature in the 3120–4500 K region are given by Breitung [26] and also recommended by Fink [1]:

$$\alpha_{v,\ell}(T) = 0.9285/[8860 - 0.9285(T - 3120)] \quad (1/\mathrm{K}), \tag{18}$$

$$\rho_\ell(T) = 8860 - 0.9285(T - 3120) \quad (\mathrm{kg/m^3}). \tag{19}$$

The relative uncertainties of these values are 4%.

3.3. Variable dependence and remarks

The fuel density is a function of the fuel composition, temperature, fraction of theoretical density (% TD) or porosity, burnup, O/M ratio or deviations from stoichiometry, x. The density decreases with temperature due to thermal expansion. The density also decreases with increasing porosities or with smaller fractions of the TD. The PuO_2 or MOX fuel is a little heavier than UO_2 fuel. Deviations from stoichiometry increase the thermal expansion and decrease the density. Finally, the burnup also affects the density by changing the porosity. At low burnups (less than 15 MWd/kg) the density increases by fuel densification; at higher burnups, the density decreases (porosity increases) by fuel swelling.

4. Enthalpy and heat capacity

4.1. Review of available data and correlations

Table 3 shows in chronological order some of the available data and correlations on enthalpy and heat capacity for UO_2, PuO_2, and MOX. Because of the large amount of UO_2 data, only selected data are presented in the table. The majority of the UO_2 data can be found in the data sources employed in developing the different UO_2 correlations.

We start with the review of the UO_2 correlations presented in Table 3. In 1972 Kerrisk and Clifton [31] developed correlations for enthalpy and heat capacity for UO_2 using five different sets of data. The correlations are physically based and comprise three terms, one for the lattice phonon contribution, one for the thermal expansion contribution, and the last one for the defect formation. In 1982, Fink [3] developed correlations for UO_2, PuO_2, and MOX employing three terms also, but the last term was an electronic contribution term. More recently in 2000, Fink reviewed all the UO_2 data and developed improved correlations for UO_2 [1]. Two sets of equations were developed by Fink for the enthalpy and the heat capacity of solid UO_2: one with exponentials and the other one with polynomials in temperature.

The MATPRO correlations [18] were developed based on the same model of Kerrisk and Clifton [31] and were modified in 1997 with the addition of the effect of gadolinium. The MATPRO correlations employ the following input variables: temperature, fuel composition (UO_2, PuO_2, and gadolinium), and O/M ratio or deviation from stoichiometry. MATPRO calculates a weighted average for the heat capacity based on the fractions of each component.

Fig. 6 shows predictions from MATPRO and the most recent Fink correlations (exponential equation (2) and polynomial equation (4) of [1] and [2]) for the heat capacity of UO_2 compared to some experimental data.

Table 3
Available data and correlations on enthalpy and heat capacity of UO_2, PuO_2, and MOX fuels

Reference	UO_2	PuO_2	MOX	Comments/variables
Sandenaw [27] 1963		Data $13 < T < 325$ K		
Kruger and Savage [28] 1968		Data $192 < T < 1400$ K		Equations
Engel [29] 1969	Data	Data $300 < T < 1100$ K		
Ogard [30] 1970		Data $1500 < T < 2715$ K		Equation
Kerrish et al. [31] 1972	Correlation			T
Leibowitz [32] 1972			Data	Equation
Leibowitz [33] 1974			Data	Equation
Gibby [34] 1974			Data	Equations and table
Flotow [35] 1976		Data $4 < T < 350$ K		For ^{242}Pu and ^{244}Pu
Oetting [36] 1982		Data $298 < T < 1610$ K		Formula and table up to 2400 K
Fink [3] 1982	Correlation	Correlation	Correlation	T
Cordfunke [37] 1990		Correlation		T
Lucuta [38–41] 1992–1997	Data, formula			T, O/M, B
Ronchi [42] 1993	Data (liquid) and correlation			T
MATPRO [18] 1997	Correlation	Correlation	Correlation	T, y, O/M, Ga
Ronchi [43] 1999	Data (solid)			
Fink [1] 2000	Correlations			T

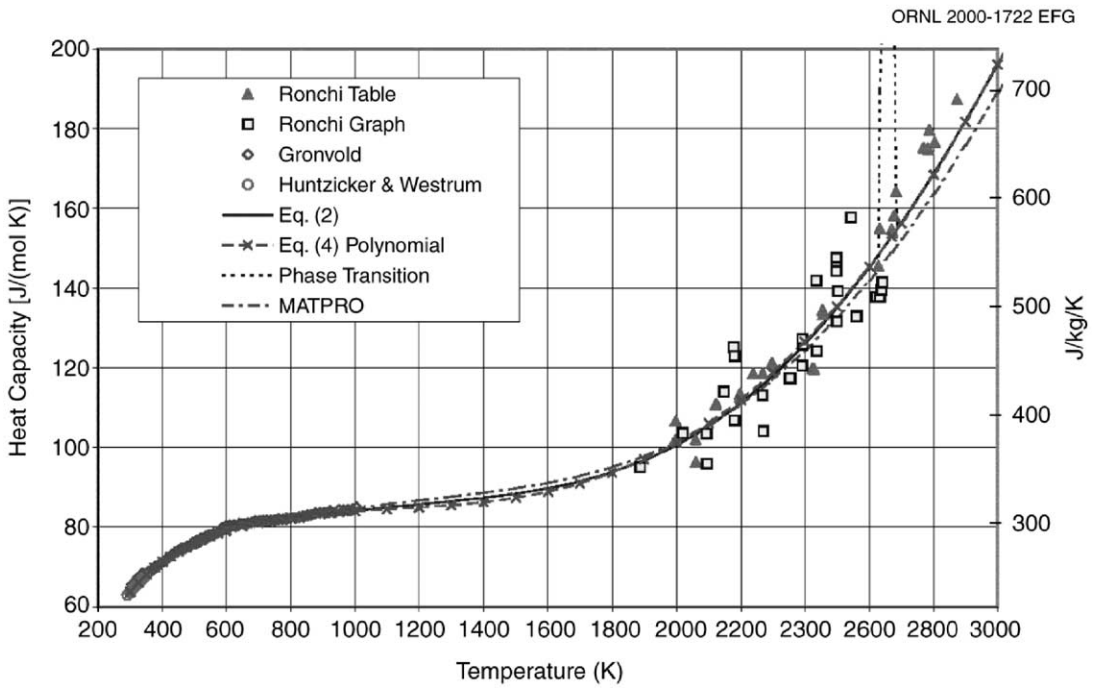

Fig. 6. Comparison of MATPRO calculated heat capacity for UO_2 with Fink Eqs. (2) and (4) of Refs. [1] and [2] and with experimental data. *Source:* Reproduced from [2].

The Fink correlations agree with the 1999 high-temperature data of Ronchi [43] better than the MATPRO correlation. For temperatures above 2000 K, the Fink correlations yield higher values than the MATPRO correlation. For temperatures below 2000 K, the correlations agree well with each other, with the MATPRO

correlation yielding slightly higher values than Fink's. Both MATPRO and Fink correlations employ the same value of 235.5 J/kg/K for C_P at 298.15 K based on the 1971 measurements of Huntzicker and Westrum [44].

A λ-phase transition has been detected for the heat capacity of UO_2 at 2670 ± 30 K by several investigators, such as Hutchings [45] and Hiernaut et al. [46]. At the transition, the heat capacity increases sharply in a very narrow temperature range.

Lucuta et al. [38–41] measured the specific heat of simulated high-burnup UO_2-based fuel (SIMFUEL) with an equivalent burnup from 3 to 8 at.% between room temperature and 1673 K. The results indicate that the burnup effect caused by fission products is very small. The specific heat measurements of SIMFUEL have shown:

1. the specific heat increases slightly with burnup, as predicted by the Kopp–Neumann rule;
2. higher oxygen contents increase the specific heat slightly.

Equations for the enthalpy and heat capacity of liquid UO_2 were obtained by Fink [1]. They are a combined fit of the liquid UO_2 heat capacity data of Ronchi et al. [42] and the enthalpy data of Leibowitz et al. [47] and Hein et al. [13].

Enthalpy and heat capacity data for PuO_2 are not abundant. In 1963 Sandenaw measured enthalpies and heat capacities for temperatures between 13 and 325 K [27]. Flotow [35] data for ^{242}Pu and ^{244}Pu oxides are also for low temperatures up to 350 K. In 1968 Kruger and Savage [28] measured data between 193 and 1400 K, and they developed equations for enthalpy and heat capacity that can be used up to 1800 K. In 1969 Engel [29] reported heat capacity data (for PuO_2 and also for UO_2) for temperatures between 300 and 1000 K. In 1970 Ogard [30] provided data between 1500 and 2715 K; he also developed an equation for the enthalpy as a function of temperature. Finally, Oetting [36] data are for temperatures between 298 and 1610 K, and he developed equations and tables with enthalpies and heat capacities in the range 298–2400 K.

There are basically two correlations fitting the PuO_2 data: Fink [3] and MATPRO [18]. The equations of Fink were refitted to polynomials by Cordfunke and Konings [37]; this third correlation is the Fink correlation with a different form. Fig. 7 shows these three correlations compared to the available PuO_2 data.

The Fink [3] and Cordfunke–Konings [37] correlations agree perfectly. The MATPRO [18] correlation was developed using only the data of Kruger–Savage [28] and, as expected, agrees very well with these data. The Kruger–Savage [28] equation also agrees perfectly with their database. A heat capacity equation was obtained from Ogard's [30] enthalpy equation (by calculating the first derivative). Heat capacity values calculated by this equation have been plotted for the complete range 300–2700 K, but the database was for temperatures above 1500 K. Ogard's [30] values above 1500 K are similar (but higher) to Oetting's [36] values.

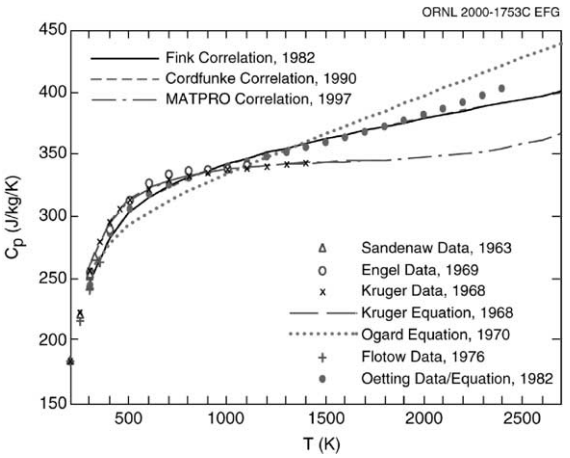

Fig. 7. Comparison of data and correlations for heat capacity of PuO_2.

Overall, the Fink correlation [3] (or the equivalent Cordfunke–Konings [37] correlation) provides the best fit to all the data. The MATPRO correlation fits perfectly the Kruger–Savage data, but only these data; and it yields significantly lower values than the Fink correlation for temperatures above 900 K.

Table 4 shows measured values of PuO_2 heat capacity at 298.15 K and values employed by different correlations. It can be seen that the Fink correlation employs a lower value, based on Flotow [35], than the MATPRO correlation. Fig. 7 shows that the Fink correlation yields values slightly lower than the MATPRO correlation at 298.15 K and at temperatures under 900 K.

Finally, for MOX fuel, data and equations fitting the data are available from [32–34], and correlations were developed by Fink [3] and MATPRO [18]. The MATPRO MOX correlation is a weighted average of the MATPRO UO_2 and PuO_2 correlations.

4.2. Recommendation

For solid UO_2, the most recent equations of Fink [1] for enthalpy and heat capacity are the best fit to all the experimental data and are therefore recommended. The equations are valid between 298.15 and 3120 K (the melting temperature of UO_2). The constants for these equations are given in Table 5. Constants are given for two different units: J/mol and J/kg for the enthalpy and J/mol/K and J/kg/K for the heat capacity.

$$H_s(T) - H_s(298.15) = C_1\theta\left[\frac{1}{e^{\theta/T}-1} - \frac{1}{e^{\theta/298.15}-1}\right] + C_2[T^2 - (298.15)^2] + C_3 e^{-E_a/T}. \quad (20)$$

Table 4
C_P of PuO_2 at 298.15 K

Reference	Reported value	Reported units	Value in J/kg/K
Sandenaw [27] 1963	16.4	cal/mol/K	253.2
Kruger–Savage [28] 1968	16.5	cal/mol/K	254.4
Ogard [30] 1970	16.4	cal/mol/K	253.2
Flotow [35] 1976	66.25	J/mol/K	241.8
Oetting [36] 1982	66.25	J/mol/K	241.8
Fink correlation [3] 1982	66.25	J/mol/K	241.8
MATPRO correlation [18] 1997			258.3

Table 5
Constants used in enthalpy and heat capacity correlations [Eqs. (20) and (21)]

Constant	UO_2	PuO_2	Units
C_1	81.613	87.394	J/mol/K
	302.27	322.49	J/kg/K
C_2	2.285×10^{-3}	3.978×10^{-3}	J/mol/K^2
	8.463×10^{-3}	1.4679×10^{-2}	J/kg/K^2
C_3	2.36×10^{7}	0	J/mol
	8.741×10^{7}	0	J/kg
θ	548.68	587.41	K
E_a	18,531.7		K

$$C_P = \frac{\partial H}{\partial T} = \frac{C_1\theta^2 e^{\theta/T}}{T^2(e^{\theta/T}-1)} + 2C_2T + \frac{C_3E_a e^{-E_a/T}}{T^2}. \quad (21)$$

Fink also developed polynomial functions for both the enthalpy and the heat capacity that fit the experimental data very well. These equations for the enthalpy and the heat capacity are also given here, together with the constants to be used in Table 6,

$$H_s(T) - H_s(298.15) = c_1 + c_2t + c_3t^2 + c_4t^3 + c_5t^4 + c_6t^5 + c_7t^{-1}, \quad (22)$$

Table 6
Constants used in enthalpy and heat capacity correlations [Eqs. (22) and (23)]

Constant	UO_2	PuO_2	Units
c_1	−21.1762	−32.0342	J/mol
	−78.4303	−118.2062	J/kg
c_2	52.1743	84.495	J/mol/K
	193.238	311.7866	J/kg/K
c_3	43.9735	5.3195	J/mol/K^2
	162.8647	19.629	J/kg/K^2
c_4	−28.0804	−0.20379	J/mol/K^3
	−104.0014	−0.752	J/kg/K^3
c_5	7.88552	0	J/mol/K^4
	29.2056	0	J/kg/K^4
c_6	−0.52668	0	J/mol/K^5
	−1.9507	0	J/kg/K^5
c_7	0.71391	1.90056	J K/mol
	2.6441	7.0131	J K/kg

$$C_P = c_2 + 2c_3t + 3c_4t^2 + 4c_5t^3 + 5c_6t^4 - c_7t^{-2}. \quad (23)$$

These equations employ the variable $t = T/1000$ instead of T to minimize the size of the coefficients.

For solid PuO_2, the 1982 exponential equations of Fink [3] for enthalpy and heat capacity are also the best fit to the experimental data and are also recommended. Their range of validity is between 298.15 and 2701 K (the melting temperature of PuO_2). The PuO_2 constants for Eqs. (20) and (21) are also in Table 5. These equations do not have the last exponential term ($C_3 = 0$).

In 1990, Cordfunke and Konings [37] developed polynomials that fit perfectly the Fink exponential equations for C_P of PuO_2. Enthalpy polynomials were obtained by integrating the C_P equations. The constants for PuO_2 to be used in Eqs. (22) and (23) are also given in Table 6. These equations have been modified to employ the variable $t = T/1000$.

The uncertainty in the recommended enthalpy increments is ±2% from 298 to 1800 K and ±3% from 1800 K to the melting point. The heat capacity uncertainty is ±2% from 298 to 1800 K and ±13% from 1800 K to the melting point.

The small effect of burnup on specific heat can also be incorporated in the analytical expression of the heat capacity by modifying the constant C_2 of Eq. (21). Lucuta et al. [41] obtained the following expression:

$$C_2^* = C_2(1 + 0.011B) \quad (24)$$

with B burnup (at.%). Lucuta et al. [41] developed this correction for the constant C_2 of the MATPRO [18]

correlation, which has a similar form to the Fink correlations [Eqs. (20) and (21)].

For the enthalpy of liquid UO_2 from 3120 to 4500 K, we recommend the following expression from Fink [1]:

$$H_\ell(T) - H_s(298.15) = 2.977 \times 10^6 + 0.931T - 4.9215 \times 10^9/T \quad (\mathrm{J/kg}). \quad (25)$$

The uncertainty in this enthalpy equation is ±2% from 3120 to 3500 K and ±10% from 3500 K to 4500 K. Values above 4500 K have large errors and were not considered. In addition, temperatures above 4500 K are not likely to be reached even in accident calculations.

The specific heat capacity of UO_2 in the liquid state from 3120 to 4500 K is given by Fink [1] as the first derivative of Eq. (25):

$$C_{P,\ell}(T) = 0.931 + 4.9215 \times 10^9/T^2 \quad (\mathrm{J/(kgK)}). \quad (26)$$

The heat capacity uncertainty is ±10% from T_m to 3400 K and increases linearly from ±10% at 3400 K to 25% at 4500 K. For PuO_2 or MOX there are no available data, and the values for UO_2 may be used.

The solid solutions, formed in the system UO_2–PuO_2, are almost ideal. The Kopp–Neumann rule is true for an ideal system. We recommend the calculation of enthalpy and specific heat of solid MOX fuel $[(U_{1-y}Pu_y)O_2]$ by the Kopp–Neumann rule: for a mixture of UO_2 and PuO_2, either property of the solid is determined by combining the contribution from each constituent in proportion to its mole fraction. For the specific heat,

$$C_P(T, \mathrm{MOX}) = (1-y)C_P(T, \mathrm{UO_2}) + yC_P(T, \mathrm{PuO_2}). \quad (27)$$

When the material is partially molten, the heat capacity is determined similarly with a weighted sum of the solid and liquid portions.

Because the MOX fuel has a higher melting temperature (~3000 K) than PuO_2 fuel (~2700 K), values above 2700 K (the upper limit of validity) need to be calculated by Eq. (21) or (23) to be used in Eq. (27) for the weighted average of the heat capacity.

Fig. 8 shows calculated values for the heat capacity of UO_2, PuO_2, and MOX (with 5%, 20%, and 25% PuO_2 contents). As expected, the MOX values for 5% PuO_2 are very close to the UO_2 values (that contribute to 95% of the total value). Experimental data for MOX fuel are also shown from [32–34]. The Leibowitz data of 1972 [32] and 1974 [33] are the same, but they have different equations fitting the data. The Gibby data for MOX with 25% PuO_2 agree well with the calculated values for 25% PuO_2. The equation from [33] agrees better with calculated values than the one from [32].

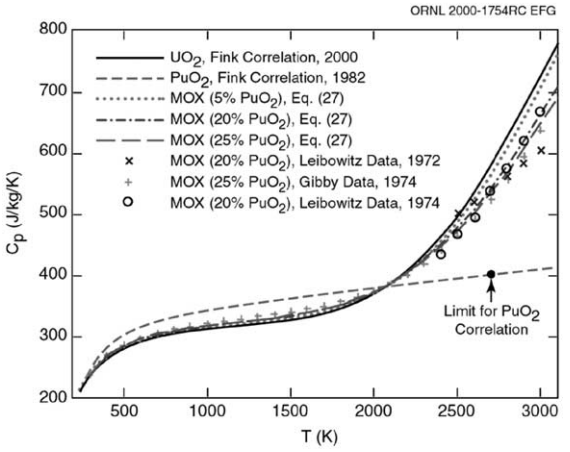

Fig. 8. Comparison of data and correlations for heat capacity of MOX.

4.3. Variable dependence and concluding remarks

The enthalpy and the heat capacity are functions of the temperature (T), fuel composition (UO_2 and PuO_2 fractions, and gadolinium content), O/M ratio or deviation from stoichiometry (x), and burnup (B). The main influencing variables are the temperature and the fuel composition. Both the enthalpy and the heat capacity increase with temperature. The heat capacity reaches a maximum at the melting point, decreasing afterward. The heat capacity of solid UO_2 is lower than the heat capacity of solid PuO_2 (or MOX) up to ~2000 K; the inverse is true at higher temperatures. The effect of the other variables (O/M ratio and burnup) is small. Their effect is to increase the heat capacity slightly.

The Fink correlations for UO_2 [1] and for PuO_2 [3] have been recommended because they have the best agreement with the experimental data. At low temperatures (less than 2000 K for UO_2 and less than 1000 K for PuO_2), the MATPRO correlations yield slightly higher values for the heat capacities of both UO_2 and PuO_2 (Figs. 6 and 7) than the recommended Fink [1,3] correlations, but at high temperatures they yield significantly lower values. These lower heat capacities are non-conservative for some transients and conservative for others. For the same fuel temperature, lower heat capacities result in less energy stored in the fuel than the actual values, which will result in lower cladding or coolant temperatures (non-conservative) when the stored energy is released (as occurs in a loss-of-coolant accident). In contrast, for those transients that increase the energy deposited into the fuel, lower heat capacities will result in higher than actual temperature increases, a conservative result.

Finally, for liquid UO_2 or MOX, the equations of Fink for the enthalpy and heat capacity are recom-

mended. The heat capacity of liquid UO_2 (or MOX) decreases with temperature, up to 4500 K.

5. Heat of fusion of UO_2, PuO_2, and MOX fuels

5.1. Review of available data

Table 7 shows in chronological order the available data on the heat of fusion of UO_2, MOX, and PuO_2 fuels. Few experimental data have been found for UO_2, only one value for MOX, and no experimental values for PuO_2. The reported values for PuO_2 are all calculated from equations. Epstein [48] has two different calculations for the heats of fusion of UO_2 and PuO_2. His calculated heats of fusion for PuO_2 are lower than for UO_2. However, Adamson calculated higher heats of fusion for PuO_2 than for UO_2 [16].

5.2. Recommendation

We recommend the value for the heat of fusion of UO_2 calculated by Fink [1] from the equations of liquid and solid enthalpy [Eqs. (20) and (25)] of UO_2 at the melting point (3120 K). This value is

$$\Delta H_m(UO_2) = 70 \pm 4 \text{ kJ/mol} = 259.3 \pm 14.8 \text{ kJ/kg}. \quad (28)$$

This value is also recommended by the INSC database [2], and is close to the experimental data of Hein et al. [13] and Leibowitz et al. [47].

For MOX fuel, we recommend the experimental value of Leibowitz obtained for MOX with 20% PuO_2 [33]:

$$\Delta H_m(\text{MOX}) = 67 \pm 3 \text{ kJ/mol} = 248 \pm 12 \text{ kJ/kg}. \quad (29)$$

This heat of fusion is smaller (by 3 kJ/mol or 12 kJ/kg) than the heat of fusion recommended for UO_2. Leibowitz experimental data for UO_2 [47] and MOX [33] yields a difference of 7 kJ/mol between both heats of fusion.

For PuO_2, there are inconsistencies in the reported values, and we cannot recommend any value. Epstein calculated a lower heat of fusion for PuO_2 than for UO_2 [48], but Adamson calculated the opposite [16].

5.3. Variable dependence

The only variable that we found to influence the heat of fusion was the fuel composition. We found inconsistencies in the reported values, but we believe the heat of fusion of MOX fuel (and probably PuO_2) is lower but very similar to the heat of fusion of UO_2.

6. Thermal conductivity

6.1. Review of available data and correlations

The thermal conductivity is a property that does not follow the law of mixtures. Therefore, PuO_2 values of thermal conductivity were not reviewed because they cannot be used to calculate the thermal conductivity of MOX.

There is a large body of data and correlations on thermal conductivity of UO_2 fuel. The data are not so extensive for MOX fuel. Table 8 shows in chronological order the most relevant references that cover mainly correlations and reviews of other works.

The data reviewed show that the thermal conductivity of fuel (both UO_2 and MOX) decreases with temperature until reaching a minimum at ~1800–2000 K, and then it increases again with temperature. Some thermal conductivity correlations have three terms, but most correlations consist of two terms: the first one that decreases with temperature (it has a polynomial of the temperature in the denominator), and the second one that increases with temperature (by using an exponential

Table 7
Available data on the heat of fusion (kJ/mol) of the system UO_2–PuO_2

Reference	UO_2	MOX	PuO_2	Comments
Epstein [48] 1967	77.8 ± 0.5		66.5 ± 0.5	Two different calculations
	88.7 ± 5.4		70.3 ± 5.4	
Hein et al. [13] 1968	76.1 ± 2.0			Experiment, drop calorimetry
Leibowitz et al. [47] 1971	74 ± 3			Experiment, drop calorimetry
Leibowitz et al. [33] 1974		67 ± 3 for $(U_{0.8}\ Pu_{0.2})O_2$		Experiment, drop calorimetry
Rand et al. [15] 1978	74.8 ± 3			Calculated
Fink et al. [49] 1981	74.8 ± 3			Calculated
Adamson et al. [16] 1985	86.9		90.5	Calculated
MATPRO [18] 1997	74			Taken from Leibowitz [47]
Fink [1] 2000	70 ± 4			Calculated

Table 8
Data and correlations on fuel thermal conductivity

Reference	UO_2	MOX	Variables
Washington [50] 1973	Graphs, tables, and formulas	Graphs, tables, and formulas	T, U/Pu, O/M, p
Martin [51] 1982	Formulas	Formulas	T, x, p
Harding and Martin [52] 1989	Formula		T, p
Philipponneau [53] 1992		Data and formula	T, x, B, p
Lucuta [54] 1996	Data and formulas		T, x, B, p
Wiesenak [55] 1997	Formula		T, B
Ohira and Itagaki [56] 1997	Formula		T, B, p
MATPRO [18] 1997	Formula	Formula	T, U/Pu, O/M, B, Ga, p
Ronchi [43] 1999	Data and formula		T
Duriez et al. [57] 2000		Data and formula	T, x, p
Fink [1] 2000	Formula		T, p

or a polynomial of temperature). These two terms correspond to two physical contributions to the thermal conductivity: a *phonon lattice* term (decreasing with temperature) and a *small-polaron ambipolar* term (increasing with temperature). The last term of some correlations may represent other contributions, such as radiation or electronic contributions that also increase with temperature.

Analysis of the available data shows that the thermal conductivity of MOX fuel is lower than the thermal conductivity of UO_2; addition of small amounts of PuO_2 to the fuel decreases the thermal conductivity. However, variation of the PuO_2 content between 3% and 15% does not appear to further decrease the thermal conductivity [57]. If the amount of PuO_2 is increased above 15%, then there is an additional decrease of the thermal conductivity of MOX fuel [57]. Commercial MOX fuel has PuO_2 concentrations below 5%.

The data also show that the thermal conductivity decreases with burnup and with deviations from stoichiometry. It appears that the burnup also changes the stoichiometry of the fuel, particularly in MOX fuel [53,57], but not so much in UO_2 fuel, unless the fuel has defects [54]. Few data are available at high temperatures (above 2000 K), and the data have large errors. The high-temperature data show either no dependence or very small dependence on burnup and on deviations from stoichiometry. The UO_2 and MOX data overlap on this region [58].

A brief review of some important UO_2 references follows. Washington [50] developed working tables and graphs that yield thermal conductivities as a function of temperature, composition, and deviations from stoichiometry. The 1989 formula of Harding and Martin [52] has been widely used by computer codes or as the basis for other correlations. The work of Lucuta et al. [54] is of particular importance because it separated the different effects of burnup, radiation, and deviation from stoichiometry by using SIMFUEL, a fuel with extended burnup simulated by adding stable (non-radioactive) additives to the UO_2 fuel matrix. Lucuta's correlation employs the basic expression for thermal conductivity from Harding and Martin [52] for fully dense, unirradiated UO_2 fuel multiplied by four factors that account for the effects of dissolved solid fission products, precipitated solid fission products, porosity, and radiation damage. There is a fifth factor, deviation from stoichiometry; but Ref. [54] states that under normal operating conditions, UO_2 fuel does not deviate from stoichiometry, and this factor is 1. However, for fuel with defects or under accident conditions, Ref. [54] recommends a lattice expression that accounts for the deviations from stoichiometry, and this expression may be used instead of the basic Harding and Martin formula.

The 1997 Wiesenak formula [55] for UO_2 was developed from data from the Halden Reactor Project. It is a very simple formula with only two variables: fuel temperature and burnup. It was developed for fuel with 95% TD. The MATPRO correlations [18] were developed a long time ago, and they have been improved recently by adding the effects of burnup (using a 1992 Lucuta correction [38]) and gadolinium. In 1999 Ronchi obtained new experimental data and developed a correlation for the thermal conductivity with two terms (the phonon lattice and ambipolar contribution) [43]. Finally, in 2000 Fink developed a new correlation, using the same ambipolar term of Ronchi and an improved lattice term [1]. The Fink correlation fits all the available data better than the Ronchi correlation. The Ronchi and Fink correlations have temperature dependence only and are for 95% TD fuel.

Fig. 9 compares four of these correlations with available experimental data of 95% TD UO_2 fuel with no burnup. The correlations are Wiesenak [55], a combined Lucuta/Ronchi described by Eq. (32) below, Fink [1] Eq. (31) below, and Harding and Martin [52]. The Fink correlation clearly provides the best fit to the data, in particular to the high-temperature data of Ronchi [43], and it yields the lowest calculated values of the four

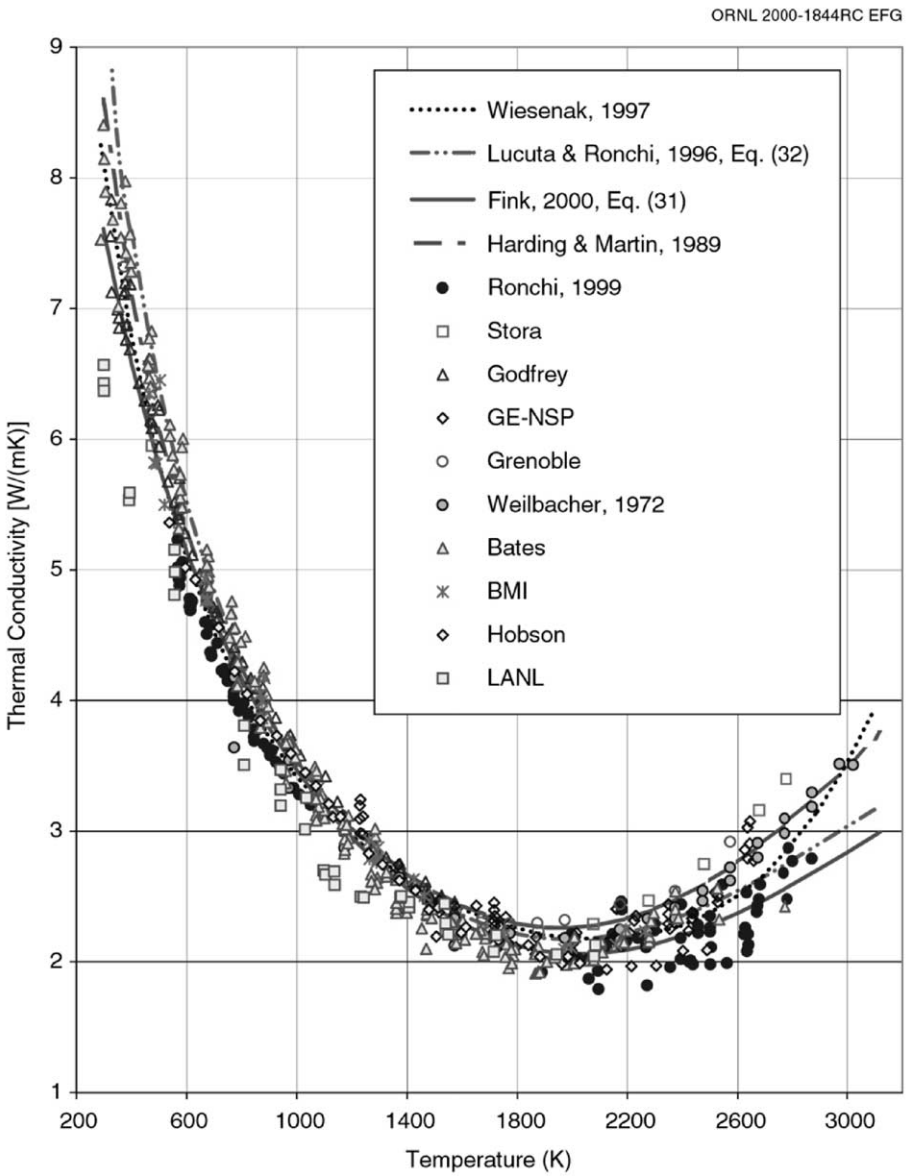

Fig. 9. Comparison of data and correlations for thermal conductivity of UO_2 with 95% TD and no burnup. *Source:* Modified from [2].

correlations for temperatures above 1400 K. The combined Lucuta/Ronchi correlation [Eq. (32)] also agrees well with the data.

For MOX fuel, the correlations developed by Philipponneau [53] and Duriez et al. [57] agree very well with experimental data. The Philipponneau correlation considers temperature, burnup, deviation from stoichiometry, and porosity. Duriez et al. consider the same variables, except burnup.

The MATPRO [18] correlation for MOX fuel has not been evaluated enough to be recommended. A preliminary evaluation of this correlation indicated that increasing fractions of PuO_2 result in decreasing values of the thermal conductivity, with the lowest value for 100% PuO_2. Some experimental data [59] indicate that the thermal conductivity of MOX decreases with increasing PuO_2 fraction until a minimum (around 70% of PuO_2) is reached; then it increases again, with values for pure PuO_2 similar to those of UO_2.

6.2. Recommendation

Because the changes taking place in the fuel during irradiation are independent of the kind of fuel (UO_2 or

MOX fuel), we recommend the physically based Lucuta et al. model [54] with separate factors as follows:

$$\lambda(T,B,x,p) = \lambda_o(T,x)\mathrm{FD}(B,T)\mathrm{FP}(B,T)\mathrm{FM}(p)\mathrm{FR}(T) \quad (\mathrm{W/m/K}), \tag{30}$$

where $\lambda_o(T,x)$ is the basic expression for unirradiated fully dense fuel. One basic expression will be used for UO_2 fuel and a different one for MOX fuel. The variable x (deviation from stoichiometry) is here because some basic expressions have this variable dependence. However, for stoichiometric, unirradiated fuel, $x = 0$. The remaining non-dimensional factors account for dissolved solid fission products from burnup (FD), precipitated solid fission products from burnup (FP), fuel porosity (FM), and radiation damage (FR). The basic expression for the thermal conductivity of UO_2 fuel in Lucuta's model is the Harding and Martin correlation [52]. As suggested by Fink [1], we also recommend using the Fink correlation [1] as the basic expression for UO_2 fuel

$$\lambda_o(T) = 1.158\left(\frac{100}{7.5408 + 17.692t + 3.6142t^2} + \frac{6400}{t^{5/2}}\exp^{-16.35/t}\right) \quad (\mathrm{W/m/K}) \tag{31}$$

with $t = T/1000$ (temperature in K), and the factor 1.158 is used to convert the original Fink correlation from 95% TD fuel to 100% TD fully dense fuel using Eq. (36). The range of validity of this correlation is from 298 to 3120 K (the melting temperature of UO_2), and the uncertainties for this formula are 10% from 298 to 2000 K and 20% from 2000 to 3120 K. The Fink correlation [1] agrees better with experimental data than other correlations as shown in Fig. 9. The Fink correlation [1], however, cannot account for deviations from stoichiometry that, according to Lucuta, are not common in UO_2 fuel [54]. For UO_2 fuel with defects that introduce deviations from stoichiometry, the following correlation, which combines the lattice term recommended by Lucuta et al. [54, Eq. (13)] and the ambipolar term of Ronchi [43] can be used

$$\lambda_o(T,x) = \frac{1}{0.0257 + 3.336x + (2.206 - 6.85x)t/10} + 1.158\frac{6400}{t^{5/2}}\exp^{-16.35/t} \ (\mathrm{W/m/K}) \tag{32}$$

with $t = T/1000$ and x deviation from stoichiometry.

The first term (lattice term) is for 100% TD fuel and does not need to be multiplied by the factor 1.158. Comparison of Eq. (32) with 95% TD stoichiometric data also shows very good agreement (Fig. 9).

The lattice term provided by Lucuta et al. is good only for temperatures below 1800 K. For higher temperatures, an ambipolar term needs to be added. We have chosen the Ronchi [43] ambipolar term because, as Fink did [1], it agrees very well with UO_2 data at high temperatures. The Ronchi term does not have dependence on x, but the experimental data reviewed show that at high temperatures, the effect of x is not important. Ref. [60] notes that the thermal conductivity of UO_2 fuel change very little with deviations from stoichiometry at high temperatures.

The variable x is considered *only* in the lattice term in all of the correlations for UO_2 [51,54] and for MOX [51,53,57] fuel that have been reviewed.

For fully dense MOX fuel, we recommend the following basic expression, which is a combination of the lattice term of Duriez [57] that agrees well with data at low temperatures and the ambipolar term of Ronchi [43] that provides better agreement with high-temperature MOX data than the ambipolar Duriez term

$$\lambda_o(T,x) = 1.158\left(\frac{1}{A + Ct} + \frac{6400}{t^{5/2}}\exp^{-16.35/t}\right) \quad (\mathrm{W/m/K}), \tag{33}$$

where

$A(x) = 2.85x + 0.035$ (mK/W),
$C(x) = (-0.715x + 0.286)$ (m/W),
$t = T/1000$ (temperature in K).

As in Eq. (31), the factor 1.158 converts from 95% TD to 100% TD per Eq. (36). This correlation has temperature and deviation from stoichiometry dependence and is valid from 700 to 3100 K, x less than 0.05, and for PuO_2 concentrations between 3% and 15%. As stated before, the PuO_2 concentration does not affect the thermal conductivity in this range. The uncertainties for these equations are estimated to be 7% between 700 and 1800 K, increasing to 20% at 3100 K.

The original Duriez correlation [57] with its ambipolar term can also be used as the basic expression for MOX fuel. This Duriez correlation fits very well the data used to develop it, but the combined Duriez/Ronchi correlation, Eq. (33), fits better other high-temperature data, such as laboratory-produced MIMAS fuel [57] and data of Ref. [53,58,61,62].

Fig. 10 compares the original Duriez correlation [57] and the recommended Duriez/Ronchi correlation, Eq. (33), with high-temperature MOX thermal conductivity data. Only experimental data above 1400 K are considered because both correlations are almost identical for temperatures below 1400 K. It is clear that the Duriez/Ronchi correlation, Eq. (33), fits the high-temperature data better than the original Duriez correlation.

Fig. 11 compares the ambipolar terms of Duriez [57], Ronchi [43], and Harding and Martin [52] for 95% TD fuel. As shown in Figs. 10 and 11, the Duriez/Ronchi correlation yields lower values than the original Duriez correlation at temperatures above 1500 K. The Duriez ambipolar term is the largest of the three terms; when

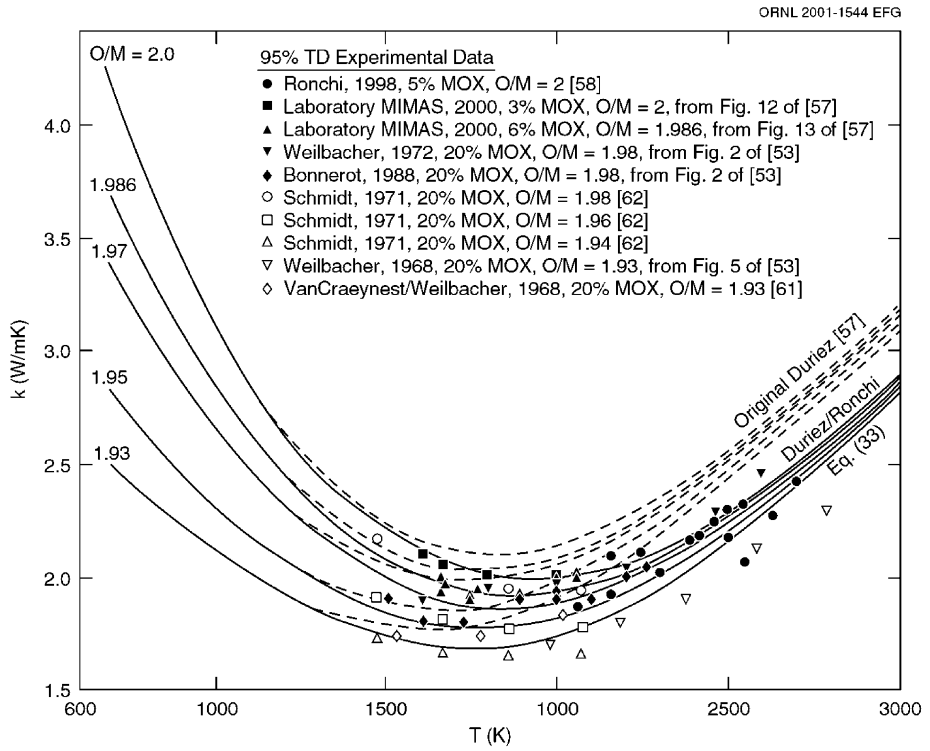

Fig. 10. Comparison of the original Duriez and the Duriez/Ronchi correlations with high-temperature, 95% TD, MOX thermal conductivity data.

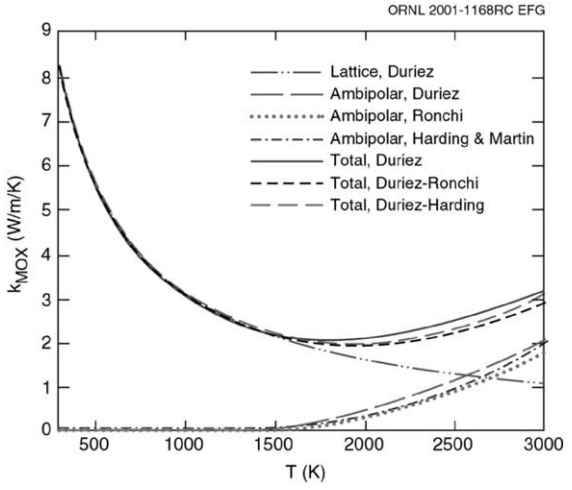

Fig. 11. Comparison of ambipolar terms and total thermal conductivity for 95% TD MOX fuel.

added to the Duriez lattice term, it also results in the largest total thermal conductivity. Because of this, the combined Duriez/Ronchi correlation fits some high-temperature data better than the original Duriez correlation [57].

Again, as in the case of UO_2 fuel [Eq. (32)], the effect of x, deviation from stoichiometry, is not important for MOX fuel at high temperatures. The MOX experimental data of Ref. [61] show that both the thermal diffusivity and the thermal conductivity changes very little with x at temperatures above 1773 K. Neither the ambipolar term of Duriez et al. [57] nor the one of Philipponneau [53] has dependence on x.

Fig. 12 shows the total thermal conductivity of stoichiometric, zero burnup UO_2 and MOX fuels calculated by Eqs. (31) and (33), showing the contributions from the lattice and the ambipolar terms. The ambipolar contribution (from Ronchi) is the same for UO_2 and MOX. The UO_2 lattice contribution is larger than that of MOX; therefore, the total thermal conductivity of UO_2 is larger than that of MOX. Above 2600 K, the total thermal conductivity of MOX fuel is slightly higher than the thermal conductivity of UO_2 fuel. Overlap of UO_2 and MOX fuel thermal conductivity values has been seen in some experiments [58]. If a basic correlation different than Fink's is used for UO_2 fuel, such as the combined Lucuta/Ronchi correlation, Eq. (32), or Harding and Martin [52] or Wiesenack [55], all of them shown in Fig. 9, the UO_2 thermal conductivity at temperatures above 2600 K will be noticeably higher, and the MOX values will not overlap with the UO_2

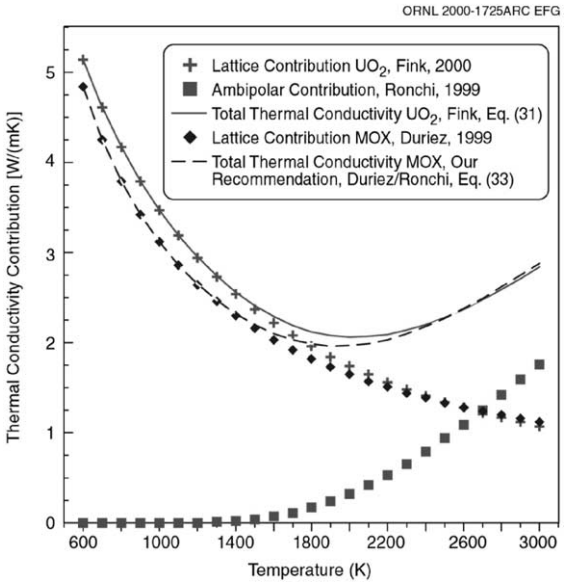

Fig. 12. Thermal conductivity contributions and total thermal conductivity of 95% dense, stoichiometric unirradiated UO_2 and MOX fuels [Eqs. (31) and (33)].

values. Conversely, if the original Duriez correlation [57] is used for MOX fuel, the overlap between the MOX and the UO_2 calculated values will be more pronounced.

The remaining factors of Eq. (30) are from Lucuta et al. [54] and are the same for both UO_2 and MOX fuels.

The effect of the dissolved fission products is calculated by a burnup and temperature-dependent factor FD:

$$\mathrm{FD} = \omega[\arctan(1/\omega)], \tag{34}$$

where $\omega = 1.09/B^{3.265} + 0.0643(T/B)^{1/2}$, T (temperature in K), and B is the burnup (in at.%).

The effect of the precipitated fission products is calculated by a burnup and temperature-dependent factor FP:

$$\mathrm{FP} = 1 + \frac{0.019B}{(3 - 0.019B)[1 + \exp -(T - 1200)/100]} \tag{35}$$

with temperature T (in K) and burnup B (in at.%).

The effect of porosity, p, is accounted for by the well-known Maxwell–Eucken equation [54]; also recommended in [53,57]

$$\mathrm{FM} = (1 - p)/(1 + 2p). \tag{36}$$

For $p = 0.05$, $\mathrm{FM} = 0.8636$, and $1/\mathrm{FM} = 1.158$, which is the factor used in Eqs. (31)–(33) to convert from 95% TD fuel (with $p = 0.05$) to 100% fully dense fuel.

There are other expressions to account for the porosity; as an alternative, the modified Loeb equation [51,52] may be used.

The radiation effect is calculated by the factor FR:

$$\mathrm{FR} = 1 - \frac{0.2}{1 + \exp(T - 900)/80}. \tag{37}$$

This factor has a significant effect at temperatures below 900 K, sharply decreasing as temperatures increase above 900 K. This factor is not dependent on the burnup.

Fig. 13 shows thermal conductivity values calculated by Eqs. (31) and (33) for UO_2 and MOX fuels, with and without radiation damage and with and without burnup (5% at burnup is 46.875 MWd/kg). The radiation damage is independent of burnup and reduces the thermal conductivity at temperatures below 1100 K.

For liquid fuel, a value of 2.5 ± 1 W/m/K is recommended by Fink for UO_2 fuel [1]. Because no values are available for MOX, the UO_2 value is also recommended for MOX.

Values of the thermal conductivity of solid fuel at the melting temperature of ~3100 K are around 3 W/m/K for both UO_2 and MOX (Figs. 9, 10, 12 and 13). These values are within the error band of the thermal conductivity of liquid fuel.

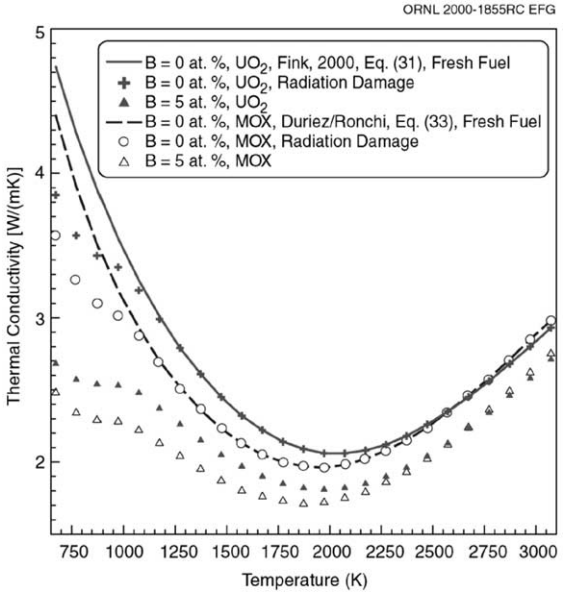

Fig. 13. Effect of radiation damage and burnup, B, on the recommended Eqs. (31) and (33) for the thermal conductivity of stoichiometric 95% dense UO_2 and MOX fuels.

6.3. Variable dependence and concluding remarks

The thermal conductivity of the fuel is a function of the temperature, fuel composition, fuel porosity, burnup, and deviation from stoichiometry. The thermal conductivity decreases with temperature up to ~2000 K and then increases with temperature. Addition of PuO_2 to the fuel or increasing porosities reduces the thermal conductivity. Burnup and/or deviations from stoichiometry significantly decrease the thermal conductivity. The last two effects are not so important at temperatures above 2200 K. The burnup may change the stoichiometry of the fuel by reducing the O/M ratio (or increasing x), so both effects are interrelated.

Fuel pins with MOX fuel or with burnup have lower thermal conductivities than fuel pins with UO_2 fuel or no burnup. Therefore, MOX fuel will have, for the same power, higher temperatures (in particular, the center of the fuel pellet) and more stored energy than UO_2 fuel.

The Lucuta's separate effect model has been selected as the best correlation for the thermal conductivity of fuel. A different basic thermal conductivity expression will be used for UO_2 (Fink [1] or combined Lucuta [54] and Ronchi [43] for fuel with defects) and for MOX (combined Duriez [57] and Ronchi [43]).

7. Conclusions

A comprehensive review of thermophysical properties of fuels, with emphasis on MOX fuel, has been completed. The properties reviewed are solidus and liquidus temperatures of the uranium/plutonium dioxide system, thermal expansion and density, enthalpy and specific heat, enthalpy of fusion, and thermal conductivity. Available properties for UO_2 and MOX fuels have been analyzed and compared, and the best set of correlations for both UO_2 and MOX fuels has been selected. These correlations can be used in codes for safety calculations.

As expected, the properties of UO_2 and MOX fuels (with up to ~5% PuO_2) are very similar, but some differences were clearly identified. The most significant differences follow:

1. MOX fuel has a *lower melting temperature*, *lower heat of fusion*, and *lower thermal conductivity* than UO_2 fuel. For the same steady-state power conditions, MOX fuel will result in *higher temperatures* and *more stored energy* than equivalent UO_2 fuel.
2. MOX fuel is *slightly heavier* than UO_2 fuel because ^{239}Pu is heavier than ^{235}U, the isotope that plutonium is replacing in MOX fuel.
3. Burnup and/or deviation from stoichiometry reduce the thermal conductivity of both UO_2 and MOX fuels significantly.

No good data were found on the heat of fusion of PuO_2, and only one data point was found for MOX fuel.

Acknowledgements

This paper has been a collaborative effort of the 'Kurchatov Institute', Russian Federation, and Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US Department of Energy under contract DE-AC05-00OR22725.

References

[1] J.K. Fink, J. Nucl. Mater. 279 (2000) 1.
[2] World Wide Web, INSC Materials Properties Database, http://www.insc.anl.gov/matprop.
[3] J.K. Fink, Int. J. Thermophys. 165 (1982) 3.
[4] International Atomic Energy Agency, Thermophysical properties of materials for water-cooled reactors, IAEA-TECDOC-949, June 1997.
[5] S.W. Pijanowski, L.S. DeLuca, Knolls, KAPL-1957, 1960.
[6] T.D. Chikalla, Hanford, HW-69832, 1961.
[7] W.L. Lyon, W.E. Baily, General Electric, GEAP-4640, 1964.
[8] R.E. Latta, R.E. Fryxell, Trans. Am. Nucl. Soc. 8 (2) (1965).
[9] H. Hausner, J. Nucl. Mater. 15 (1965) 179.
[10] W.L. Lyon, W.E. Baily, J. Nucl. Mater. 22 (3) (1967) 332.
[11] E.A. Aitken, S.K. Evans, General Electric, GEAP-5672, May 1968.
[12] H.C. Brassfield et al., GEMP-482, April 1968.
[13] R.A. Hein, P.M. Flagella, J.B. Conway, J. Am. Ceram. Soc. 51 (5) (1968) 291.
[14] R.E. Latta, R.E. Fryxell, J. Nucl. Mater. 35 (1970) 195.
[15] M.H. Rand et al., Rev. Int. Hautes Tempér. Réfract. Fr. 15 (1978) 355.
[16] M.G. Adamson, E.A. Aitken, R.W. Caputi, J. Nucl. Mater. 130 (1985) 349.
[17] J. Komatsu et al., J. Nucl. Mater. 154 (1988) 38.
[18] SCDAP/RELAP5 Development Team, SCDAP/RELAP5/MOD3.2 Code Manual, Volume IV: MATPRO – A Library of Materials Properties for Light-Water Reactor Accident Analysis, NUREG/CR-6150, vol. IV (INEL-96/0422), Rev. 1, October 1997.
[19] S. Yamanouchi et al., J. Nucl. Sci. Technol. 25 (1988) 538.
[20] K. Konno, T. Hirosawa, J. Nucl. Sci. Technol. 35 (1998) 494.
[21] D.G. Martin, J. Nucl. Mater. 152 (1988) 94.
[22] M. Tokar et al., Nucl. Technol. 17 (1973) 147.
[23] M. Benedict, T. Pigford, H.W. Levi, Nuclear Chemical Engineering, McGraw-Hill, New York, 1981.
[24] S.A. Hodge, Fission Gas Release and Pellet Fuelling Within the Capsule Assembly During Phase IV of the Average Power Test, Sect. 6.2.2.1, ORNL/MD/LTR-184, July 2000.
[25] D.D. Lanning et al., FRAPCON-3: Modifications to Fuel Rod Material Properties and Performance Models for High-Burnup Application, NUREG/CR-6534, vol. 1, PNNL-115113, October 1997.
[26] W. Breitung, K.O. Reil, Nucl. Sci. Eng. 105 (1990) 205.
[27] T.A. Sandenaw, J. Nucl. Mater. 10 (3) (1963) 165.
[28] O.L. Kruger, H.J. Savage, J. Chem. Phys. 49 (1968) 4540.

[29] T.K. Engel, J. Nucl. Mater. 31 (1969) 211.
[30] A.E. Ogard, in: Proceedings of the 4th International Conference on Plutonium and Other Actinides, Santa Fe, NM, 1970, p. 78 (Part 1).
[31] J.F. Kerrish et al., Nucl. Technol. 16 (1972) 531.
[32] L. Leibowitz et al., J. Nucl. Mater. 42 (1972) 113.
[33] L. Leibowitz et al., ANL-8082, February 1974.
[34] R.L. Gibby et al., J. Nucl. Mater. 50 (1974) 155.
[35] H.E. Flotow et al., J. Chem. Phys. 65 (3) (1976) 1124.
[36] F.L. Oetting, J. Nucl. Mater. 105 (1982) 257.
[37] E.H.P. Cordfunke, R.J.M. Konings, Thermochemical Data for Reactor Materials and Fission Products, North-Holland, Amsterdam, 1990.
[38] P.G. Lucuta et al., J. Nucl. Mater. 188 (1992) 198.
[39] P.G. Lucuta et al., J. Nucl. Mater. 223 (1995) 51.
[40] P.G. Lucuta et al., J. Nucl. Mater. 228 (1996) 251.
[41] P.G. Lucuta et al., J. Nucl. Mater. 247 (1997) 121.
[42] C. Ronchi et al., Nucl. Sci. Eng. 113 (1993) 1.
[43] C. Ronchi et al., J. Appl. Phys. 85 (1999) 776.
[44] J.J. Huntzicker et al., J. Chem. Thermod. 3 (1971) 61.
[45] M.T. Hutchings, J. Chem. Soc. Faraday Trans. II 83 (1987) 1083.
[46] J.P. Hiernaut et al., Int. J. Thermophys. 14 (1993) 259.
[47] L. Leibowitz et al., J. Nucl. Mater. 39 (1971) 115.
[48] L.F. Epstein, J. Nucl. Mater. 22 (3) (1967) 340.
[49] J.K. Fink, M.G. Chasanov, L. Leibovitz, J. Nucl. Mater. 102 (1981) 17.
[50] A.B.G. Washington, UK Atomic Energy Authority, TRG R-2236, September 1973.
[51] D.G. Martin, J. Nucl. Mater. 110 (1982) 73.
[52] J.H. Harding, D.G. Martin, J. Nucl. Mater. 166 (1989) 223.
[53] Y. Philipponneau, J. Nucl. Mater. 188 (1992) 194.
[54] P.G. Lucuta, H.J. Matzke, I.J. Hastings, J. Nucl. Mater. 232 (1996) 166.
[55] W. Wiesenack, in: Proc. ANS Inter. Topical Meeting on LWR Fuel Performance, Portland, OR, 1997, p. 507.
[56] K. Ohira, N. Itagaki, in: Proc. ANS Inter. Topical Meeting on LWR Fuel Performance, Portland, OR, 1997, p. 541.
[57] C. Duriez, J.-P. Alessandri, T. Gervais, Y. Philipponneau, J. Nucl. Mater. 277 (2000) 143.
[58] C.R. Ronchi, ITU Annual Report, EUR187515, 76 (1998).
[59] R.L. Gibby, J. Nucl. Mater. 38 (1971) 163.
[60] R. Brant, G. Neuer, J. Non-Equilib. Thermodyn. 1 (1976) 3.
[61] J.C. Van Craeynest, J.C. Weilbacher, J. Nucl. Mater. 26 (1968) 132.
[62] H.E. Schmidt, High Temp. High Press. 3 (1971) 345.