CHEMICAL FORM OF FISSION PRODUCTS IN HIGH BURNUP FUELS

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Abstract

In order to make a proper assessment of candidate materials for advanced high-burnup fuels, thermochemical studies of fuel materials have been performed. Using data from the ECN thermochemical database (TBASE), which has been updated and extended for the present work, the suitability of various advanced fuel materials and inert matrices is studied. Detailed thermodynamic equilibrium calculations are performed for $Pu_{0.42}U_{0.58}O_2$ and $Pu_{0.40}U_{0.60}N$ for values of the burnup up to 200 MWd/kgHM. The formation of metallic phases, the pressure buildup and the stability of nitride or oxide phases is studied for each fuel type. The results for the chemical form of the solid fission products are given.

The chemical aspects of the use of the inert matrix spinel ($MgAl_2O_4$) in combination with oxide fuel will be discussed. Experimental research on the compatibility of various types of inert matrices (nitrides, spinel) is in progress at ECN.

1. INTRODUCTION

Fuels with burnup far beyond current values are presently considered for incineration of plutonium. This can be achieved by the use of MOX fuels in LWRs or LMRs, but also by the use of advanced fuels like nitride or inert matrix fuels, which seem more suited for LMRs. Development of such fuel concepts is presently underway, but extensive research is required to evaluate the fuel performance under such extreme conditions.

At high burnup, significant changes in the chemical composition of the fuel occur, since a large number of fission products is formed in the fuel matrix. Many of these fission products will dissolve in the fuel matrix, but some will be gases that collect in pores and some can precipitate in separate phases. It is important to know the chemical changes that occur at high burnup since such changes may affect the gas release and mechanical and thermal properties of the fuel.

Because information on the chemical composition at high burnup cannot be obtained easily from experiments (due to the long irradiation times), thermochemical calculations are an important tool to understand the chemical processes in nuclear fuels, as will be shown in the present paper. The thermochemical approach is used to evaluate the equilibrium composition of various fuel types as a function of burnup.

2. THERMOCHEMICAL DATABASE: ECN-TBASE

In order to predict the chemical state of high-burnup fuel, accurate thermochemical data are a necessity. In 1985, a project on the evaluation of physico-chemical properties of fission products and reactor materials was started at the Netherlands Energy Research Foundation ECN. This ongoing program has resulted in a thermochemical database which presently

contains data of about 800 compounds. A selection of 197 compounds was published previously [1]. Each compound is carefully assessed. The evaluated thermochemical properties are the enthalpy of formation and the entropy at room temperature and a set of coefficients of the enthalpy increments for each temperature range. For the condensed compounds, the transition enthalpies and crystallographic data are also stored. In addition, each compound has a short description about the assessment or the references. The thermodynamic database of ECN (TBASE) is available in electronic form. The database can be consulted by software (TBASE-consult) which can generate thermodynamic tables and graphs, evaluate chemical reactions calculate stability diagrams (Fig. 1). The Gibbs energy functions can be exported to Chemsage [2] datafiles for calculation of phase equilibria in, for example, high burnup fuels.
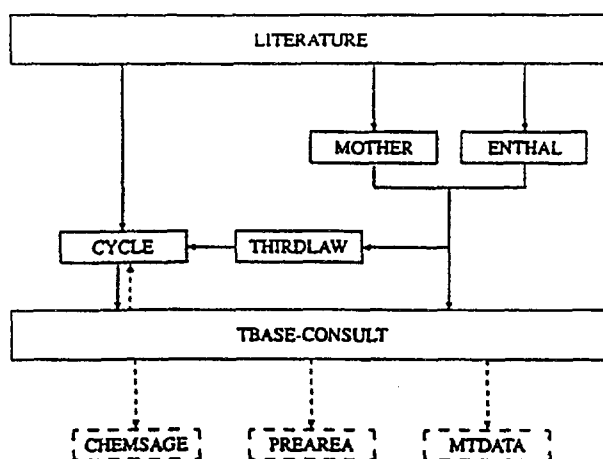

FIG. 1.   Flow diagram of the ECN computer programmes used in the assessment of thermochemical properties.

Recently, the database has been updated with compounds relevant for actinide incineration studies. This includes data for inert matrices for both oxide and nitride fuels. The completion of the database with inert matrix data also requires data for the reaction products of these matrices with the fission products. Especially in high-burnup fuels the chemical reaction of the inert matrix with the fission products may affect the fuel integrity.

3.   PHASE DESCRIPTION OF THE FUEL

Thermochemical calculations can predict the chemical behaviour of the fuel at high values of the burnup and may give a better understanding of the chemical processes in the fuel. The results of these calculations can be used as guidelines for the choice of fuel materials. In this section we will describe the input data files for the thermochemical calculations. Two data-input files for use with Chemsage were constructed; one is specific for oxide fuels, the other contains data for nitride fuels.

The predictive power of thermochemical calculations depends very much on the accuracy of the data and the completeness of the database that is used. Here we have chosen to take 30 elements into consideration. For the oxide fuel database these elements are: Ag, Al, Am, Ln, Ba, Ce, Cm, Cs, I, Kr, La, Mg, Mo, Nb, Nd, Np, O, Pd, Pr, Pu, Rb, Rh, Ru, Sr, Tc, Te, U, Xe, Y and Zr. Here the symbol Ln refers to lanthanide elements (=Pm, Sm,Eu,Gd,Tb,Dy,Ho,Er) that are treated as one representative lanthanide element. The elements Mg and Al are added to allow for the calculation of spinel matrices. All compounds that contain any of these elements are automatically selected within the ECN-Tbase and are exported to a Chemsage datafile. The compounds are grouped in different phases, so that phase separation phenomena during fission can be easily traced. The oxide fuel database is divided in five parts:

- GAS. This phase contains all gases. A total of 109 gases was considered.

- METAL. This phase represents the so-called five metal inclusions (Ru,Rh,Pd,Mo,Tc), the intermetallic compounds $(U,Pu)(Ru,Rh,Pd)_3$ and also metallic Ag and Te.

- OXIDE. This is the main oxide phase which contains 17 oxide compounds: actinide and lanthanide oxide (MO_2, M_2O_3) and solvents $(BaO,MgO$ and $SrO)$.

- GREY. This phase contains 9 perovskite compounds $(Ba,Sr)(U,Pu,Zr)O_3$ which form the so-called grey phase.

- Remaining condensed compounds(84) (e.g. CsI, Cs_2Te and spinel)

For the nitride fuel database the selected elements are: Ag, Am, Ln, Ba, C, Ce, Cm, Cs, I, Kr, La, Mo, N, Nb, Nd, Np, O, Pd, Pr, Pu, Rb, Rh, Ru, Sr, Tc, Te, U, Xe, Y and Zr. No OXIDE or GREY phase was defined here. The nitride datafile has the following structure:

- GAS. This phase contains all gases. A total of 116 gases was considered.

- METAL. This phase is identical to the METAL phase for the oxide datafile.

- NITRIDE. This phase contains all condensed nitride compounds (18). This includes the actinide and lanthanide mononitrides compounds (UN,PuN,LaN,CeN etc.) and U_2N_3, Mo_2N, Sr_3N_2 and Ba_3N_2.

- Remaining condensed compounds (119) (e.g. CsI and Cs_2Te)

All the mixture phases (GAS, METAL, NITRIDE,OXIDE and GREY) are assumed to be ideal mixtures phases. This is of course a very crude assumption which was made to get a quick insight in phase separation. In the future, it may however be necessary to add excess Gibbs energy terms for compounds with low solubility.

4. PHASE EQUILIBRIUM CALCULATIONS

The thermochemical calculations were performed for 1 cm^3 of oxide or nitride fuel. The temperature was fixed at 1500 K. The gas volume was assumed to consist of the porosity

of the fuel plus the available plenum volume in the pin per cm^3 of fuel. The calculations are performed as a function of the burnup. The nuclide inventory for $Pu_{0.42}U_{0.58}O_2$ and for $Pu_{0.40}U_{0.60}N$ was calculated for a fast reactor fuel inventory by use of coupled spectrum and burnup calculations [3].

4.1 Mixed oxide fuel

One of the most important parameters for oxide fuel is the oxygen potential. Since it is very hard to predict the oxygen potential in these large-scale thermodynamic calculations, the oxygen potential is fixed at a constant value of -300 kJ/mol. This is the approximate value of the oxygen potential of $Pu_{0.42}U_{0.58}O_2$ at 1500 K [4]. The actual oxygen potential may increase during fission, although a buffering reaction of the Mo/MoO_2 couple may limit the oxygen potential at a lower level: -325 kJ/mol.

The present composition is a reference oxide, other systems such as oxide fuel + inert matrices can be compared with the results of this system. The density of this oxide is 95.5%T.D. Evaluation of a typical fast reactor pin design shows that the free volume is 1.66 cm^3 per cm^3 of fuel pellet. It is assumed that the total available gas volume is the gas space in the solid (given by the porosity) plus the free volume. The gas volume for this system is therefore: (1-0.955)*1cm^3 + 1.66cm = 1.71 cm^3. The gas pressure during fission is mainly determined by the noble gases; the gas phase consists for $\approx$ 90% of Xe and Kr. The pressure increases linearly with the burnup and reaches a maximum of 157 bar at 203 MWd/kgHM (Fig. 2(a)). The calculated pressures are the maximum pressures in the plenum in case all gases are released to the plenum, the actual pressures inside gas bubbles in the solid may be larger.

The phase behaviour of the fuel during fission is depicted in Fig. 2(b). At the lowest burnup the (fresh) fuel consists of one phase: the OXIDE phase. As the burnup increases, the concentration of the fission products increases and new compounds and phases are formed. One of the well-known phases is the METAL phase which represents the metallic inclusions that are found in irradiated fuel [5]. In addition to the METAL phase, oxide precipates were found to consist mainly of Cs_2MoO_4 and $BaMoO_4$. The GREY phase was not formed, presumably because the oxygen potential is too high.
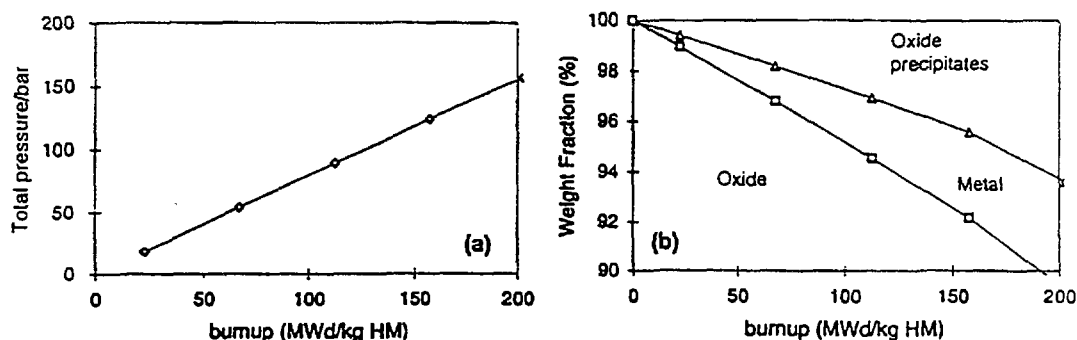

FIG. 2.   Behaviour of the MOX fuel as a function of burnup at T=1500 K and oxygen potential of -33 kJ/mol.
(a) Pressure; (b) Weight percentage of the different solid phases.

As an example, the speciation of Mo and Cs in the solid phases was calculated. The mole fraction of these elements in different phases is plotted in Fig. 3(a) and (b). Molybdenum is found to occur both in the METAL phase and as molybdate in the oxide precipitates. All the iodine of the fuel is converted in CsI.
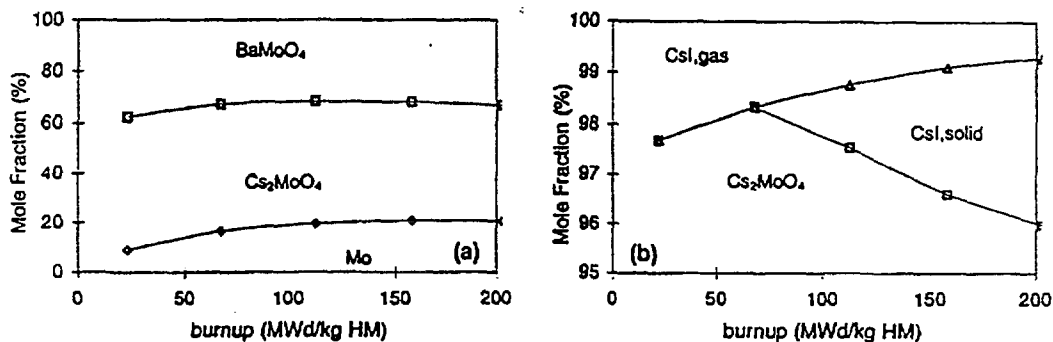

FIG. 3.   Speciation of (a) Mo and (b) Cs in oxide fuel at $T = 1500$ K and an oxygen potential of -300 kJ/mol.

4.2   Nitride fuel

Here we will evaluate the behaviour of a mixed nitride fuel $Pu_{0.40}U_{0.60}N$. It is assumed that the fuel is free of oxygen. The density of the nitride fuel is 85 % T.D. The gas volume for this system is therefore: $(1-0.85)* 1cm^3 + 1.66cm^3 = 1.81cm^3$. The development of the gas pressure as a function of the burnup is shown in Fig. 4(a). Again the gas atmosphere consists mainly of Xe and Kr. The gas pressure is deflected downwards at high burnup, which is related to the condensation of cesium. In contrast to the oxide fuel calculations, there are very few cesium compounds that can be formed in the nitride fuel. From the estimates in Ref. [6] it seems highly unlikely that cesium nitride (Cs_3N) will be formed.

The phase behaviour of the nitride fuel is shown in Fig. 4(b). As the burnup increases the amount of NITRIDE phase decreases and a METAL phase and "precipitates" in the form of Cs_2Te,Cs and CsI are formed. The METAL phase consists for more than 50 w% out of the very stable intermetallic compounds $(U,Pu)(Ru,Rb,Pd)_3$. The amount of METAL phase is slightly larger than the METAL phase of the oxide fuel. This is partly due to the high Mo content of the METAL phase, which is shown in Fig. 5(a). More than half of all the Mo can be found in the metallic phase, whereas for the oxide fuel (Fig.3(a)) only 20% of the Mo is metallic. At low values for the burnup more than 50% of the cesium is gaseous, the gas pressure of cesium increases to about 20 bars at 100 MWd/kgHM. At that burnup, the saturation pressure of cesium is reached and condensation of cesium metal starts. Part of the cesium reacts with Te and forms Cs_2Te.

The nitrogen pressure is shown in Fig. 6(a). The pressure remains below 0.1 bar and is controlled by the UN/U_2N_3 couple. As the burnup increases, the UN density decreases and U_2N_3 is formed (Fig. 6(b)). Uranium nitride (U_2N_3) plays an important role in the nitrogen balance, it takes up almost all nitrogen that is released during fission.
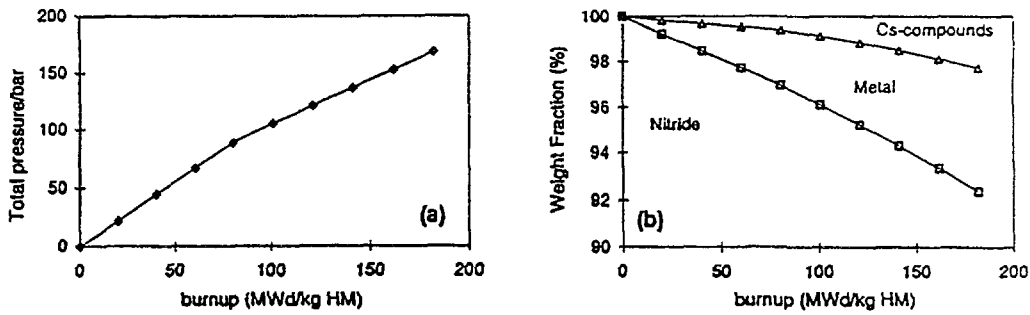
FIG. 4.   Behaviour of the nitride fuel as a function of burnup at $T = 1500 \ K$.
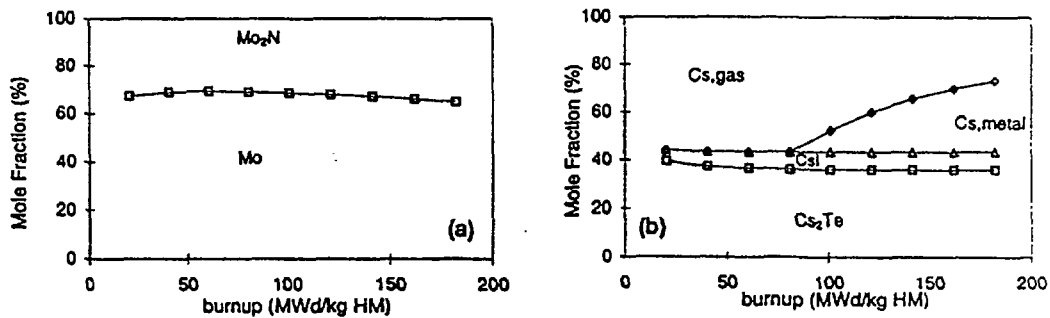(a) Pressure; (b) Weight percentage of the different solid phases.

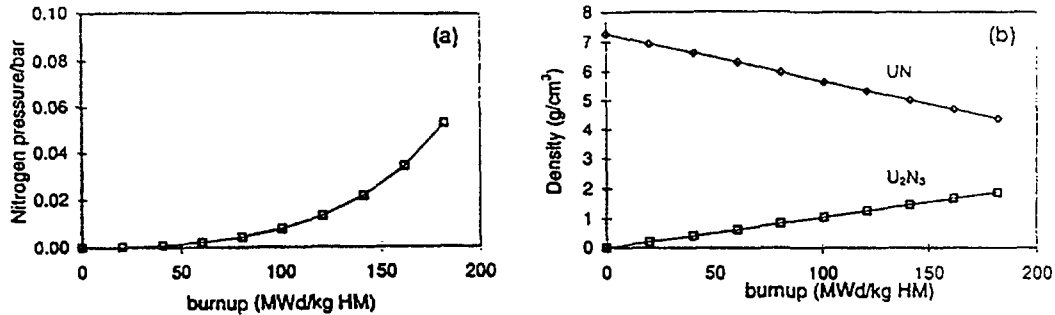FIG. 5.   Speciation of (a) Mo and (b) Cs in nitride fuel at $T = 1500 \ K$.

FIG. 6.   (a) Nitrogen pressure in the gas plenum and
(b) Amount of UN/U_2N_3 in the solid at $T = 1500 \ K$.

## 5.   COMPATIBILITY OF SPINEL WITH OXIDE FUEL

Spinel ($MgAl_2O_4$) is one of the candidate materials for use as an inert matrix in oxide fuels. Apart from neutronic requirements (low activitation of Mg, Al and O) the inert matrix should have good chemical compatibility with the fuel and the fission products. Ideally, an inert matrix mixes in all proportions with the fuel and does not react with the fission products. Even at high burnup, when a large amount of fission products is dissolved in the fuel, the inert matrix should remain intact and chemical reactions may not affect the physical integrity of the fuel pellet.

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One of the reactions with fission products that may occur in spinel-based fuel pellets is the reaction with the lanthanide elements:

$$MgAl_2O_4 + 2\ Ln + 1\frac{1}{2}O_2 \rightarrow 2LnAlO_3 + MgO$$
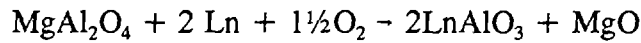
The lanthanide aluminates are stable compounds at normal operating conditions, so formation of these compounds may be expected. A calculation of the chemical state of spinel in a mixture of $PU_{0.42}U_{0.58}O_2$ + 60 vol% spinel was performed. All the lanthanide elements (Ln) were represented by lanthanum, and the lanthanide aluminates were represented by $LaAlO_3$. The thermochemical data of the lanthanide aluminates are given in Ref [7].

In Fig. 7 the speciation of Al in the different phases is shown. At 203 MWd/kgHM 95.5 w% of the initial amount of spinel is left. Aluminium is not only found in the spinel phase and as $LnAlO_3$ but also in Al_2O_3. This can be explained by the following reaction:

$$MgAl_2O_4 \rightarrow Al_2O_3 + MgO\ (OXIDE)$$
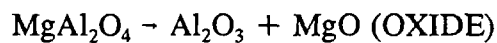
In this evaluation it was assumed that MgO dissolves in the OXIDE phase, which promotes this partial decomposition of spinel. Even when no lanthanide elements are present, spinel will decompose in Al_2O_3 and MgO. Lanthanum is found for more than 90% in the form of $LnAlO_3$, the rest is dissolved in the OXIDE phase as Ln_2O_3. The assumption that MgO forms an ideal mixture with the oxides is not completely correct. In fact, the evaluation of the MgO-PuO_2 phase diagram [8] shows that at 1500 K 0.6 mole% MgO can dissolve in PuO$_2$. According to [9] the solubility of MgO in UO_2 is approximately 35 mole% at 1600-1700°C. The calculated concentration in of MgO in the OXIDE phase (ideal mixing) is 4.8 mole% and does not depend on the burnup. Additional calculations showed that when MgO cannot dissolve in the OXIDE phase, no Al_2O_3 will be formed.

The compatibility of various inert matrices with fission products was examined at ECN. Interaction experiments were performed with spinel and lanthanide oxides. Lanthanide sesquioxide (Ln_2O_3, Ln=La,Nd and Eu) were mixed with spinel and heated at T=1473 K. The formation $LnAlO_3$ was confirmed by X-ray diffraction. This supports the thermochemical predictions for the formation of lanthanide aluminates. The question however is, if plutonium will form $PuAlO_3$ with spinel. PuAlO$_3$ was formed from PUO$_2$ and Al$_2$O$_3$ or Al(OH)$_3$ in
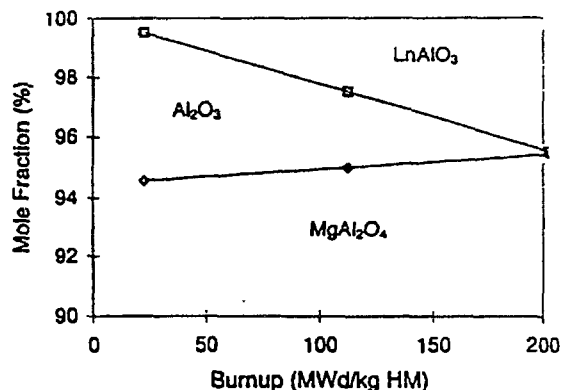

FIG. 7.   Speciation of Al in spinel-based oxide fuel. The mole fraction Al is plotted as a function of the burnup at T = 1500 K.

strongly reducing environments (carbon powder or hydrogen atmosphere) [10]. Thermochemical data for $PuAlO_3$ are required to predict the compatibility of PuO_2 with spinel.

6. CONCLUSION

A thermochemical analysis of high burnup MOX and mixed nitride fuel was performed. For both the oxide and the nitride fuel it was found that a metal phase of about 4-5w% is formed at a burnup of 180 MWd/kgHM. The speciation of Mo showed that in oxide fuel molybdenum is predominantly present as cesium- or barium-molybdate, whereas in the nitride fuel it is mainly found in the metallic phase. The cesium pressure in the gas plenum of the nitride fuel reaches the saturation pressure at high burnup so that metallic cesium will be formed.

The chemical compatibility of spinel with oxide fuel was examined. It seems that the formation of lanthanide aluminates from spinel and the lanthanide elements is likely at normal thermodynamic conditions (T=1500 K, oxygen potential=-300 kJ/mol). At 203 MWd/kgHM about 4.5w% of the initial amount of spinel is decomposed. The solubility of MgO in the OXIDE phase seems to be important for the stability of spinel, already at low values of the burnup.

The presented thermochemical calculations are based on ideal mixture phases. More detailed models including excess parameters will be an item for future research.

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