

2.3 High-Temperature Reactor developments in The Netherlands

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Abstract

The high-temperature reactor development in the Netherlands is embedded in the WHITE reactor program, in which several Dutch research institutes and engineering companies participate. The activities within the WHITE program are focused on the development of a small scale HTR for combined heat and power generation. In 1995, design choices for a pebble bed reactor were made at ECN. The first concept HTR will have a closed cycle helium turbine and a power level of 40 MWth. It is intended to make the market introduction of a commercially competitive HTR feasible. The design will be an optimization of the Peu-à-Peu (PAP) concept of KFA Jülich. Computer codes necessary for the evaluation of reactor physics aspects of this reactor are developed in cooperation with international partners. An evaluation of a 20 MWth PAP concept showed that the maximum fuel temperature after depressurization does not exceed 1300 °C.

As a part of the HTR program at ECN, chemical aspects of HTR fuel and coated particles are studied. Experimental work on the oxidation resistance of coating materials and fission product attack on coating materials as well as thermochemical calculations of the fuel particles are done at ECN. The concept-HTR of ECN is fuelled with UO₂, but the use of thorium is considered. The composition of the fuel determines the oxygen potential, which plays a key role in chemical safety of the fuel. Thermochemical calculations of the chemical form of cesium inside the HTR fuel particles were performed for a wide oxygen potential range. The chemical form of cesium determines the cesium pressure inside the fuel particle, which in turn determines the release behavior of Cs from defective particles. At normal operating temperatures and low oxygen potentials, the chemical form of cesium is C₆₀Cs. It is known that cesium carbon compounds decompose above 650 °C in vacuum. The stability of these compounds in the fuel particles at high temperatures (1000-1600 °C) is questioned. Decomposition of these compounds may result in high cesium pressures even at normal operating conditions. Experimental work on the thermodynamic properties of cesium compounds at high temperatures is currently performed.

1 Introduction

In 1993, ECN started the WHITE (Widely applicable High Temperature Reactor) program, for the development of a safe and environmental-friendly high-temperature reactor HTR. This modular-type HTR is considered as an interesting option for small scale combined heat and power generation in the Netherlands. In 1995 some design choices were made and at present the WHITE program focuses on an optimized concept based on the Peu-à-Peu design of KfA Jülich [1]. A small pebble bed reactor with a closed cycle gas turbine is chosen, the power level of the current concept is 40 MWth. The design is very simple; no emergency cooling system, backup shutdown systems or containments should be needed. The reactor will shut down after a core heat accident due to the negative temperature coefficient. Even in the worst case, the fuel temperature does not exceed 1300 °C. The TRISO-coated fuel particles contain uranium oxide fuel kernels. The use of thorium will also be considered.

The activities of ECN within the WHITE program include studies of the reactor physics of the HTR, as well as chemical aspects of the fuel. Physics aspects of the HTR being studied include safety analyses, optimization of the design and the thorium fuel cycle. The chemical studies concern the oxidation and Pd-attack of coating materials, the stability of carbide fuel, and the thermochemical processes inside the fuel particles during normal and off-normal conditions.

Thermochemical properties of reactor materials are vital for fuel fabrication, reprocessing and behaviour of the fuel during reactor operation. The understanding of the processes in the fuel particle, such as thermal migration and corrosion of the SiC coating, requires thorough knowledge of chemical reactions inside the particles. The release of fission products from defect particles, the interaction of fission products with the coating layers are important issues of HTR safety. The long term stability of stored HTR-waste (i.e. the integrity of the fuel particle and elements, the corrosion resistance of the coating layers) may be estimated by means of thermochemical assessments based on accurate experimental data.

In order to study the above mentioned processes, the nuclear chemistry group at ECN performs thermodynamic measurements of compounds that appear in nuclear systems. Data of various compounds are collected and continuously updated in a Thermodynamic Database (TBASE), part of which is published [2]. As an example of this thermochemical research, the chemical form of one of the hazardous fission products, Cs, in the HTR fuel particle will be discussed in this paper.

In the interior of the TRISO-coated fuel particle, a porous carbon layer is used for the retention of fission products. Fission products such as cesium are absorbed on carbon [3] but can also form lamellar cesium carbon (CsC_n) compounds. Kwasny, Hilpert and Nickel [4] have

performed an extensive series of measurements of the sorption of cesium on various types of graphite at 950-1820 K. The formation and decomposition of intercalation compounds with the formula CsC_n ($n=8,10,24,36,48,60$) was studied by Aronson and Salzano [5]. The same authors also measured the cesium vapour pressure of these compounds in the temperature range 670-1070 K [6, 7].

Thermochemical calculations of Minato *et al.* [8], show that the predominant chemical form of cesium inside the carbon buffer layer is Cs_2MoO_4 for temperatures up to 1600-1800 K. For temperatures higher than 1800 K cesium carbon compounds, CsC_n , are formed. Aronson and Salzano [5] have studied the decomposition of lamellar cesium graphite compounds and found that all compounds (CsC_n) have decomposed at 923 K *in vacuo*. Tromp and Cordfunke [9] state that the stability of KC_n compounds in a purified helium-flow is limited to a temperature of 875 K. The question that rises is: Are the CsC_n compounds stable at temperatures up to 1600 K? It may be that the cesium carbon compounds are stabilized by their own Cs pressure inside the HTR fuel particle, even at elevated temperatures. Decomposition of the cesium carbon compounds may result in a sudden increase of the cesium pressure inside the fuel particle. However, no thermodynamic measurements of CsC_n above 1080 K are available in literature.

Obviously, the chemical form of the relatively large amount of cesium inside the HTR fuel particle is of great importance for estimates of the release of cesium under normal/off-normal conditions.

2 Formation of cesium carbon compounds

Salzano and Aronson studied the stability and the equilibrium Cs vapour pressures of CsC_n compounds in the temperature range 400-800 Celsius using Knudsen effusion in conjunction with a tracer technique [5, 6, 7, 10]. From the vapour pressure measurements, they derived the Gibbs energy of formation of CsC_n [7], described by:



The thermodynamic parameters of the formation of cesium intercalates are given in Reference [7]. We have used these data and the thermodynamic data of C(s) [11] and Cs(g) [2] to calculate the Gibbs energy function of CsC_n . These thermodynamic data were used for further thermodynamic calculations.

The vapour pressure of cesium in a carbon environment is plotted in Figure 1. In the figure the threshold Cs-pressure for the formation of Cs intercalates is shown. From their vapour pressure measurements Aronson and Salzano [10] derived the equation:

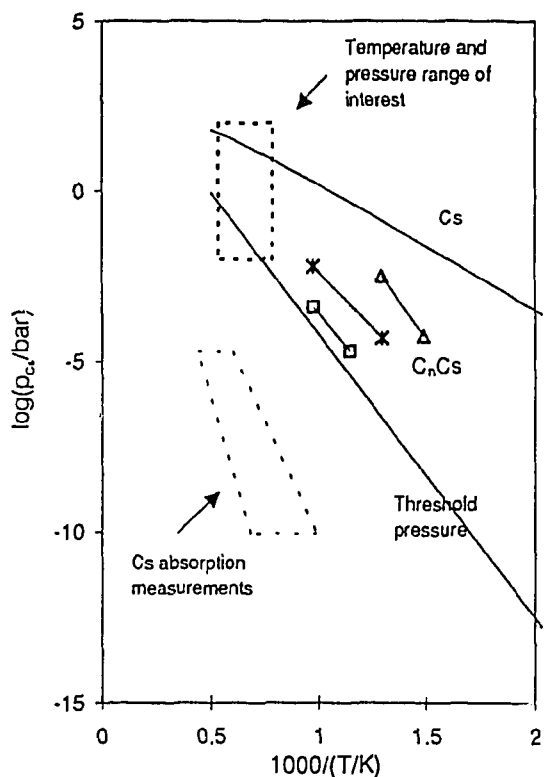


Figure 1: Cesium vapour pressures [7]: (□): $C_{60}Cs/C_{48}Cs$; (*) $C_{24}Cs/C_{10}Cs$; (Δ): $C_{10}Cs/C_8Cs$. Dashed area refers to the sorption measurements [3]. Upper solid line is the vapour pressure of pure Cs, the lower solid line is the threshold pressure for the formation of intercalation compounds 2. The dashed box refers to the temperature range of 1273-1873 K for which no thermodynamic data of CsC_n are available.

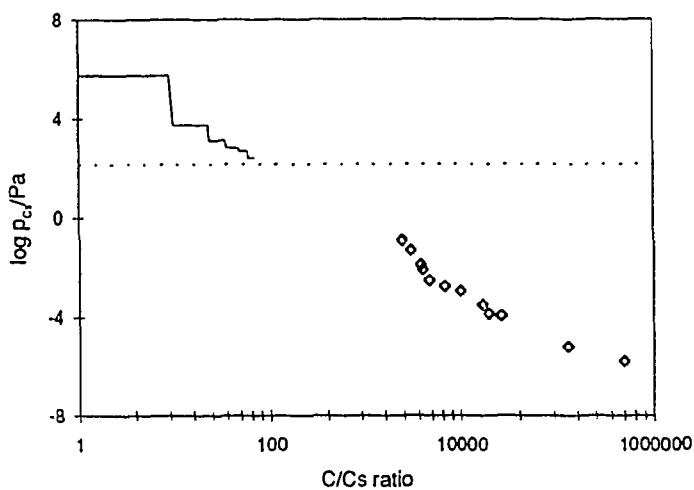


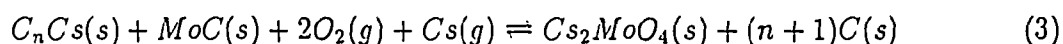
Figure 2: Cesium pressure versus C/Cs ratio, $T=1200$ K. Solid line: Intercalates [7]; Dashed curve: threshold pressure (Eq. 2). ◇ Sorption measurements [4]

$$\ln p_{Cs}/\text{bar} = -\frac{158992}{RT} + \frac{78.34}{R} \quad (2)$$

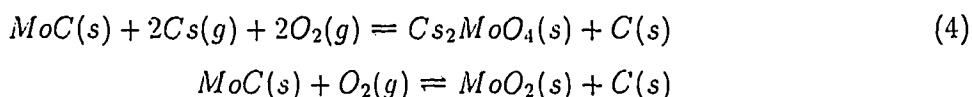
For cesium pressures below the threshold pressure cesium absorbs on carbon and above the threshold pressure cesium intercalates are formed. The predicted threshold pressure was experimentally verified by Merz and Scharf [12] for pyrographite and reactor graphite. As the threshold pressure is exceeded, $C_{60}Cs$ is formed. Further increase of the pressure leads to formation of $C_{48}Cs$, $C_{36}Cs$ etc. and finally a C_8Cs/Cs mixture remains. Note that the measurements of Aronson and Salzano are performed in a limited temperature range. Extrapolation of the $C_8Cs/C_{10}Cs$ vapour pressure curve shows that C_8Cs cannot be stable above 1000 K, even if the cesium pressure is increased. The question is whether the other intercalates are stable at temperatures up to the maximum fuel temperature of the HTR (1873 K). Below the threshold pressure sorption of Cs on graphite takes place, as was extensively studied by Kwasny, Hilpert and Nickel [4]. Vapour pressures of cesium were measured using Knudsen effusion and mass spectrometry for different cesium concentrations. In Figure 2 the cesium vapour pressures for the intercalates [7] and of chemisorbed cesium Kwasny [4] extrapolated to 1200 K are shown. The data are plotted versus the carbon/cesium ratio in the condensed phase. For large cesium concentrations (small C/Cs ratio) the cesium pressure changes stepwise at C/Cs = 8,10,24 etc. Below the threshold pressure sorption of cesium on carbon is expected. In the HTR fuel particle, the overall C/Cs ratio can be as large as 160 (see Table 1), so that formation of intercalates may be expected.

3 Chemical form of cesium

Both the cesium pressure and the oxygen potential play an important role for the chemical form of cesium in the condensed phase. As was pointed out by Lindemer [13] cesium molybdate is the stable form of Cs if a certain oxygen potential is exceeded. Since MoC is the stable form of Mo in a carbon environment, the formation of cesium molybdate from MoC has to be considered:



The formation of Cs_2MoO_4 and MoO_2 are given by the following reactions:



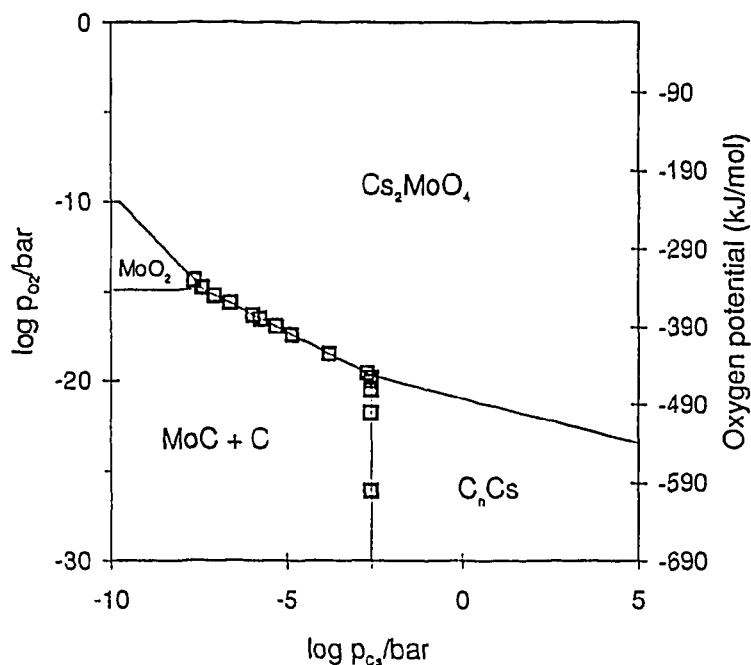


Figure 3: Predominance area diagram of the C-Cs-Mo-O system at 1200 K. The boxes refer to the calculations of the HTR fuel at 5.5 % FIMA and 1200 K.

As was shown by Cordfunke and Konings [14] Cs_2ZrO_3 can be formed at low oxygen potentials from ZrO_2 . At $T=1200\text{ K}$ Cs_2ZrO_3 is formed below an oxygen potential of $-508\text{ kJ}\cdot\text{mol}^{-1}$ at a minimum cesium pressure of 0.16 bar.

At the normal fuel temperature of the HTR (1200 K) the threshold oxygen potential for the formation of Cs_2MoO_4 out of C_{60}Cs is $-460\text{ kJ}\cdot\text{mol}^{-1}$. C_nCs is more stable than Cs_2ZrO_3 according to the present calculations, but it should be stressed that these calculations are based on extrapolations of the thermodynamic measurements of C_{60}Cs [6, 7] that were performed in the range 670-1070 K. The thermodynamic parameters Cs_2ZrO_3 at room temperature were taken from [2], and were recently updated with enthalpy increment measurements up to 640 K. The thermodynamic properties of both cesium compounds at HTR fuel conditions are presently experimentally determined at ECN.

4 Thermodynamic calculations of the HTR particle

During the lifetime of a fuel particle both the burnup and the fuel temperature will change. The burnup and the temperature are the most important parameters for the thermochemical description of the fuel, for they determine the inventory of the particle, the oxygen potential,

Table 1: Inventory of the HTR fuel particle at 5.5 % FIMA [8]

	Amount (10^{-8} mol)	mol %
C	755.00	62.44
UO ₂	411.00	34.00
Total F.P.	43.0	3.56
Kr	0.74	0.06
Rb	0.70	0.06
Sr	1.78	0.15
Zr	6.49	0.54
Mo	5.74	0.47
Tc	1.47	0.12
Ru	3.63	0.30
Rh	1.03	0.08
Te	0.57	0.05
I	0.29	0.02
Xe	5.32	0.44
Cs	4.79	0.40
Ba	1.57	0.13
La	1.46	0.12
Ce	2.75	0.23
Nd	4.62	0.38
Eu	0.07	0.01

the chemical form of the fission products and the pressure inside the fuel particle. For the present calculations TRISO-coated UO₂ fuel particles will be considered. The fuel kernel is coated with a porous carbon layer, an inner PyC layer, a SiC coating and an outer PyC layer, but in the present case only the fuel kernel and the porous carbon layer are taken into account. It will be assumed that the PyC layers and the SiC coating remain intact, and no gas transport through these layers will take place. Normal conditions are assumed; the fuel temperature is 1200 K, and the burnup is 5.5 % FIMA. Both the particle dimensions and the inventory at 5.5 % FIMA are taken from the study of Minato *et al.* (Reference [8]) and are summarized in Table 1. The buffer volume of the porous carbon layer is 3.14×10^{-11} m³ [8], and the total amount of carbon is 7.55×10^{-6} mole and the initial amount of uranium oxide is 4.35×10^{-6} mole. At 5.5 % FIMA 4.11×10^{-6} mole of UO₂ remains and 0.48×10^{-6} mole of fission product is formed, which are specified in Table 1. It is commonly assumed that the oxygen potential increases with increasing burnup [15], although this could not be confirmed experimentally by Matzke [16]. Since the burnup dependence of the oxygen potential remains a point of discussion in literature, the calculations are performed as a function of the oxygen potential. The thermochemical calculations are performed using the ChemSage code [17]. The

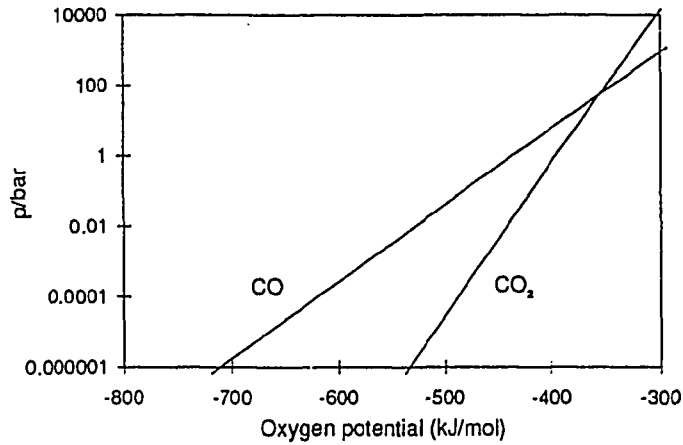


Figure 4: Pressure of CO and CO₂ as a function of the oxygen potential assuming an excess of carbon. T=1200 K

thermochemical data were taken from the ECN thermodynamic database [2]. The condensed compounds that were used in the present calculations are listed in Table 2.

Because of the excess amount of carbon inside the fuel particle, the CO and CO₂ pressures can become quite large. This is demonstrated in Figure 4, where both pressures are plotted as function of the oxygen potential at 1200 K. The CO/CO₂ equilibrium plays an important

Table 2: List of compounds used in thermochemical calculations [2]

Solids				Gases			
Ba	CeO ₂	La	SrUO ₄ (β)	Ba	Cs ₂ I ₂	La ₂ O ₂	SrO
BaMoO ₄	Cs	La ₂ O ₃	SrZrO ₃	Ba ₂	Cs ₂ MoO ₄	LaO	Tc
BaO	Cs ₂ Mo ₂ O ₇	La ₂ Zr ₂ O ₇	Tc	BaMoO ₄	Cs ₂ O	Mo	Te
BaU ₂ O ₇	Cs ₂ MoO ₄	Mo	Te	BaO	Cs ₂ O ₂	Mo ₂	Te ₂
BaUO ₃	Cs ₂ O	MoC	TeO ₂	C	CsI	Nd	TeO
BaUO ₄	Cs ₂ Te	MoO ₂	U	C ₂	CsO	NdO	TeO ₂
BaZrO ₃	Cs ₂ U ₂ O ₇	Nd	UO ₂	C ₃	CsTe	NdO ₂	UO
C	Cs ₂ U ₄ O ₁₂	Nd ₂ O ₃	UO ₃ (β)	C ₄	Eu	O	UO ₂
C ₈ Cs	Cs ₂ UO ₄	Rb	UO ₃ (γ)	C ₅	Eu ₂ O	O ₂	UO ₃
C ₁₀ Cs	Cs ₂ ZrO ₃	Rh	Zr	Ce	Eu ₂ O ₂	O ₃	Xe
C ₂₄ Cs	CsI	Ru	ZrO ₂	CeO	EuO	Rb	Zr
C ₃₆ Cs	Eu	Sr		CeO ₂	I	Rb ₂	ZrO
C ₄₈ Cs	Eu ₂ O ₃ (β)	Sr ₂ ZrO ₄		CO	I ₂	Rh	ZrO ₂
C ₆₀ Cs	Eu ₂ O ₃ (γ)	Sr ₃ Zr ₂ O ₇		CO ₂	Kr	Ru	
Ce	EuO	Sr ₄ Zr ₃ O ₁₀		Cs	La	Sr	
Ce ₂ O ₃	I ₂	SrO		Cs ₂	La ₂ O	Sr ₂	

role in the thermal migration (or amoeba effect) of the fuel kernel up the temperature gradient. When the PyC layer becomes defective due to the amoeba effect, CO gas can oxidize the SiC layer.

The thermodynamic calculations of the HTR fuel particle based on the inventory of Table 1 showed that the total pressure inside the buffer volume (at $T=1200$ K and 5.5 % FIMA) is 200 bar, which is essentially the sum of the Xe (170 bar) and the Kr (24 bar). The actual noble gas pressure may be lower since part of the noble gases remains dissolved in the fuel kernel. Only at high oxygen potentials (larger than ≈ -390 kJ·mol⁻¹) the contribution of the CO and CO₂ pressure to the total pressure is significant which is shown in Figure 5. In the same plot the partial pressure of some cesium compounds are shown. The predominant chemical form of Cs in the gas phase is a saturated CsI vapour with a partial pressure of 0.033 bar. Cesium iodine (CsI) is the dominant chemical form of Iodine in both the condensed and the gas phase. Only 6 % of the total amount of cesium is present as CsI. (Figure 6). The CsI pressure is independent of the oxygen potential which shows that condensed CsI is a very stable compound. C₆₀Cs is the most stable compound up to -460 kJ·mol⁻¹, and Cs₂MoO₄ is found at higher oxygen potentials. At -390 kJ·mol⁻¹ Cs₂Te disappears and more Cs₂MoO₄ is formed.

Post-irradiation studies on uranium oxide revealed that molybdenum is found in metallic precipitates ("white inclusions") in the fuel [15]. The present study indicates that the thermodynamic stable form of Mo in the carbon-rich environment of the HTR particle is molybdenum carbide. The chemical form of Mo in the condensed phase is shown in Figure 7. Oxidation of Mo occurs at oxygen potentials larger than -342 kJ·mol⁻¹. At lower oxygen potentials Cs₂MoO₄ (-452 kJ·mol⁻¹) and BaMoO₄ (-370 kJ·mol⁻¹) are formed.

In Figure 8 it is shown that a large portion (about 27 %) of the porous carbon layer used for the formation of C₆₀Cs. For oxygen potentials larger than -452 kJ·mol⁻¹ cesium forms cesium molybdate and C₆₀Cs disappears.

It is interesting to compare the thermodynamic calculations with the predominance diagram Figure 3. The cesium pressures were calculated in the oxygen potential range from -800 to -330 kJ·mol⁻¹, and the results are plotted in Figure 3. For the lowest oxygen potentials the cesium pressure is controlled by the C/C₆₀Cs equilibrium. For larger oxygen potentials (> -452 kJ·mol⁻¹) the cesium pressure decreases moves along the MoC/Cs₂MoO₄ phase line. For the highest oxygen potentials (> -342 kJ·mol⁻¹) MoO₂ is formed. This plot shows that as the oxygen potentials increases the partial cesium pressure decreases. The total amount of Cs in the vapour phase, however, is governed by the CsI pressure which was constant for all oxygen potentials. When both C₆₀Cs and Cs₂ZrO₃ are not stable at 1200 K, however, the cesium pressure can reach high values. When no cesium compounds exist at this temperature the cesium pressure can increase to a maximum of 152 bar at 5.5 % FIMA.

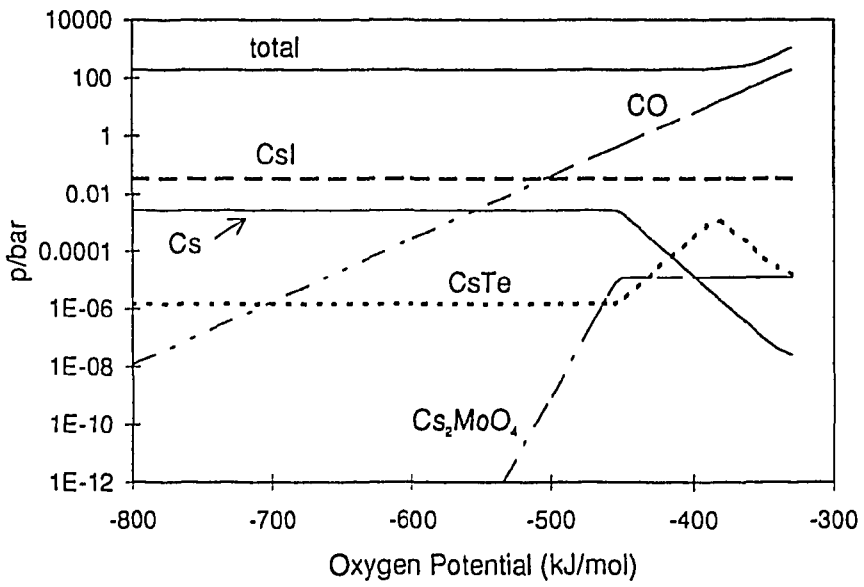


Figure 5: Pressure of different compounds in the HTR-particle buffer volume at T = 1200 K, and 5.5 % FIMA

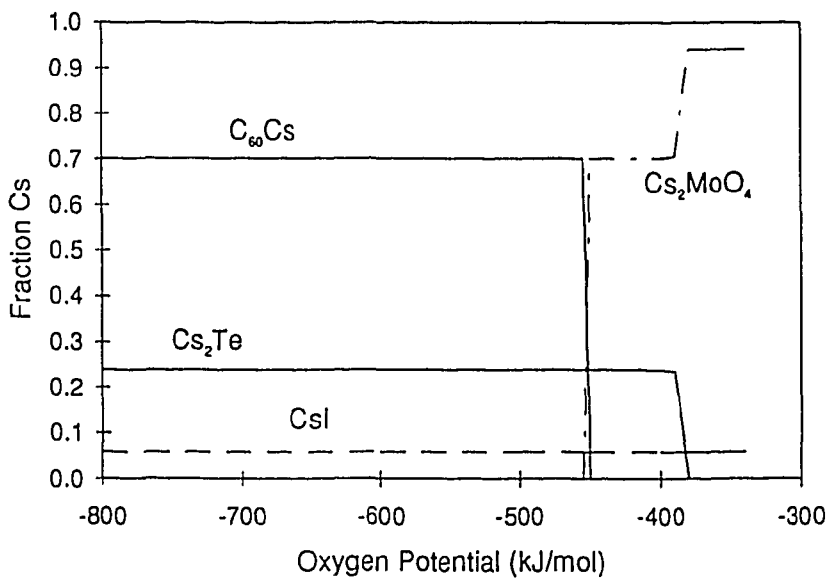


Figure 6: Fraction of Cs in the condensed phase

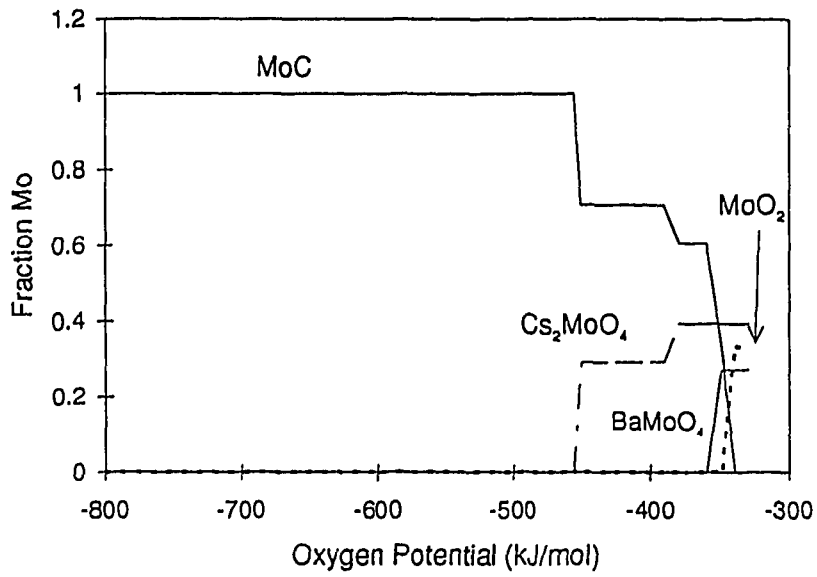


Figure 7: Fraction of Mo in the condensed phase

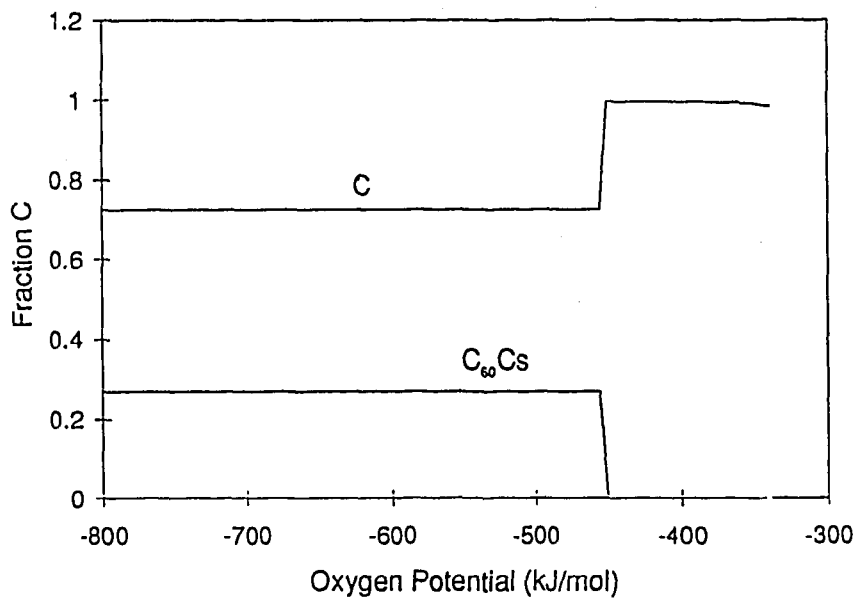


Figure 8: Fraction of C in the condensed phase

5 Conclusion

After a familiarization phase the Dutch HTR program is well underway. The HTR developments have resulted in design choices for a small Peu-à-Peu HTR. The reactor will be fuelled with spherical fuel elements, filled with UO_2 fuel particles. Part of the HTR research at ECN deals with the chemistry of the TRISO-coated fuel particles. Thermochemical calculations show that the predominant chemical form of Cs in the condensed phase inside the HTR fuel particle is, depending on the oxygen potential, either C_{60}Cs or Cs_2MoO_4 . In the vapour phase inside the buffer volume of the fuel particle, CsI is the predominant form of Cs. For these calculations, extrapolated thermochemical data of the cesium intercalates and Cs_2ZrO_3 had to be used. Stability measurements of both compounds in the temperature range 1200-1800 K are required. Decomposition of these compounds in this temperature range can give a considerable increase in the cesium pressure.

References

- [1] H. Gerwin E. Teuchert and K.A. Haas. Simplification of the pebble bed high-temperature reactor. In *International Specialists' Meeting on Potential of Small Nuclear Reactors for Future Clean and Safe Energy Sources, Tokyo, October 23-25, 1991*.
- [2] E.H.P. Cordfunke and R.J.M. Konings. *Thermochemical data for reactor materials and fission products*. Elsevier Science Publishers, 1990.
- [3] R. Moormann and K. Hilpert. Chemical behavior of fission products in core heatup accidents in high-temperature gas-cooled reactors. *Nucl. Technol.*, 94:56-67, 1991.
- [4] J. Kwasny, K. Hilpert, and H. Nickel. Investigation of the sorption of cesium by graphitic reactor materials. Juel-2353, Forschungszentrum Jülich GmbH, 1990.
- [5] F.J. Salzano and S. Aronson. Kinetic study of the decomposition of cesium-graphite lamellar compounds. *J.Chem.Phys.*, 42(3):1323-1330, 1965.
- [6] F.J. Salzano and S. Aronson. Thermodynamic properties of the cesium-graphite lamellar compounds. *J.Chem.Phys.*, 43(1):149-154, 1965.
- [7] F.J. Salzano and S. Aronson. Stability of phases in the cesium-graphite system. *J.Chem.Phys.*, 45(6):2221-2227, 1966.
- [8] K. Minato, T. Ogawa, K. Fukuda, M. Shimizu, Y. Tayama, and I. Takahashi. Fission product behavior in Triso-coated UO_2 fuel particles. *J.Nucl.Mater.*, 208:266-281, 1994.

- [9] P.J.J. Tromp and E.H.P. Cordfunke. A thermochemical study of the reactive intermediate in the alkali-catalyzed carbon gasification. I. x-ray diffraction results on the alkali-carbon interaction. *Thermochim. Acta*, 77:49–58, 1984.
- [10] F.J. Salzano and S. Aronson. The compatibility of Graphite with Cesium. *Nucl.Sci.Eng.*, 28:51–54, 1967.
- [11] L.V. Gurvich, I.V. Veyts, and C.B. Alcock. *Thermodynamic properties of individual substances*. Hemisphere Publishing Corporation, 4th edition, 1991.
- [12] E. Merz and H. Scharf. Zum Verhalten von Spalt-Caesium in graphithaltigen Brennelementen. *Atomkernenergie*, 17(4):287–292, 1971.
- [13] T.B. Lindemer. Chemical thermodynamics of iodine species in the HTGR fuel particle. *Calphad*, 7(2):87–102, 1983.
- [14] E.H.P. Cordfunke and R.J.M. Konings. The release of fission products from degraded UO_2 fuel: Thermochemical aspects. *J.Nucl.Mater.*, 201:57–69, 1993.
- [15] H. Kleykamp. The chemical state of the fission products in oxide fuels. *J.Nucl.Mater.*, 131:221–246, 1985.
- [16] A. Nakamura and T. Fujino. Thermodynamic analysis on point defects of UO_{2+x} at relatively small deviation from stoichiometry between 600 and 1400 °C. *J.Nucl.Mater.*, 140:113–130, 1986.
- [17] G. Eriksson and K. Hack. ChemSage - A computer program for the calculation of complex chemical equilibria. *Metall. Trans.*, 21B:1013–1023, 1989.