

Experimental evidence of oxygen thermo-migration in PWR UO₂ fuels during power ramps using in-situ oxido-reduction indicators



Ch. Riglet-Martial^{*}, J. Sercombe, J. Lamontagne, J. Noirot, I. Roure, T. Blay, L. Desgranges

Commissariat à l'Energie Atomique et aux Energies Alternatives, Direction de l'Energie Nucléaire, Département d'Etudes des Combustibles, Centre d'Etudes de Cadarache, 13108, Saint-Paul-lez-Durance Cedex, France

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ABSTRACT

The present study describes the in-situ electrochemical modifications which affect irradiated PWR UO₂ fuels in the course of a power ramp, by means of in-situ oxido-reduction indicators such as chromium or neo-formed chemical phases. It is shown that irradiated fuels (of nominal stoichiometry close to 2.000) under temperature gradient such as that occurring during high power transients are submitted to strong oxido-reduction perturbations, owing to radial migration of oxygen from the hot center to the cold periphery of the pellet. The oxygen redistribution, similar to that encountered in Sodium Fast Reactors fuels, induces a massive reduction/precipitation of the fission products Mo, Ru, Tc and Cr (if present) in the high temperature pellet section and the formation of highly oxidized neo-formed grey phases of U₄O₉ type in its cold section, of lower temperature.

The parameters governing the oxidation states of UO₂ fuels under power ramps are finally debated from a cross-analysis of our results and other published information. The potential chemical benefits brought by oxido-reductive additives in UO₂ fuel such as chromium oxide, in connection with their oxygen buffering properties, are discussed.

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1. Introduction

The composition and the thermochemical properties of nuclear fuel materials greatly affect their behavior under nominal or off-nominal operating conditions. Several important properties, such as thermal conductivity, solid-state diffusion, creep rate, or volatile fission gas (such as I, Te) speciation and release are directly correlated to temperature and oxygen partial pressure (or the O/M ratio) in the fuel [1,2]. As those two parameters are likely to vary noticeably both in space and time during the fuel irradiation, significant changes in the macroscopic material properties as well as in the speciation of the corrosive volatile gases, responsible for

cladding ruptures are expected [3,4].

Thus, the difficulty in establishing a coherent spatial and temporal map of the properties of an irradiated fuel stems essentially from the misunderstanding of the oxygen potential conditions taking place locally in the material, as a function of temperature, burn-up and irradiation history. Some direct oxygen potential measurements of irradiated fuels of UOX or MOX type in nominal operating conditions are described in the literature, for burn-ups varying between 30 and 100 GWd/tM and temperature values varying between 700 °C and 1000 °C [5–8]. Most of the reported values, found in the vicinity of –400 kJ/mol O₂, are consistent with a material which is oxygen buffered by the (MoO_{2(sc)}/Mo_(sc)) redox system resulting from the uranium fission, which is also in agreement with thermochemical predictions [3,4]. In the temperature range higher than 1000 °C, quantitative experimental data are very scarce. An estimation is given in a study of Kleykamp [9], assuming

^{*} Corresponding author.

E-mail address: chantal.martial@cea.fr (Ch. Riglet-Martial).

that the two phase character of the molybdenum precipitates in the fuel sample (of 41 GWd/tM average burn-up) is indicative of low oxygen potential values ranging between -376 and -418 kJ/mol O_2 at 1700 °C. Another study from Adamson et al. [10] refers to ex-reactor oxygen potential measurements using an emf oxygen probe, in oxide BWR fuels submitted to power ramps generating a temperature gradient ranging from around 500 °C at the fuel surface to above 1600 °C at the fuel center. The measurements varying between -460 and -560 kJ/mol O_2 are indicative of some radial oxygen re-distribution phenomena inside the fuel under temperature gradient. In all published studies, the reported oxygen potential data are based on either direct measurements using advanced emf oxygen probe or indirect estimates deduced from oxidation state observations of in-situ redox indicators such as fission products, impurities and the cladding.

In a previously published study from our laboratory [11] dealing with the thermodynamics of chromium in UO_2 fuel, we pointed out a direct correlation between chromium solubility in UO_2 and oxygen partial pressure within the stability areas of $Cr_{(sc)}$ and $CrO_{(l)}$ phases in the 1500 °C – 2000 °C temperature range. This suggests that chromium might be advantageously used as an oxido-reduction indicator in irradiated UO_2 fuel pellets submitted to high temperature, provided that the material including the fission products may be considered as a diluted solid solution, which is acceptable for fuels at low burn-up (<30 GWd/tU).

The present study describes the in-situ-chemical modifications which affect chromium inside a UO_2 fuel initially doped with $Cr_2O_{3(sc)}$ in the course of a power ramp of long holding time at high maximum power. Quantitative oxygen potential data in the 1500 °C – 2000 °C temperature range are deduced from the solubility measurements of chromium and the calculated temperature profile inside the pellet. The oxido-reductive properties of irradiated UO_2 fuels submitted to a temperature gradient are finally discussed from a cross-analysis of our results and other published information. The potential chemical benefits brought by oxido-reductive additives in UO_2 fuel are estimated.

2. Notations

PWR: Pressurized Water Reactor
 BWR: Boiling Water Reactor
 SEM: Scanning Electron Microscopy
 EPMA: Electron Probe MicroAnalysis
 SIMS: Secondary Ion Mass Spectroscopy
 XAS: X-ray Absorption Spectrometry
 FP: Fission Products
 emf: electro-motive force
 (sc): solid compound
 (ss): solid solution
 (l): liquid compound

3. Experimental section – materials and methods

Fuel rods of UO_2 doped with $Cr_2O_{3(sc)}$ irradiated in commercial reactors were cut into sections and remanufactured into rodlets that experienced power ramps in OSIRIS experimental reactor [12]. Two power ramps named LHT, with a 12 h holding time, at high power were performed. The main characteristics of the rods, the rodlets and the power ramps are given in Table 1.

The rodlets were transferred into hot cells after power ramp. Slices from the vicinity of the maximum power flux were cut and prepared in order to obtain sections which were further analyzed by means of various techniques: SIMS (described in Ref. [13]), EPMA and SEM. The sample preparation procedure is described in

Refs. [14] and [15]. On each sample, quantitative radial profiles of chromium and molybdenum were recorded by EPMA (see Figs. 1 and 3) from a line scan over the pellet radius with a step of 1 point / 10 μ m. In addition, three distinct areas located in periphery, mid-radius and in the center of the pellet were observed in details by EPMA, X-ray maps and electronic images (SEM).

4. Experimental observations

The radial profiles of chromium recorded on each power-ramped sample are shown in Fig. 1a and b. Likewise Fig. 2 compares the X-ray maps of chromium, oxygen, molybdenum and ruthenium in the pellet center for the sample LHT2. Superimposed in Fig. 1a and b are the radial temperature profiles calculated with ALCYONE, the CEA multi-dimensional fuel performance code dedicated to pressurized water reactors (PWR), co-developed by CEA-AREVA and EDF within the PLEIADES platform and validated on a very large database of base irradiations, power ramps and annealing tests [16].

Consistent observations are drawn from these two power-ramp tests. In the low temperature range of the pellet (cold section), between the periphery and the radial position that reached approximately 1400 °C, the soluble fraction of chromium in the UO_2 matrix is measured around a constant value of 0.1 wt% Cr, regardless of temperature. The chromium fraction in excess is precipitated in UO_2 as an oxide secondary phase. The chromium speciation (both soluble and insoluble forms) in the cold section of the rodlets is similar to that recorded on a pre-irradiated 5 cycles (burn-up ~ 62 GWd/tM) rod of the same type under nominal operating conditions (temperature varying between 500 °C and 1000 °C). In the high temperature range of the pellet (hot section), between the radial position that reached 1500 °C and the center of the pellet, the soluble fraction of chromium in UO_2 decreases significantly down to the range $[0.04 \text{ wt\%} - 0.09 \text{ wt\%}]$ and an abundant precipitation of metallic chromium is observed as a secondary phase. As shown on the X-ray maps in Fig. 2, chromium precipitates are both linked to a lack of oxygen and associated to some intermetallic FP solid phases including Mo and Ru. This co-localization is clearly highlighted when the EPMA profiles of molybdenum and chromium are superimposed as shown in Fig. 3. In the narrow transition area located at about mid-radius of the pellet (~ 1500 °C), a drastic drop of the chromium solubility is observed and precipitates in secondary phase are present under two different redox states (oxidized and metal). It is shown from X-ray maps that chromium oxide is detected as large precipitates whereas metallic chromium is identified as small precipitates.

The observed Cr EPMA signal in the $[1500 - 2000$ °C] range is significant as it exceeds the detection limit of the experimental technique. In addition, the change in the signal shape between the cold and the hot sections of the pellet is significant for both chromium and molybdenum and it is clearly related to a change in the chemical form of the precipitates. At last, in as much as chemical transformations are mostly thermodynamically controlled at high temperature, it is likely that chromium in solid solution in UO_2 be in equilibrium with the chromium metallic solid phase [11]. The measured chromium concentration is therefore representative of the solubility of chromium metal in UO_2 in the $[1500$ °C – 2000 °C] range (see §.5.2.1.). In fact, the chromium solubility at given T and pO_2 corresponds to the maximum soluble concentration of chromium in UO_2 in those conditions.

5. Interpretation

5.1. Low temperature range (<1460 °C): Cold section of the pellet

The chromium content in solid solution for each ramped rodlet

Table 1
Characteristics of the power-ramped samples investigated.

	LHT 1	LHT 2
Irradiation time	2 Cycles	2 Cycles
Average burn-up GWd/tM	29.7	29.9
Cladding	Zy4	Zy4
Fuel	UO ₂ - 0.2% Cr ₂ O _{3(sc)}	UO ₂ - 0.2% Cr ₂ O _{3(sc)}
235 U content %	4.5%	4.5%
Maximum power during ramp W/cm	468	531
Holding time	12 h 04	12 h 11
Power at the sample position W/cm	450	520

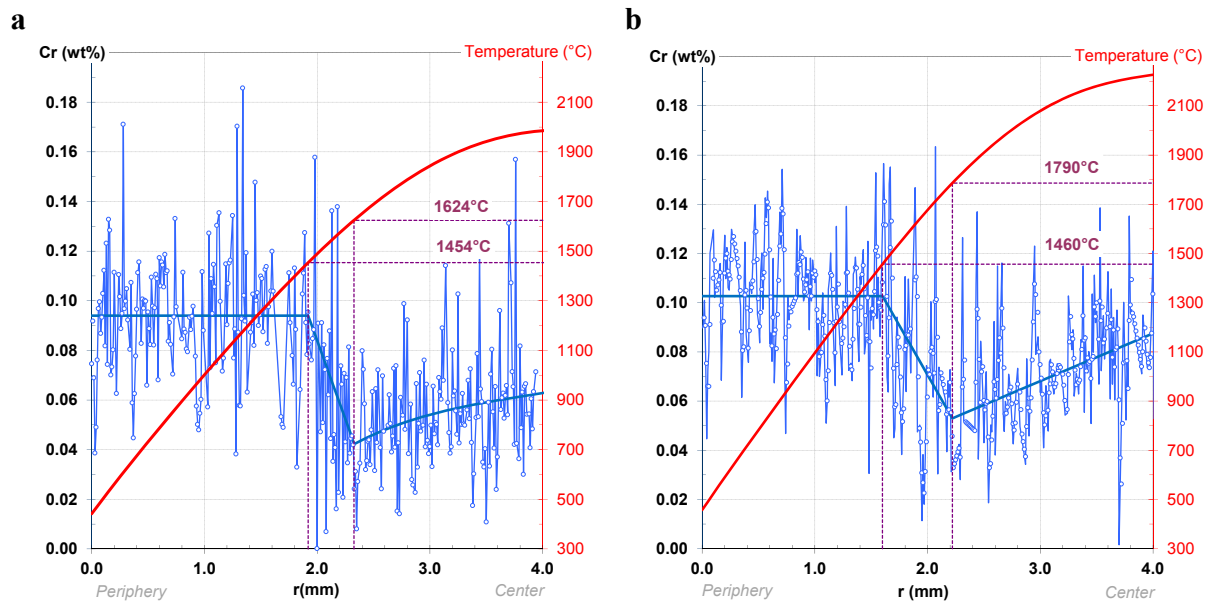


Fig. 1. Radial temperature profiles and concentration profiles of chromium measured by EPMA for ramp tests LHT1 (Fig. 1a) and LHT2 (Fig. 1b).

was measured in the vicinity of 0.1 wt% Cr regardless of temperature, in the whole range [20 $^{\circ}C$ - 1400 $^{\circ}C$]. The chromium soluble content was equivalent to that of the initial un-irradiated fuel after sintering, measured to $0.102 \pm 0.004\%$ [11,17,18]. In addition, as compared to the initial un-irradiated fuel, the chemical form of the chromium precipitates of type Cr₂O_{3(sc)} did not change during nominal condition irradiation, not even during ramp tests, regardless the burn-up and the characteristics of the ramp (power, duration...). It may then be stated that neither the temperature, nor the burn-up, nor either the mode of irradiation affects the chromium speciation in the temperature range [20 $^{\circ}C$ - 1460 $^{\circ}C$]. Nevertheless, we verified in a previous study [11] that both the stability of the Cr-O solid/liquid phases and the solubility of chromium in UO₂ were strongly dependent on temperature beyond 1500 $^{\circ}C$. The fact that the solubility of chromium is unrelated to temperature at $T < 1450$ $^{\circ}C$ indicates that the spontaneous thermodynamic transformations of chromium in the UO₂ matrix occurring at $T > 1500$ $^{\circ}C$ are strongly slowed, even inhibited a low temperature owing to the fact that the thermal energy brought to the system is not sufficient to exceed the energy barrier of the chemical transitions (highest energetic barrier for solid-solid type transformations). For that reason, in the low temperature range of a power ramp (< 1450 $^{\circ}C$) or in nominal operating conditions, chromium in the UO₂ fuel stays in its initial stage reached after sintering.

These assumptions were confirmed in our laboratory by further tests of long-time thermal annealing of UO₂ pellets (initially doped

with 1600 ppm Cr₂O_{3(sc)}) at the temperature of 1400 $^{\circ}C$ and 1600 $^{\circ}C$, all tests being carried out under reducing conditions (Ar / 5% H₂) consistent with the thermodynamical stability of metal chromium. The analyses by XAS of the annealed samples showed that, at 1400 $^{\circ}C$, the microstructure of the pellet did not change (absence of precipitate, chemical environment of solubilized chromium) as compared to its initial stage whereas a massive metal chromium precipitation was observed at 1600 $^{\circ}C$, as thermodynamically expected. To conclude, at temperature lower than 1450 $^{\circ}C$, chromium in UO₂ does not change as compared to its initial stage reached after sintering, irrespective of both the oxygen potential conditions prevailing in that section of the pellet and the power cycle. Chromium is thus present in UO₂ in disequilibrium with respect to oxido-reduction. Neither the stoichiometry of the solid precipitates (if present), nor the solubility of chromium in the matrix are consistent with the actual thermochemical conditions of the material.

5.2. High temperature range (> 1460 $^{\circ}C$): Hot section of the pellet

5.2.1. Thermodynamic equilibrium state

Beyond the temperature of 1460 $^{\circ}C$, an abrupt decrease of chromium dissolved in UO₂ was evidenced by EPMA. This variation was coupled with a massive metal chromium precipitation in secondary phase. We think that this evolution is an indication of a switch from a kinetically controlled chemical system to a thermodynamically controlled one, the thermal energy brought to the

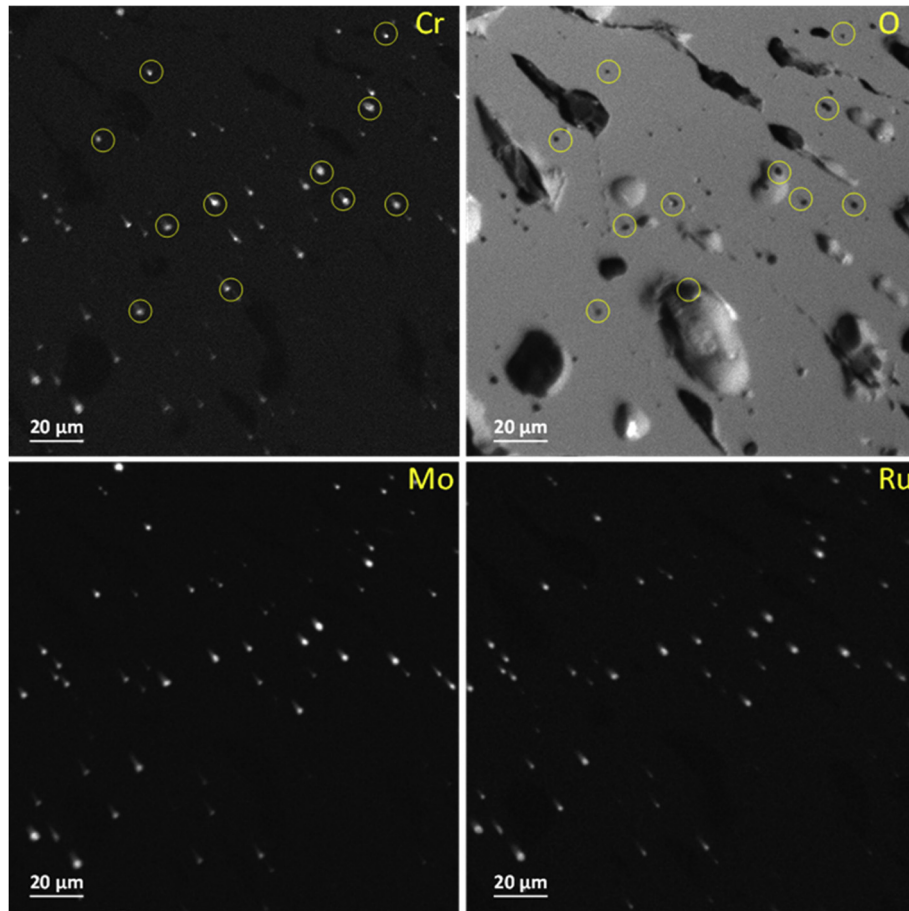


Fig. 2. X ray maps of the elements Cr, Mo, Ru and O in the pellet center for the LHT2 ramp test.

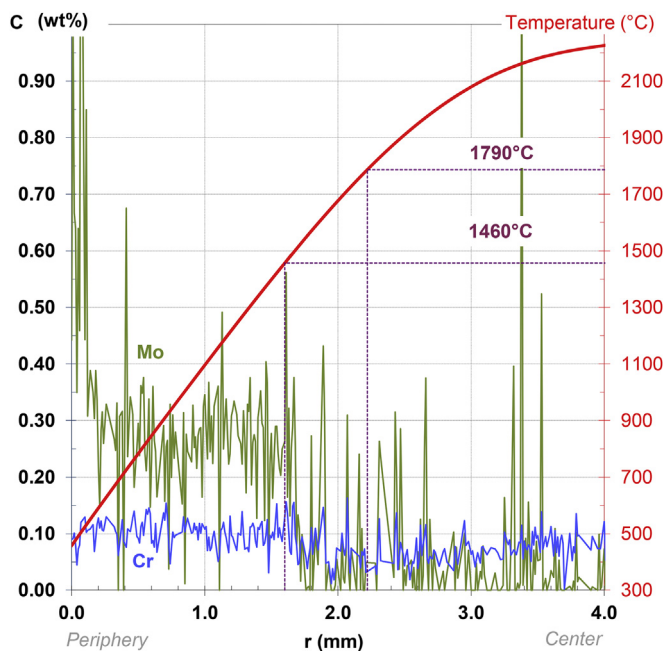


Fig. 3. Comparison of the radial concentration profiles of Cr and Mo measured by EPMA for the LHT2 ramp test.

system beyond 1450 °C exceeding the energy barrier of the chemical transitions. This is accredited by the following

observations. For temperatures ranging between about 1500 °C and 2000 °C, the EPMA measurements collected in the ramped UO_2 fuel vary continuously (Fig. 4) in the interval [0.04 wt% - 0.09 wt%] in consistency with solubility measurements previously collected on laboratory samples submitted to similar experimental conditions [11]. Such a solubility variation was interpreted with a simple thermodynamic model with temperature and oxygen potential as main parameters [11]. Additionally, by plotting the variation of the chromium solubility in the LHT1 and LHT2 fuel samples as a function of temperature (Fig. 4), an excellent reproducibility is obtained in the [1800 °C - 2000 °C] range in spite of different radial temperature gradients across the pellet. All these observations agree with the assumption of a chemical system evolving under thermodynamic control at high temperature.

5.2.2. Chromium as an oxido-reduction tracer

In Ref. [11], a direct correlation was established between the chromium solubility in UO_2 and the oxygen partial pressure within the stability areas of $\text{Cr}_{(\text{sc})}$ and $\text{CrO}_{(\text{l})}$ phases in the 1500 °C - 2000 °C temperature range. As a consequence, the solubility of chromium might be advantageously used as an *in-situ* oxido-reduction tracer in UO_2 fuel pellets submitted to high temperatures (off-nominal operating conditions). The oxygen potential variations in the power ramped UO_2 rodlets of the LHT1 and LHT2 tests may be determined therefore from the solubility measurements of chromium in the [1500 °C - 2000 °C] range, using the solubility laws established earlier and the calculated temperature profiles over the pellet (coming from simulations with the fuel performance code

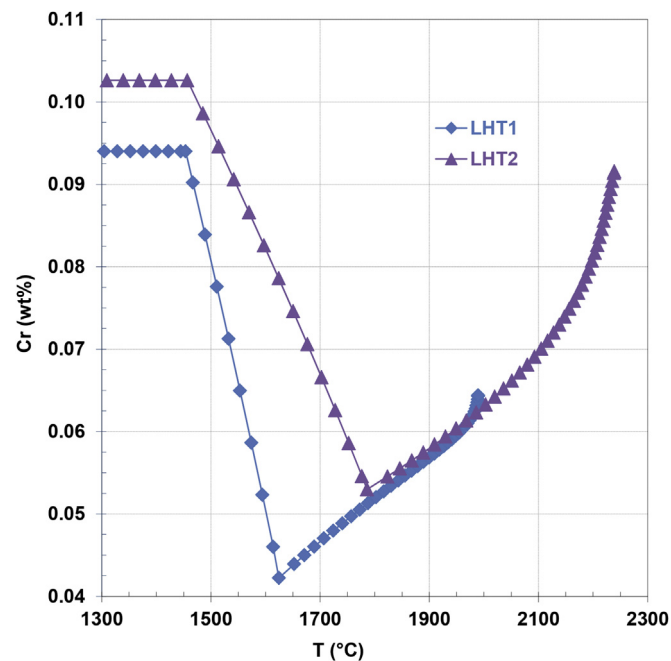


Fig. 4. Comparison of the Chromium profiles measured by EPMA for ramp tests LHT1 (Fig. 1a) and LHT2 (Fig. 1b) as a function of temperature.

ALCYONE). This interpretation is based on the assumptions that: i) thermodynamic equilibrium in the hot section of the pellet is reached (as discussed in section 5.2.1.), ii) the chromium solubility laws previously established on un-irradiated fuels are applicable i.e. the effect of fission products on chromium solubility is negligible at low burn-up (less than 30 GWd/tU).

A full interpretation of the experimental data on the power-ramped samples is given in Fig. 5, depicting the oxygen potential variation of the rodlets at equilibrium as a function of temperature in the [1500 °C - 2000 °C] range. The data were interpreted as developed in section 5.2.2 using the chromium solubility laws given in Ref. [11] and recalled in Table 2. The interval [1500 °C - 1800 °C] corresponds to the validity range of the solubility model.

The calculated oxygen potential values are representative of the final thermochemical state of the Cr₂O_{3(s)} doped UO₂ rodlets, after 12 h of holding time at high power (450 - 520 W/cm) without cladding failure. From the chromium iso-solubility curves shown in Fig. 5, it appears that in the range [1500 °C - 2000 °C], the region in accordance with solubility values ranging between around 0.04 wt % and 0.08 wt% corresponds to the metallic chromium Cr_(sc) stability one. The solubility being the lowest in that area as compared to the Cr₂O_{3(s)} or CrO_(l) areas, a high precipitation of Cr_(sc) is predicted, which is in agreement with the experimental observations.

6. Discussion

6.1. Evidence of a reductive perturbation at high temperature during a power transient

The correlation depicted in Fig. 5 shows that the oxygen potential of the ramped rodlets of the LHT1 and LHT2 tests of initial burn-up close to 30GWd/tM varies continuously between -450 and -380 kJ/mol O₂ in the interval [1500 °C - 2000 °C]. However, the oxygen potential of the initial Cr₂O_{3(s)}-doped pellets is to be expected in the vicinity of the limit between the Cr₂O_{3(s)} and CrO_(l) stability domains [11] (Fig. 6) after sintering, which is a bit more

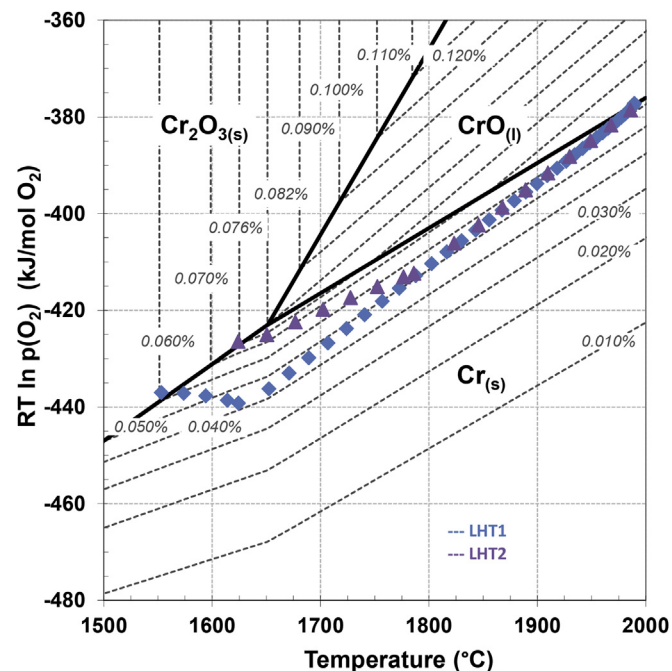


Fig. 5. Oxygen potential profile in the pellet at the end of the power ramp (12 h holding time) for the ramp tests LHT1 (diamonds) and LHT2 (triangles) in the [1500 °C - 2000 °C] temperature range. Continuous segments indicate the phase stability diagram of the Cr-O system [11]. An extrapolation up to 2000 °C of the solubility model [11] (validity up to 1800 °C) is made. The solubility of chromium in UO₂ refers to the maximum soluble concentration in UO₂ in equilibrium with the corresponding solid phase (as a function of T and pO₂). Chromium iso-solubility curves are shown in dashed lines. Figures in italics indicate the iso-solubility values expressed in %wt Cr.

Table 2

Parameters of the chromium solubility laws in UO₂ in the [1500°C - 2000°C] temperature range, from Ref. [11]. The solubility law is of type $\log_{10}(y_{Cr}) = p \log_{10}(pO_2) + V + U/T$, with pO_2 the oxygen partial pressure in Bar, T the temperature in K and y_{Cr} the soluble chromium molar fraction in UO₂. An uncertainty of 7% is associated to the calculated solubility data expressed in weight % Cr.

Chromium phase	Slope p	V	U (x10 ⁻⁴)
Cr ₂ O ₃	0.00	0.1385	-0.4827
CrO	0.25	-4.872	1.034
Cr (T > 1651 °C)	0.75	-8.391	2.816
Cr (T < 1651 °C)	0.75	-6.076	2.370

oxidative. In addition, it is expected, from both experimental observations [5,6] and thermochemical simulations [3,4] that the oxygen potential of irradiated UO₂ fuels of burn-up ranging from 30 to 60 GWd/tU be even more oxidative as it is estimated in the vicinity of the (MoO_{2(s)}/Mo_(sc)) redox couple. Therefore, as shown in Fig. 6, the oxygen potential of the rodlets after completion of the power transient decreases drastically. Such a drop in oxygen potential is significant enough to initiate the reduction into metal of the initial chromium oxide, as observed experimentally. In addition, the oxygen potential range reached after power ramp is also consistent with the stability of metallic molybdenum and ruthenium (Fig. 6), which are often encountered as intermetallic phases. Thus, under high power-ramp conditions, metallic chemical phases of Mo, Ru and Cr are expected to precipitate in the hot section of the pellet, which agrees with the current observations. In consistency with thermochemical predictions, the observations confirm the existence of a strong reductive perturbation occurring in the hot section of the pellets during a power transient.

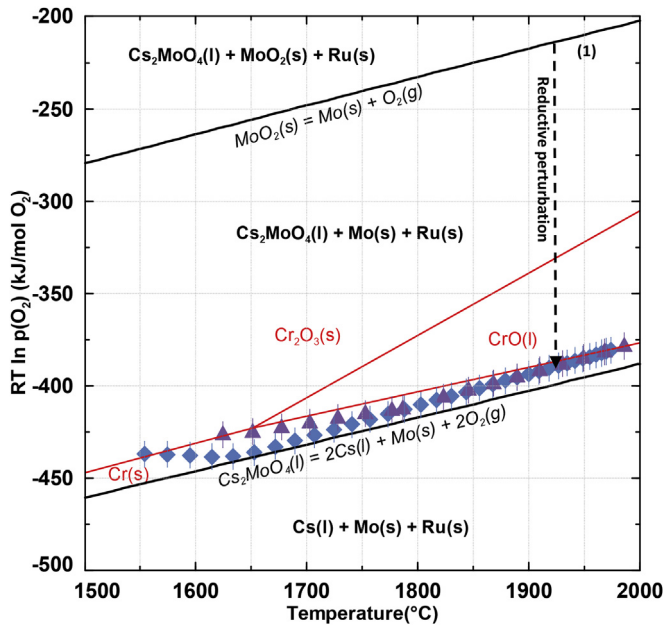


Fig. 6. Evidence of a significant reductive perturbation in the high temperature section of the pellets (center) during a power ramp - Diagram established with the FactSage software - Curve (1): simulated equilibrium state of a stoichiometric UO_2 fuel irradiated at 30 GWd/t U. This initial state is controlled in the vicinity of the $(\text{MoO}_{2(\text{sc})}/\text{Mo}_{(\text{sc})})$ redox systems. Experimental points: equilibrium state achieved by the rodlets LHT1 (diamonds) and LHT2 (triangles), subjected to a power transient, after a 12 h holding time at high power (468 and 530 W/cm) without cladding failure. An uncertainty of ± 7 kJ/mol O_2 is estimated from the variations of the measured Cr solubility data (cf. Fig. 4). The final state is approximately controlled by the $(\text{Cs}_2\text{MoO}_{4(\text{l})}/\text{Cs}_{(\text{l},\text{g})} + \text{Mo}_{(\text{sc})})$ redox system. This is consistent with the stabilization of intermetallic phases of molybdenum, ruthenium and chromium as observed experimentally, as well as a high release of gaseous cesium controlled by the equilibrium $\text{Cs}_2\text{MoO}_{4(\text{l})} = \text{Cs}_{(\text{g})} + \text{Mo}_{(\text{sc})} + 2\text{O}_{2(\text{g})}$ or $\text{Cs}_{(\text{l})} = \text{Cs}_{(\text{g})}$.

6.2. Evidence of an oxidative perturbation at low temperature during a power transient

One can figure out the possible behavior of the fuel in the cold section of the pellet from the recent paper of Desgranges et al. [15] supporting the formation of a new highly oxidized solid phase around the grain boundaries near the pellet chamfer of a standard UO_2 fuel rod (named LHT0 in Table 3) ramped in similar conditions as that of the LHT1 and LHT2 specimens. Such a phase had never been reported in operating PWR fuel [15]. This new phase of composition U_4O_9 which may form at the periphery of the pellet of low temperature (around 400 °C) can only be stabilized in conditions significantly more oxidative than that imposed by the reference $(\text{MoO}_{2(\text{sc})}/\text{Mo}_{(\text{sc})})$ redox couple (Table 3 and Fig. 6). Thus, the occurrence of an oxidized uranium phase at the pellet chamfer gives evidence of a strong oxidative perturbation occurring in the cold section of the pellet during a power transient. As the system is closed, this oxidative perturbation is clearly correlated to the reductive perturbation taking place at the same time in the hot central part of the pellets. Note that the amplitude of the oxidative perturbation is particularly dependent (cf. §. 6.3) of the burn-up (amount of oxygen freed by the fission of UO_2) and the radial temperature gradient over the pellet, which is directly related to the linear power rating imposed to it. Consequently, the oxidised grey phases of U_4O_9 type are detected in case of fuel of burn-up higher than ~ 30 GWj/t U and maximum power transient higher than ~ 400 W/cm (ramp LHT0) only. Those grey phases are not expected to form in the LIT/B4 and LIT2/3 conditions (Table 3), for which little oxygen redistribution would occur (insufficient for

stabilizing the U_4O_9 phase). However, the variations of cladding oxidation, representative of the amount of oxygen coming to the clad, observed for LIT2/3 and LIT/B4 [10] are also an indication of the oxidative perturbation taking place in the cold section of the pellets during a power ramp.

6.3. Oxygen redistribution in irradiated oxide fuels

Published experimental oxygen activity data measured with various independent techniques, for irradiated UO_2 fuels submitted to temperature gradients, are summarized in Table 3, together with the data issued from the current study. It is clear from the results of all tests that the fuel oxygen potential is drastically reduced as compared to the reference initial values $(\text{MoO}_{2(\text{sc})}/\text{Mo}_{(\text{sc})})$ redox couple) in the central area of the pellet whereas the region at the edge of the pellet may display a significant oxidation. The plot given in Fig. 7 gives thus evidence that irradiation under a temperature gradient, such as that occurring during high power transient, causes radial oxygen redistribution from the hot central region of the pellet to the cold peripheral one, in consistency with the predicted direction of oxygen transport in hypo-stoichiometric oxide fuels ($\text{O}/\text{M} < 2$) [19]. Hence, in accordance with most of the previously published data ([20] and references herein), the present results confirm that UO_2 fuels of nominal stoichiometry close to 2.000 remain approximately quasi-stoichiometric or become slightly hypo-stoichiometric when irradiated up to 75 GWd/tM, particularly as a result of the accumulation with increasing burn-up of fission products of oxidation state lower than +4 (Rare Earths), which are highly soluble in UO_2 . As expected then, those fuels behave as hypo-stoichiometric fuels as regard the O_2 thermo-migration, when submitted to high power transients.

In the two sub-sections below is given our own analysis of the oxido-reductive behavior of irradiated fuels, including the potential chemical benefits brought by oxido-reductive additives in UO_2 fuel such as chromium oxide.

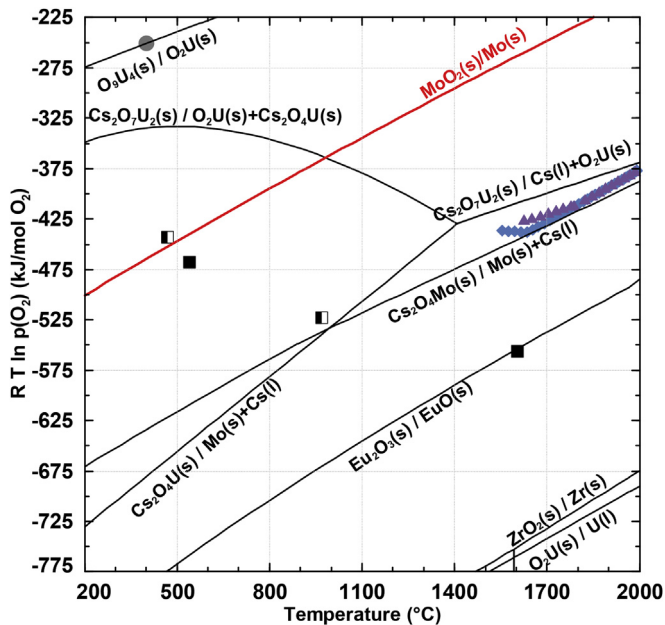
6.3.1. Parameters governing the amount of re-distributed oxygen

The amount of oxygen that is available for migration depends on both the initial stoichiometry and the burn-up (O_2 freed by the fission of UO_2) of the fuel, as well as the amount of additive in oxide form (O_2 freed by reduction of the oxide) in the material, as long as this additive is involved in a redox couple that is likely to activate throughout the central reductive perturbation (like $\text{Cr}_2\text{O}_{3(\text{sc})}$ – Fig. 6): thus, the higher the burn-up and the amount of oxydo-reductive additive, the larger the amount of oxygen available for transport. It is acknowledged moreover that the oxygen migrating to the cold peripheral region of the pellet contributes to increase the cladding oxidation [10,21], which may greatly help to protect the later from corrosion by I-SCC during a power transient. This effect probably results from the chemical competition between iodine and oxygen on zircaloy which would be displaced in favor of oxygen. In fact, the reaction $\text{Zr}_{(\text{sc})} + \text{I}_{2(\text{g})} = \text{ZrI}_{4(\text{g})}$, leading to the gaseous corrosion phase $\text{ZrI}_{4(\text{g})}$, is suspected to be the main chemical reaction responsible for clad rupture by I-CSC. However, the detrimental effect of iodine on zirconium may be overcome grace to the beneficial effect of oxygen leading to the formation of $\text{ZrO}_{2(\text{sc})}$, according to $\text{Zr}_{(\text{sc})} + \text{O}_{2(\text{g})} = \text{ZrO}_{2(\text{sc})}$. Pre-formed or neo-formed $\text{ZrO}_{2(\text{sc})}$ layers are likely to protect the clad from iodine attack [21, 22] to a certain extent.

From these observations, it is deduced that an excess of oxygen in the UO_2 fuel, coming either from an initial hyper-stoichiometry of the fuel or the presence of an oxido-reductive compound (like chromium oxide), or both, might be efficient to prevent clad failure by I-SCC during a high power transient. An optimization of the amount of additive needed is to be performed however as a

Table 3Oxygen activity data versus temperature for high burn up UO_2 fuel rods, nominally stoichiometric, under power ramps.

Fuel specimen	Initial enrichment	Additive Cr_2O_3	Initial pellet diameter	Average burn-up	Maximum power	Holding time	Temperature, μO_2 ($^\circ\text{C}$; kJ/mol O_2)		Methodology	Reference
	% U-235	ppm	mm	GWd/tU	W/cm	h	Fuel surface	Fuel center		
LIT/B4	2.34	0	12.2	18.9	230	nd ^b	(470; –443)	(970; –523)	emf ^a	[10]
LIT2/3	2.55	0	12.4	11.4	394	nd ^b	(540; –463)	(1605; –556)	emf ^a	[10]
LHT0	4.0	0	8.2	32.4	463	12	(400; –251)	(1800; –)	Phase analysis	[15]
LHT1	3.7	2000	8.2	26.7	470	12	(400; –)	(1935; –375)	Cr solubility	This work
LHT2	3.7	2000	8.2	29.9	540	12	(400; –)	(2200; –375)	Cr solubility	This work

^a ElectroMotive Force measurements with a (NiO/Ni) reference electrode at 750 $^\circ\text{C}$.^b Not documented.**Fig. 7.** Literature survey of oxygen potential measurements on UO_2 fuel subjected to temperature gradients. Black squares: test LIT2/3 [10]; Black and white squares: test LIT/B4 [10]; Filled Circle: test LHT0 [15]; Diamonds and triangles: tests LHT1 and LHT2 [present work].

function of the burn-up of the fuel, the power transient conditions (which govern the oxygen and corrosive fission products migration to the clad) and the nature of the dopant.

In addition, the amount of oxygen which effectively migrates from the center to the edge of the pellet depends on the radial temperature gradient over the pellet directly related to the linear power rating imposed to it. It seems clear indeed from Adamson's results on the LIT/B3 test that the most severe cladding oxidation, that is the highest amount of oxygen coming to the clad, is linked to the strongest temperature gradient [10].

6.3.2. O_2 re-distribution and oxygen potential shift at high temperature

As mentioned before, the shift of oxygen potential induced by the O_2 re-distribution is directly linked to the amount of oxygen available for migration, also called the oxygen buffering capacity of the fuel, which is the total amount of oxygen available for transport, including the oxygen possibly coming from the additive. This oxygen buffering capacity increases with both the burn-up of the tested fuel and the amount of oxido-reductive additive (such as $\text{Cr}_2\text{O}_3(\text{sc})$). As shown in Fig. 7, the LIT2/3 rod of lower buffering capacity (11.4 GWj/tU, no additive) shows at 1600 $^\circ\text{C}$ a higher oxygen

potential drop than the LHT1 and LHT2 rods, of higher buffering capacity ($\sim 30\text{GWj/t U}$, 2000 ppm $\text{Cr}_2\text{O}_3(\text{sc})$). Thus, the larger the buffering capacity, the shorter the oxygen potential drop in the hot region of the pellet. Larger oxygen buffering capacities allow therefore a relative control of the material as regards its properties dependent on $p\text{O}_2$ [23,24] (buffering effect) which can be advantageous to compensate the strong perturbations induced by power ramps. Thus, as reported in Ref. [3], by addition of chromium oxide to UO_2 , the oxygen potential or O/M of the fuel can be stabilized in a domain where the amount of chemically reactive gases ($\text{CsI}(\text{g})$, $\text{I}_2(\text{g})$, $\text{TeI}_2(\text{g})$, $\text{Te}_x(\text{g})$) in the fuel is the lowest. Furthermore, in this controlled oxygen potential domain, the major gaseous species is $\text{CsI}(\text{g})$ which has little volatility and is quite unreactive towards the Zr cladding [14, 25]. From that point of view, chromium oxide added to UO_2 fuel is likely to act on both the fission gas release (as Cr-doped fuels have a larger grain size leading to an enhanced retention of fission gases [11]) and the corrosion risk of the cladding (by stabilizing the chemically reactive gases that form in the fuel during a power ramp into chemical species unreactive towards Zr).

More generally, in connection with its buffering properties, one benefit of adding an oxido-reductive dopant inside an oxide fuel consists in reducing the possible drawbacks induced by strong redox perturbations on the material. Thus, the fuel creep is known to vary greatly with the O/M of the material [23,26], the release of noble gases increases with the O/M ratio [27]. Moreover, adding an oxido-reductive dopant contributes to increase the oxygen buffering capacity of the fuel, which may be beneficial for the prevention of clad-failure by I-CSC (iodine-oxygen competition displaced in favor of oxygen).

7. Conclusion

The property of in-situ redox indicator of chromium was used to estimate in the [1500 $^\circ\text{C}$ - 2000 $^\circ\text{C}$] range, the oxygen potential radial profile of some chromium doped UO_2 fuels submitted to a power ramp of long holding time, without failure. It is shown that the oxygen potential of the rod in the range [1500 $^\circ\text{C}$ - 2000 $^\circ\text{C}$] decreases down to [–394 - 410] kJ/mol O_2 during the power ramp, which is in the vicinity of the ($\text{Cs}_2\text{MoO}_4(\text{l})$, $\text{Cs}(\text{l})$ + $\text{Mo}(\text{sc})$) buffer system. These results imply that irradiated fuels submitted to temperature gradient such as power ramps are submitted to strong oxido-reductive perturbations, owing to radial migration of oxygen from the center to the periphery of the pellet. This phenomenon of oxygen redistribution, similar to that encountered in Sodium Fast Reactors fuels may induce a massive reduction/precipitation of the fission products Mo, Ru, Tc and Cr (if present) in the high temperature pellet center and the formation of oxidized grey phases of cesium uranates or U_4O_9 type in its cold part, of lower temperature.

The amplitude of the oxygen potential drop during a power ramp is expected to depend on the temperature gradient (resulting

from the linear power rating) and on the amount of oxygen available for migration (in connection with the initial sur-stoichiometry of the fuel, the burn-up of the rod and the amount of dopant if present). Thus, the addition to the fuel of an oxido-reductive dopant, such as chromium, contributes to enlarge its oxygen buffering capacity. One consequence is a reduction of the oxygen potential drop during a power ramp, as compared to standard rods of similar burn-up, which could be beneficial to buffer all key properties of the irradiated fuel dependent on oxygen (creep rate, thermal conductivity, fission gas speciation...). Another consequence is a possible better prevention against clad-failure by I-CSC during a power ramp, by displacing the iodine-oxygen competition to the clad inner surface in favor of oxygen.

It is therefore of great importance in PWR fuel performance codes to model oxygen radial redistribution during power ramps, not only for its impact on fuel properties, but also for its effect on corrosive volatile fission gas release. An extension of this work will consist in applying the present methodology to other fuel rods submitted to varying power ramp conditions in order to improve the model of oxygen re-distribution implemented in the ALCYONE code [3,4].

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References

- [1] M. Conte, J.P. Gatesoupe, M. Trotabas, J.C. Boivineau, G. Cosoli, Study of the thermal behaviour of LMFBR fuel, in: International Conference on Fast Breeder Reactor Performance, March 1979, pp. 5–8. Monterey, CA, USA.
- [2] Bogdan Mihaila, Marius Stan, Juan Ramirez, Alek Zubelewicz, Petrica Cristea, J. Nucl. Mater. 394 (2–3) (November 2009) 182–189.
- [3] B. Baurens, Thèse de l'Université d'Aix-Marseille (Ecole doctorale 352-Physique et Sciences de la Matière), France, 17 octobre 2014.
- [4] B. Baurens, J. Sercombe, Ch Riglet-Martial, L. Desgranges, L. Trotignon, P. Maugis, J. Nucl. Mater. 452 (1–3) (September 2014) 578–594.
- [5] Matzke HJ, J. Nucl. Mater. 208 (1994) 18–26.
- [6] Matzke HJ, J. Nucl. Mater. 223 (1995) 1–5.
- [7] K. Une, Y. Tominaga, S. Kashiba, J. Nucl. Sci. Technol. 28 (1991) 409.
- [8] C.T. Walker, V.V. Rondinella, D. Papaioannou, S. Van Winckel, W. Goll, R. Manzel, J. Nucl. Mater. 345 (2005) 192–205.
- [9] H. Kleykamp, J. Nucl. Mater. 84 (1979) 109–117.
- [10] M.G. Adamson, E.A. Aitken, S.K. Evans, J.H. Davies, in: Symposium on the Thermodynamics of Nuclear Materials; Vienna, Austria, 21 Oct 1974. IAEA-SM 190/54.
- [11] Ch Riglet-Martial, Ph Martin, D. Testemale, C. Sabathier-Devals, G. Carlot, P. Matheron, X. Iltis, U. Pasquet, C. Valot, C. Delafay, R. Largenton, J. Nucl. Mater. 447 (1–3) (April 2014) 63–72.
- [12] C. Mougél, B. Verhaeghe, C. Verdeau, S. Lansiaert, S. Béguin, B. Julien, Power ramping in the OSIRIS reactor : database analysis for standard UO₂ fuel with Zy-4 cladding, in: Pellet Cladding Interaction in Water Reactor Fuels, OECD/NEA N°6004, 2005, pp. 333–345.
- [13] B. Rasser, L. Desgranges, B. Pasquet, Appl. Surf. Sci. 203–204 (2003) 673–678.
- [14] L. Desgranges, Ch Riglet-Martial, I. Aubrun, B. Pasquet, I. Roure, J. Lamontagne, Th Blay, J. Nucl. Mater. 437 (Juin 2013) 409–414.
- [15] L. Desgranges, J. Lamontagne, Ch Riglet-Martial, Th Blay, J. Nucl. Mater. 457 (February 2015) 246–251.
- [16] C. Struzik, C.V. Marelle, "Validation of Fuel Performance CEA Code ALCYONE, Scheme 1D, on Extensive Database", Top Fuel 2012, September 2012, pp. 2–6. Manchester, United Kingdom.
- [17] T. Cardinaels, K. Govers, B. Vos, S. Van den Berghe, M. Verwerf, L. de Tollenaere, G. Maier, C. Delafay, J. Nucl. Mater. 424 (2012) 252–260.
- [18] A. Leenaers, L. de Tollenaere, Ch Delafay, S. Van den Berghe, J. Nucl. Mater. 317 (2003) 62–68.
- [19] C. Sari, G. Schumacher, J. Nucl. Mater. 61 (2) (August 1976) 192–202.
- [20] J. Spino, P. Peerani, J. Nucl. Mater. 375 (1) (30 March 2008) 8–25.
- [21] J.H. Davies, E.V. Hoshi, D.L. Zimmerman, J. Nucl. Mater. 270 (1–2) (1 April 1999) 87–95.
- [22] T.T. Yang, C.H. Tsai, J. Nucl. Mater. 166 (1989) 252–264.
- [23] P.T. Sawbridge, G.L. Reynolds, B. Burton, J. Nucl. Mater. 97 (1981) 300–308.
- [24] H. Assmann, W. Dörr, G. Gradel, G. Maier, M. Peehs, J. Nucl. Mater. 98 (1981) 216–220.
- [25] K. Konashi, T. Yato, H. Kaneko, J. Nucl. Mater. 116 (1983) 86–93.
- [26] M.S. Seltzer, J.S. Perrin, A.H. Clauer, B.A. Wilcox, React. Technol. 14 (2) (1971) 99–135.
- [27] M.A. Mansouri, D.R. Olander, J. Nucl. Mater. 254 (1998) 22–33.