EUROPEAN COMMISSION

Community Research

RAPHAEL

Contract Number: 516508 (FI6O)

DELIVERABLE (D-FT1.1)

Study of the feasability of manufacturing UCO kernels by an external sol-gel process

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Reporting period: e.g. 15/04/2005-15/10/2006
Date of issue of this report : 08/12/2006
Start date of project : **15/04/2005** Duration : **18 Months**

Project co-funded by the European Commission under the Euratom Research and Training Programme on Nuclear Energy within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	
RE	Restricted to the partners of the RAPHAEL project	
CO	Confidential, only for specific distribution list defined on this document	**X**

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ReActor for Process heat, Hydrogen And ELectricity generation (RAPHAEL)		
Sub-project: SP-FT **Work package:** 1	**RAPHAEL document no:** RAPHAEL-0612-D-FT1.1	**Document type:** D=Deliverable
Issued by: CEA (FR) **Internal no.:** NT LCU 06-014		**Document status:** Final

Document title

Sub-project Fuel Technology (SP-FT)
Study of the feasability of manufacturing UCO kernels by an external sol-gel process

Abstract

This document deals with current knowledge on the manufacturing of UCO kernels and on our experimental manufacturing of these kernels based on various grids extracted from the literature.

The literature related to the manufacturing of "UCO" kernels using the Sol-Gel route by an external (Gel Supported Precipitation) and internal (Hexamethyl tetramine) gelling processes is developped including predictable experimental difficulties encountered in obtaining "UCO" kernels. The main characteristics that can be expected from the manufactured "UCO" kernels are also given.

The following chapter describes our experimental investigation in order to manufacture "UCO" kernels starting from dried kernels mainly made from a uranyl di-uranate and carbon black solution. The GSP process used to elaborate theses dried kernels is detailed step by step from the broth preparation, the droplet formation and gelation, the ageing and washing steps up to the beads drying step. Calcining and sintering steps are more detailed because of the impact of the thermal treatment process (temperature, gas nature) on the kernel's microstructure and composition. Thermal Gravimetric Analysis, X-ray Diffraction, Optical and Scanning Electronic Microscopy and EDS characterization were used as efficient techniques in order to evaluate the impact of experimental parameters on the composition, microstrucure of the final kernels.

An optimized calcining thermal treatment was found leading to a uranium dioxide phase with the presence of carbon black, preserving the carbon black and eliminating the additives resulting from the sol-gel external process. A sintering thermal treatment was also developed in order to obtain an uranium dioxide sub-stoechiometric that should favor the formation of a oxycarbide uranium phase. The kernels obtained by the could be mainly composed of a $UO_{1,96}$ phase containing a little $UC_{2-x}O_x$ phase. More experimental analysis should be added to our panel of X-ray diffraction, EDS analysis and electron microscope observations in order to confirm the phase obtained.

Proposals for further experimental grids are also detailed in order to obtain kernels with a sufficient amount of oxy-carbide phase that could be characterised with certainty.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	12/2006	First issue	A. Duhart-Barone CEA	F. Charollais CEA	M. Phelip CEA	E. Bogush AREVA-NP

DIRECTION DE L'ENERGIE NUCLEAIRE

DEPARTEMENT D'ETUDES DES COMBUSTIBLES

Service Plutonium Uranium et Actinides mineurs

Laboratoire des **Combustibles Uranium**

SPUA/LCU

NOTE TECHNIQUE

Study of the feasibility of manufacturing UCO kernels by an external sol-gel process

NT LCU 06-014	**Indice O**	**Décembre 2006**	**1/50**

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LCU

Référence : NT LCU 06-014	Indice : 0	Page : 2/50

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Summary :

This document deals with current knowledge on the manufacturing of UCO kernels and on our experimental manufacturing of these kernels based on various grids extracted from the literature. The literature related to the manufacturing of "UCO" kernels using the Sol-Gel route, either an external (Gel Supported Precipitation) or an internal (Hexamethyl tetramine) gelling processes is developped including predictable experimental difficulties encountered in obtaining "UCO" kernels. The main characteristics that can be expected from the manufactured "UCO" kernels are also given. The following chapter describes our experimental investigation in order to manufacture "UCO" kernels starting from dried kernels mainly made from a uranyl di-uranate and carbon black solution. The GSP process used to elaborate these dried kernels is detailed step by step from the broth preparation, the droplet formation and gelation, the ageing and washing steps up to the beads drying step. Calcining and sintering steps are more detailed because of the impact of the thermal treatment process (temperature, gas nature) on the kernel microstructure and composition. Thermal Gravimetric Analysis, X-ray Diffraction, Optical and Scanning Electronic Microscopy and EDS characterization were used as efficient techniques in order to evaluate the impact of experimental parameters on the composition, microstrucure of the final kernels. An optimized calcining thermal treatment was found leading to a uranium dioxide phase with the presence of carbon black, preserving the carbon black and eliminating the additives resulting from the sol-gel external process. A sintering thermal treatment was also developed in order to obtain an uranium dioxide sub-stoechiometric that should favor the formation of a oxycarbide uranium phase. The kernels obtained by this calcining-sintering treatment could be mainly composed of a $UO_{1,96}$ phase containing a little $UC_{2-x}O_x$ phase. More experimental analysis should be added to our panel of X-ray diffraction, EDS analysis and electron microscope observations in order to confirm the phase obtained. Proposals for further experimental grids are also detailed in order to obtain kernels with a sufficient amount of oxy-carbide phase that could be characterised with certainty.

Key Words	Oxicarbide, kernels, sol-gel process

N° F.A./Affaire	A-CDHTR-03-01-04/EUR655516508

IND.	DATE	REDACTEUR (nom, visa)	VERIFICATEUR (nom, visa)	APPROBATEUR (nom, visa)
0	12/2006	Anne Duhart-Barone	François Charollais	Christophe Perrais

CLASSIFICATION	Lib	X	DR		CC		CD		SD	

MISES A JOUR

INDICE	DATE	MOTIF DE LA REVISION
0	Décembre 2006	Edition originale

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1 INTRODUCTION

The sixth programme named **RAPHAEL**, meaning **R**e**A**ctor for **P**rocess heat, **H**ydrogen, **A**nd **E**lectricity generation, has been set-up to complement and support European national VHTR programmes and to contribute to the international effort on Generation IV VHTR projects.

The sub-Project Fuel Technology (SP FT) objectives are to establish a technological basis on TRISO coated particule fuel capable of withstanding VHTR requirements that is a coolant temperature of 900-1000°C and a burn-up of at least 160 000 MWd/tHM.

The R&D is oriented towards two goals; Improving knowledge of HTR and VHTR fuel and fuel behaviour and Searching for solutions for improving fuel performances in order to satisfy the VHTR temperature and burn-up objectives. The activities within the SP FT are organised into four packages related to fuel fabrication and control (WP-FT1), fuel and material irradiation (WP-FT2), safety testing and post irradiation examinations (WP-FT3), and fuel development and quantification.

The **CEA laboratory (LCU/U-based Fuel Laboratory)** is solicitated in the **WP-FT1 Fuel fabrication and control** work-package in order to improve the robustness of the fuel at higher temperature and to allow it to reach a higher burn-up. That is the reason why, we have worked on the feasibility of manufacturing UCO kernels (**task n°1**) using modified sol-gel routes in place of UO_2 kernels to minimize the amoeba effect.

This document deals with current knowledge on the fabrication of this type of fuel and on our experimental manufacturing of these kernels based on various grids of interesting data extracted from the literature.

The **first chapter** is devoted to describe the **literature manufacturing of "UCO"** kernels using the Sol-Gel route by an external (Gel Supported Precipitation) and internal (Hexamethyl tetramine) gelling processes. A general overview on the manufacturing processes of UO_2 kernels using a sol-gel route is presented because by slightly modifying the UO_2 process, UCO kernels can be produced. A last part of this chapter deals with the predictable experimental difficulties encountered in obtaining "UCO" kernels through the sol-gel route based on the know-how of our laboratory. The main characteristics that can be expected from the manufactured "UCO" kernels are also given.

The **second chapter** deals with our experimental investigation in order to manufacture "UCO" kernels. The first step was to elaborate dried kernels mainly made from a solution of uranyl nitrate and carbon black. The GSP process used to elaborate theses dried kernels is detailed step by step from the broth preparation, the droplet formation and gelation, the ageing and washing steps up to the beads drying step. The calcining and sintering steps are particularly developed, based on specific literature data because of the impact of the thermal treatment process (temperature, gas nature) on the kernel's microstructure and composition. Thermal Gravimetric Analysis, X-ray Diffraction, Optical and Scanning Electronic Microscopy and EDS characterization were used as efficient techniques in order to evaluate the impact of experimental parameters on the composition, microstructure of the final kernels.

A **general conclusion** allows us to conclude on the feasibility of uranium oxicarbide manufacturing through the external sol-gel route, essentially based on a bibliographic study and on the experimental knowledge of our laboratory. The advantages and drawbacks of our process of fabrication are summarised and allows us to conclude on the thermal treatment steps impact on the kernels composition and microstructure. Proposals for further experimental grids are also detailed in order to obtain kernels with a higher proportion of UC_2 carbide phase in the "UCO" kernel.

2 LITERATURE REVIEW OF "UCO" KERNEL MANUFACTURING

2.1 Generalities about the "UCO" fuel

High Temperature Reactor technology is currently enjoying a period of renewed interest thanks to the genuine advantages offered by this reactor type in terms of thermodynamic yield, inherent safety and its flexibility within the fuel cycle. These advantages are based primarily on the core concept, which relies heavily on refractory ceramic materials, on the use of an inert gas (helium) as a coolant, on the separation of the neutron moderation functions and on the removal of decay heat. Today, this specific reactor type is being considered for cogeneration applications for electricity and heat at a very high temperature.
Reaching these very high temperatures (1000 to 1100°C) can be accomplished with optimised HTRs. A demonstration VHTR project is now under study in the United States for commissioning in about 2017; such a VHTR would operate according to the same principles as those of the HTR, using a fuel made up of TRISO particles inserted into the compacts themselves in graphite prismatic blocks cooled by helium.
The major challenge is the resistance of the TRISO fuel particle in severe operating conditions with temperatures that would be about 150 to 200°C higher than those of the conventional HTRs that were developed earlier. This temperature hike will impact on the different constituents of the particle: the fuel nucleus and the protective layers. The temperature increase on the nucleus should result in an additional swelling (gas component), a greater release of fission gases, an increase in the diffusion speed of the fission products in various environments and for the UO_2 kernels, a much greater carbon oxide production.

The fuel referred to as « UCO » actually consists of a mixture of UO_2 oxide and UC_2 carbide that can be mixed in varying proportions. The most well known experiment performed on this fuel comes from studies carried out in American laboratories in the 1970's, particularly at the ORNL where all of the composition from 0 to 100% was explored.

The major argument governing the Americans' choice of "UCO" as an HTR reference fuel lies in the satisfactory physico-chemical behaviour of the fission products. The simultaneous presence of the oxide and carbide phases stabilizes the oxygen potential of the system up to very high burnup rates (75% FIMA) reached by fuels of the HEU.

The UC_2 phase, present in this composite fuel, reacts with part of the oxygen released by the fission of a uranium nucleus coming from the UO_2 phase resulting in the re-formation of the UO_2 according to the $UC_2 + O_2 \rightarrow UO_2 + 2\,C$ reaction.

In fact, the atmosphere is maintained at a low $P(O_2)$ potential and may be stabilized during irradiation, thereby greatly limiting the formation of carbon oxide, a phenomenon whose major consequences would result in reducing the migration of the nucleus in the particle (the "amoeba effect") and oxidation by this gas in the SiC layer.

Furthermore, by confining the initial UC_2 content to reasonable values, we also stop the risk of a corrosion of the SiC by lanthide-type fission products.

2.2 General information on the manufacturing of "UCO" kernels

The objective of the following chapter is to demonstrate the feasibility of uranium oxi-carbide kernel fabrication using a sol-gel route. The bibliographical study examining the possibilities of fabricating "UCO" kernels based on sol-gel processes has identified two routes for producing this type of uranium oxi-carbide particle: either the process called "external gelling" is used (a process used by the Germans and applied by the LCU or a process termed "internal gelling" (the process used by the Americans) is applied. The fundamental principle behind the fabrication of uranium oxicarbides is common to both processes and relies on the carbo-reduction reaction of the uranium oxide in presence of carbon. Both processes used are modified in comparison to those implemented in the elaboration of UO_2 kernels only at the preparation of the broth stage and during the last stages of the thermal treatments (calcinations and carbo-reduction sintering).

2.3 Overview on the manufacturing processes of UO_2 kernels using a sol-gel route

In the following paragraphs, we recall the definition, the basic principle and the major stages involved in the sol-gel route process as well as the elaboration processes of the UO_2 kernels through the pseudo sol-gel routes, both external and internal.

2.3.1 Definition, principle and generic stages of the sol-gel process

By definition, the sol-gel route is a process in which a transition between a sol and a gel occurs in one of the stages of its implementation. A sol is a colloidal suspension of fine particles (about a dozen at a few thousand angstroms in size) in the aqueous or alcoholic phase maintained stable by a simple Brownian agitation. A gel is a bi-phase mixture (solid and liquid phase), in which the constitutive phases form fields of a very slight dimension, and behave, at this time, like a non-crystalline solid.

The principle of the sol-gel process depends on the destabilization of the sol, obtained through modification of one of the maintenance parameters of the solvation of the particles: particle concentration, the presence of a gelling agent, temperature or pH of the sol generating its breaking. The particles of the suspension, with a size of less than 100 nm, then stick together while remaining in the liquid phase in pores formed between the particles. This precipitation in liquid phase forms a stable gel. The appearance of the gel may be linked to a transition phase which explains the transitional term, "sol-gel". In our kernel elaboration phase, the gelling phenomena must occur at the precise moment of the sol dispersion in the form of droplets.

The generic steps of the sol-gel process, resulting in the fabrication of spherical particles can be carried out in 6 major operations:

Step n°1: **Constitution of the sol** (or of the pseudo sol), based on a solution of metallic salt, called "broth",
Step n°2: **Dispersion** of the sol in the form of spherical droplets and calibrated (using a pump, the initial solution is injected into a nozzle in order to be dispersed in the form of droplets),
Step n°3: **Gelling** of the droplets thereby allowing them to retain their initial spherical form (which in the case of UO_2 kernel fabrication by GSP includes an ageing operation),
Step n°4: **Separation** of the particles from the solvent through washing,
Step n°5: **Drying** of the particles,
Step n°6: **Thermal treatment** of the particles permitting the densification and their possible chemical transformation (this is the case of "UCO" kernel fabrication). This stage corresponds to the calcination, reduction and sintering of the kernel.

According to the bibliographic research carried out on the kernel elaboration processes for nuclear fuel *(C. Perrais, J. Somers, 2002)*, the various sol-gel processes can be differentiated from each other, above all by the method used in the sol-gel transition (steps 1, 2 and 3). Steps 4, 5 and 6 are generic no matter what sol-gel process is applied.

2.3.2 Manufacturing processes using the external (GSP) and internal (HMTA) sol-gel routes

The principle of the process termed, Gel Support Precipitation (GSP) consists in mixing the initial solution (uranyl nitrate of about 400 g/L in U) with a soluble organic polymer[1] that gels at the time of droplet dispersion and acts as a support to the precipitation of the actinide[2]. This gelling polymer also enables us to adjust the viscosity of the solution. The ammonia source in diuranate ammonium triggering the uranyl nitrate precipitation comes from the fluid in which the droplets are dispersed thereby explaining the term of external precipitation. Additives such as a tensio-active (facilitating the spherical formation of the droplets) and a compound called modifier[3] (avoiding polymer degradation) are also added to the initial solution *(C. Perrais, J. Somers, 2002).*

The principle behind internal gelling involves the preparation on one hand, of a uranyl nitrate solution rich in uranium and deficient in nitrate ions ($NO_3/U \leq 1.6$), and on the other, the preparation of another solution containing a mixture of HMTA and urea, cooled at a temperature of about 0 °C. Both solutions are then mixed together and maintained at about 0 °C to avoid the premature decomposition of the HMTA[4]. The broth is afterwards dispersed for the gelling operation in an organic solvent maintained at a temperature higher than 90°C[5]. The organic solvents used are frequently tetrachloroethylene[6] used either alone or mixed with paraffin oil, silicon oils or tri-chloroethylene[7].
In the case of the sol-gel process used in the fabrication of HTR kernels, the method applied to obtain the sol-gel transition is based on a modification of the pH of the sol. The formation of the gel is obtained after destabilization of the sol through an increase in its pH (chemical gelling through contact with a basic donor). In the case of the sol-gel GSP and HMTA processes, the ammonia (or a ammonia solution according to the selected implementation) is the basic donor used; the associated nitrate may be eliminated from the cleaning, drying and thermal treatment stages (Steps 4 to 6).

Two action procedures of the basic donor may be envisioned (Figure 1) :

- Either it acts (Step n°3) from the exterior of the sol droplets through the diffusion of the ammonia from the exterior towards the interior of the kernel and creates external chemical gelling (GSP process),
- Or it is already present in the sol (Step n°1) and the chemical gelling is catalysed by a sudden temperature rise in the sol, at the time of Step 3. In this case, we may speak of an internal chemical gelling. In such a case, the **H**exa**M**ethylene**T**etr**A**mine (HMTA), stable at 0°C decomposes releasing ammonia gas[8] when it is heated up to a temperature higher than 90°C.

---

[1] Polymer type PVA (Alcool polyvinylique or Methocel)

[2] For the uranyle nitrate, the precipitation reaction is written as following:
$2UO_2(NO3)_2 + 5NH_4OH \rightarrow (UO_3)_2NH_3.3H_2O$ (ammonium diuranate) + $4NH_4NO_3$

[3] modifier type THFA (Tetrahydrofurfurilic alcool)

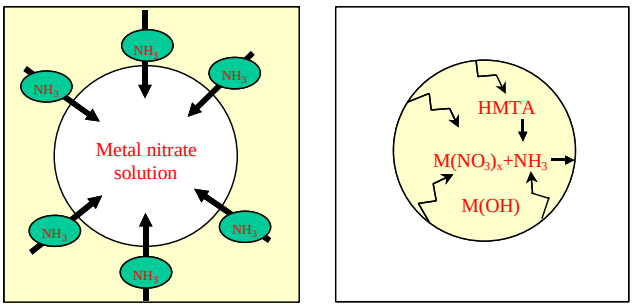
[4] HMTA : Hexa-Methyl-TetrAmine

[5] Following the desired gelification speed and the solvent used, the temperature of the solvent is mainly between 70 and 110°C.

[6] TCE (C_2Cl_4) : Tb. = 121°C

[7] the temperature is limited at 80°C because of the boiling temperature of the product (Tb. = 85°C).

[8] Decomposition in ammoniac and in formaldehyde (H_2CO)



External Gelling (GSP) Internal Gelling (HMTA)

Figure 1: Gelling processes through pH modification

Steps 4 and 5 are generic whatever the sol-gel process (GSP or HMTA). However, several differences exist given the characteristics of the gels formed.
In the case of GSP, an ageing operation (or maturation) of the gelled spheres is necessary. The spheres formed during a certain lapse of time are maintained in the ammonia solution in order to complete the gelling phenomenon (the length of time involved in this operation is determined according to the ammonia solution concentration, the temperature and size of the kernels).

The washing step (Step n°4) is usually carried out using demineralised water containing possibly some ammonia in low amounts to eliminate the ammonium nitrate[9], which is a by-product of the precipitation reaction. In order to perfect the elimination of the ammonium nitrate and to trigger the dehydration of the product, a second type of washing is carried out using isopropanol. The drying operation (Step 5) maybe performed under slightly depressurised air at a temperature higher than 80 °C or through an azeotropic distillation by the $CC1_4$ or under humid air at 180°C *(C. Perrais, J. Somers, 2002).*

For the HMTA process, the ageing operation is not necessary. The washing step (Step 4) of the spheres is carried out using demineralised water containing low amounts of ammonia. A pre-washing operation by a volatile organic solvent such as CCl_4 or petrol ether may also be used. The pre-washing operation enables us to eliminate the gelling organic solvent at viscosity and at high boiling points before the aqueous washing. The drying operation (Step n°5) is generally carried out under air at a temperature ranging between 70 and 120 °C, under humidified air or under saturated vapour at approximately 200°C *(C. Perrais, J. Somers, 2002).*

Calcination, reduction and sintering operations (Step n° 6) are not specific to this type of process. Calcination is overall carried out between 300 and 800°C allowing the organic residue[10] and the ammonium nitrate[11] to be eliminated and to consolidate the spheres and possibly to adjust the porosity. During this stage, the ammonium diuranate[12] is transformed into metallic oxide.
The reduction and sintering operations are carried out in a conventional manner under H_2 or Ar/H_2 by adapting the thermal cycle to the final desired density (final bearing between 1300 and 1700 °C). In order to obtain the UO_2 kernels, the reduction stage allows $UO_{2,00}$ to be obtained from metallic oxides formed at the end of the calcinations step. It is performed under Ar/H_2 ($5\%H_2$) and generally ranges between 400°C and 700°C. The sintering operation allows kernel densification and grain growth.

[9] The presence of NH_4NO_3 in the precipitated kernels is the main cause of their damage mainly during the thermal treatment steps. The nitrates are decomposed and the evacuation of the gas can generate the blowing up of the kernels.
[10] The organic residues are degraded by combustion with the oxygen present in the calcining atmosphere and/or coming from the reduction of the oxyde.
[11] NH_4NO_3
[12] ADU: $\mathbf{(UO_3)_2NH_3\,3H_2O}$

2.4 Descriptions of the UC_xO_y manufacturing processes

2.4.1 External sol-gel manufacturing processes

The sol-gel process, called external gelling (GSP) has been applied to the fabrication of uranium oxicarbide kernel (UC_xO_y). It has only been modified at the stage involving the preparation of the broth (Step 1, cf. §. 2.1) and in the last steps of thermal treatment (Sep 6, cf.§2.1) as indicated in the synoptics represented in Figures 2 and 3 corresponding to the German and American processes.

The German firm, HOBEG[13] has developed an external gelling fabrication process for UC_xO_y dense kernel *(M. Kadner, J.Baier, 1976 and H. Huschka, P. Vygen 1977).* The characteristics of the obtained kernels are explained in paragraph 2.5. This process has also been used to manufacture such kernels by the Institute of Chemical Technologies at the Nuclear Research Centre in Jülich *(Zimmer and al., 1975)*. The American society General Atomics has also developed a process of manufacturing dense "UCO" kernels of 360µm of diameter by an external gelling process (*R.L. Develasco and al., 1988*). The characteristics of the kernels are given in Table 5 (see chapter 2.5). In some cases, the processes were used to produce UC2 kernels. In these cases, heat treatments are quite different than for "UCO" kernels.

[13] HOBEG : Hochtemperatur-reactor-Brennelement GmbH, Hanau, Germany.

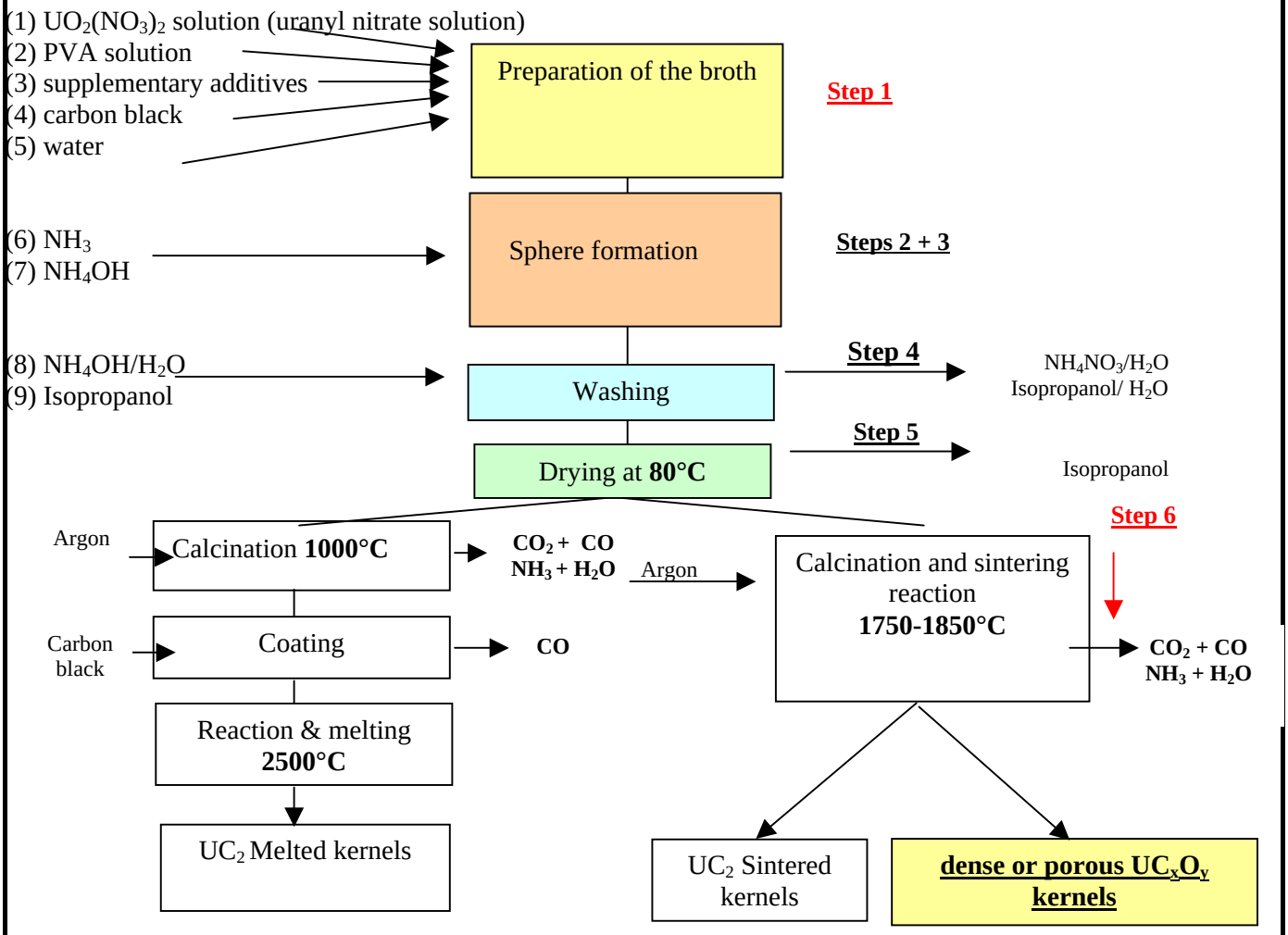


Figure 2: Fabrication of carbide and oxicarbide fissile kernel using external gelling (German firm, HOBEG)

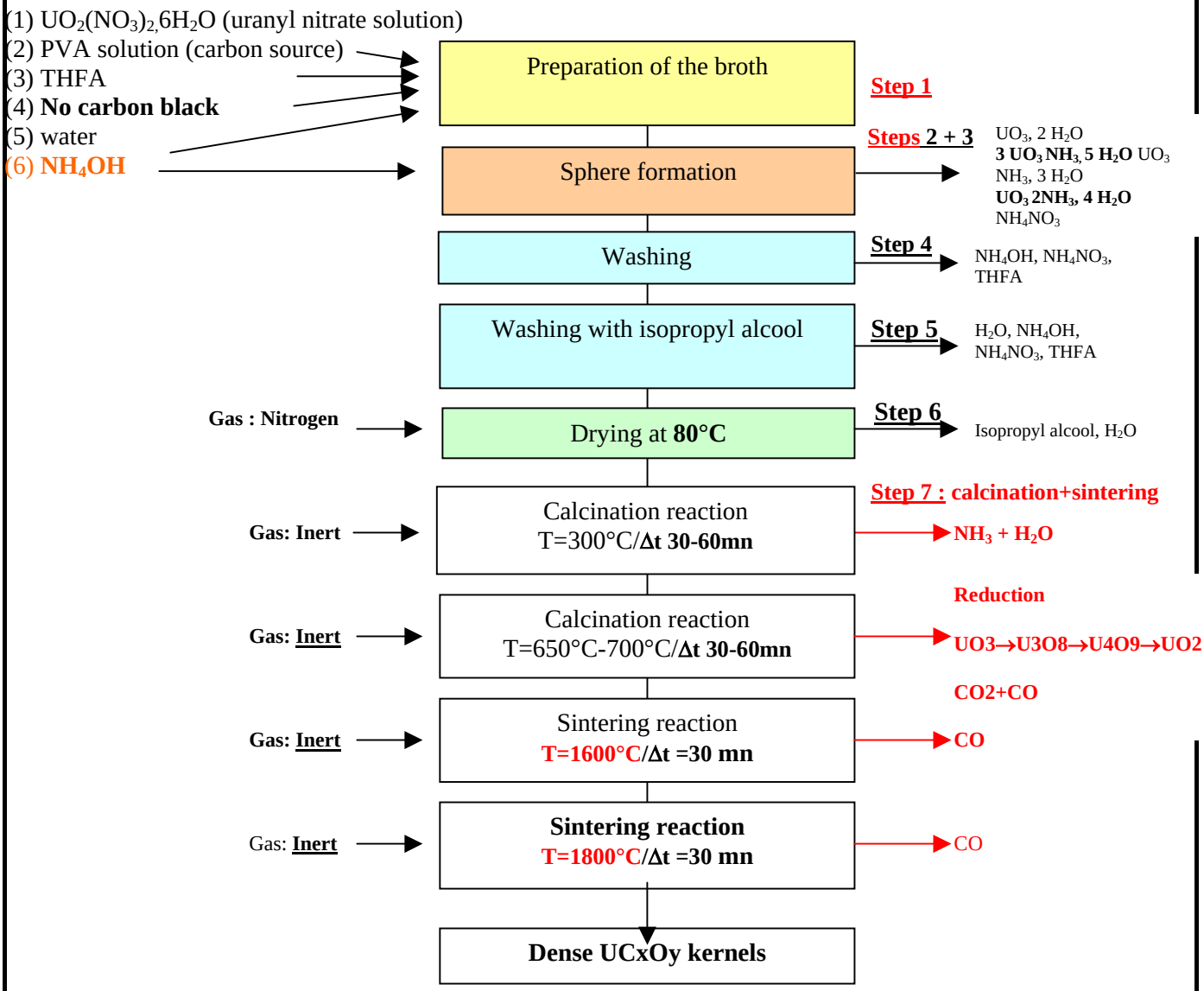


Figure 3 : Fabrication of UCO kernels using external gelling (American firm, GA)

The first modification in relation to the external gelling process used to fabricate UO_2 kernels concerns the step 1: preparation of the broth (cf. Figure 2 and Figure 3). Indeed, the kernels are obtained from a solution containing uranyl nitrate, PVA, additives[14] and water to which carbon black has been added.
The next operations are generic: the spheres are obtained through the passage of the solution through a vibrating nozzle allowing fractionation of the spray. The passage of the droplets through a thickness of 20 to 30 cm of gas ammonia leads to the instantaneous hardening of the spheres due to a chemical reaction. The solid particles are then collected in an ammonia solution. The spherical form of the particles depends, among other things, on the type and the quantity of additives introduced. These contribute to the spontaneous hardening as well as to the maintaining of their shape. Afterwards, the particles are washed in ammonia water to eliminate all traces of ammonium nitrate (NH_4NO_3), dehydrated through washing with isopropanol and dried at 80°C.

[14] Auxiliary materials: polyvinylic alcool, dioxane, acétamide, urea or glycine

Up to the drying stage, the process remains identical to the reference external gelling process (UO_2). The major difference in obtaining the "UCO" kernels lies in the calcining and sintering steps depending on the choice of the temperature and the type of gases used (Step 6, cf. figure 2).

The following table summarizes the temperature and gas conditions in order to obtain UO_2, UC_2 and UCO [*M. Kadner, J. Baier, 1976*].

References	C/U ratio in the broth	Successive Steps	Obtained kernels
M. Kadner, J. Baier, 1976, [HOBEG]	UO_2	1. Calcination UO_3 (under air, 600°C, 4H) 2. Reductive sintering $UO_{2.00}$ ($Ar+5\%H_2$, 1650°C, 2H)	UO_2 kernel Ø =200 µm ± 10 µm, d=10.5 g/cm^3 (>95% $t_{theoretical}$)
	4:1 UO_2 + 4 C Let: % molar in C = 80 % molar in U = 20	1. *Calcination* of the dried kernels (under argon) 2. Calcinated kernels coated with carbon black 3. Obtainment of the carbide (under vacuum, 2H) / graphite crucible 4. Melted kernels obtainment (2500°C) 5. Elimination of the carbon coating through « screening »	Melted UC_2 kernels Ø =200 µm ± 10 µm d=10.5 g/cm^3 (>90% $d_{theoretical}$)
	4:1 UO_2 + 4 C	1. *Calcination* of the dried kernels (sintering oven) (under argon, 4H, T=cste), 2. UC_2 kernels obtainment 3. *Sintering* (under vacuum or under argon, 1850°C)	Sintered UC_2 kernels Ø =215-220 µm d=9 g/cm^3 (>80% $d_{theoretical}$)
	4 to 6:1 UO_2 + 4 to 6 C % molar in C = 80 to 85.7 % molar in U = 20 to 14.3	*1. Calcination* of the dried kernels (cf. flow sheet-under argon) *2.* Partial conversion into carbides *3. Sintering* (cf. flow sheet-argon / cf. publication text under vacuum, 1780°C, 20 to 40 min.)	*Porous* UC_xO_y kernels Ø =300 µm d =3.5 g/cm^3 [C]> 12% (in mass)
	1 to 2:1 UO_2 + 1 to 2 C % molar in C = 50 to 66.7 % molar in U = 50 to 33.3	*1. Calcination* of the dried kernels (sintering oven) (cf.flow sheet-under argon) *2.* Conversion into carbides *3. Sintering* (cf.flow sheet-under argon , 1780 to 1850°C)	***Denses*** UC_xO_y kernels coexisting oxide and carbide[15] phases Ø =190-200 µm, d=10 to 12 g/cm^3 [C] = 2% (in mass)
R.L. Develasco and al., 1988	?	*1. Calcination of dried kernels (calcination ove) under ? at 300°C during 30 to 60 minutes followed by a cooling step under air*	***Denses kernels UO_2+UC_2*** ***d > 10.5 g/cm3*** ***[UC_2] = 20 % (molar)***

Tableau 1: Summary of UO_2, UC_2 and UOC kernels obtainment according to the imposed temperature and gases used during the calcination and sintering stages (M. Kadner, J. Baier, 1976; R.L. Develasco and al., 1988)

[15] Combines the advantages inherent to UC_xO_y kernels (low «amoeba» effect) and those inherent to melted UC2 kernels (easier handling, lower gas under irradiation release).

As for the fabrication of UO_2 kernel, calcination is carried out under air at 600°C for 4 hours while the UC_XO_Y kernel calcination is carried out under inert gas, argon (the calcination temperature is not specified). Only the American process (*R.L. Develasco and al., 1988*) gives an information on the temperature of the calcination step. The calcinations is performed in two steps at 300°C and between 650 and 700°C and lasts 24 hours with a slow temperature ramp in order to avoid a fast evaporation of water and the decomposition of metallic compounds that can damage the spheres (*O. Chihiro and al. 1976*).
In order to obtain UO_2 kernel, sintering is carried out under a reducing atmosphere (argon+5% hydrogen) at 1650°C. In the German process, in order to obtain porous UC_xO_y kernels, of low density and with more than 12% in mass of carbon, the sintering step goes up to 1750°C during 20 to 40 minutes under argon (if we refer to the flow sheet, cf. figure 2) or under vacuum (if we refer to the text in the same publication - *M. Kadner, Jürgen Baier, 1976*). The dense UC_XO_Y kernel with a low carbon percentage (2% carbon mass) are obtained after sintering under argon (cf. flow sheet, cf Figure 2) at a temperature ranging between 1780 and 1850°C.

For the UC_xO_y kernels with a density higher than 10,5 g/cm3, two processes have been used: the American and the German processes. In the first case, the sintering is performed under argon, between 1750 and 1850°C (if we refer to the flow-sheet, Figure 2). In the second case, two steps are necessary under inert gas (the type of gas is not specified) with a first soak at 1600°C and a second one at 1800°C during at least half an hours for each one. The total length of the thermal treatment cycle is of about 24 hours (if we refer to the flow-sheet, Figure 3).

No further precision on the sintering atmosphere has been added about the final composition of the UC_XO_Y kernel except for the dense kernels produced with the American process of General Atomics that mentioned a molar final composition of 20% of the UC_2 phase and 80% of the UO_2 phase. However, we can suppose that the argon atmosphere (with traces of oxygen) seems to be the most suitable for obtaining uranium oxicarbide kernel therefore the elaboration under vacuum promotes carbon obtainment.

2.4.2 Internal sol-gel manufacturing processes

The internal gelling process (HMTA) has also been applied to the fabrication of uranium oxicarbide kernel (UC_XO_Y). Just as external gelling process (GSP), this process was only modified at the §.2.3.1.
ORNL[16] (*J. M. Saurwein et al., 2002*) has developed this process for the production of uranium oxicarbide kernel (*D. P. Stinton et al., 1982*). The raw material is a UO_3 or U_3O_8 powder that is dissolved in a nitric acid solution to yield, as in the case of the GSP process, an initial solution of uranyl nitrate ($UO_2(NO_3)_2$). During Step n°1, the modification concerns the introduction of carbon black (a powder) as well as a dispersant, Tamol *(Caldwell, 1993)*, in the uranyl nitrate solution. The dispersion of the mixture is carried out using ultra-sounds *(D. P. Stinton and al., 1982)*. Urea[17] is added and then the whole solution is cooled at 0°C. The HMTA is then added to the latter solution (*Petti, D.A, et al., June 2002*) whereas in the "conventional" HMTA process used to produce UO_2 kernel, the HMTA and the urea are mixed together and the solution is afterwards cooled at 0°C then mixed with the solution containing the uranyl nitrate.

The following steps are generic to the «conventional» HMTA process. The organic solvent in which the kernels fall is hot trichloroethylene. The washing step (Step 4) of the spheres is carried out using an aqueous ammonium solution, at ambient temperature then is repeated with water.
The drying step is carried out (Step 5) under air at 60°C (*D.A Petti, and al., June 2002*).

Up to the drying step, the principle of the process is identical to the conventional HMTA process. The major difference occurs, as in the case of the "UCO" kernel elaborated in the GSP process, in the calcination and sintering steps which differ in their choice of temperature and the gasses used (Step 6).

[16] Oak Ridge National Laboratory, USA
[17] urea : H_2NCONH_2

For the UC_xO_y kernel, calcination occurs under argon at 350°C[18] during one hour (*J. Lee and al, 1993*) whereas the UO_2 kernel are calcinated under air. The particles at this stage of the process are made up of UO_3+C *(D.A. Petti, and al., June 2002).* They can also be produced at 550°C (*D. P. Stinton, et al., 1981).*

In order to obtain UO_2 kernel[19], sintering is performed under a reduction atmosphere (argon+5% hydrogen) at 1650°C. To obtain "UCO" kernels, the first thermal treatment is applied under argon at 800°C and then a reduction treatment under argon+4% of H_2 at 1600°C is carried out to reduce the UO_3+C in UO_2+UC_2 (*C. S. Caldwell, 1993*). To increase the density of the kernel obtained and to adjust the oxygen-carbon stoichiometry, a final thermal treatment under argon + 10% molar of CO at 1800°C is applied (*Petti, D.A, et al., June 2002, Caldwell, 1993)*. The final composition of the kernel is UO_2+ UC_2 but the common term given is "UCO" kernel.

Another type of thermal treatment has also been described in literature for the purpose of producing dense «UCO» kernels (*D. P. Stinton et al., 1981)*. The reaction and the sintering take place at an unusual low temperature of 1550°C. The usual thermal treatment temperatures applied are several hundred degrees higher. Two stages are necessary: the first stage involves the sintering of the kernel under an argon atmosphere + 1% molar of CO (at 1550°C for 4 hours) and a second stage under argon atmosphere + 3% molar of CO (at 1550°C for 4 hours) allowing the thermo-dynamic equilibrium to be shifted from UO_2+UC_xO_y[20] towards UO_2+UC_2. According to this paper, the thermodynamic data of the system (cf. Appendix 1) shows that the UO_2 and UC_2 phases are in equilibrium for atmospheres containing CO varying between 1.2 and 1.9 % of molar concentration at 1550°C (cf. Appendix 2). When the atmosphere contains less than 1.2 CO, the phases in equilibrium are UO_2 and UC_XO_Y, whereas an atmosphere containing more than 1.9 % CO generates no reaction, leaving the UO_2 and C in equilibrium. Experimentally, the two stages of thermal treatment previously described were implemented and allowed then to obtain sintered kernel carrying a UC_2 phase (white colour) and a UO_2 phase (grey colour) (cf. Appendix 3).

[18] : H_2NCONH_2, in order to eliminate ammonia residues, urea and water (*R. Spence, 1981*)

[19] obtained in the LBF by the GSP process but comparable because the sintering conditions are common to both processes (GSP and HMTA)

[20] the UC_xO_y phase reacts with the carbon present in the CO gas in order to form the UO_2 + UC_2 phases (*D. P. Stinton and al., 1981)*

Obtained kernel	Successive steps	Obtained kernel
UO_2	1. Calcination UO_3 (under air, 600°C) 2. reducing sintering $UO_{2.00}$ (Ar+5%H_2, 1650°C)	UO_2 kernel Ø , d=10.5 g/cm^3 (>95% $d_{theoretical}$)
« UCO »	1. Calcination under Argon (350°C) 2. Thermal treatment Argon (800°C) 3. Reduction treatment, Argon + 4% H_2 (1600°C) $UO_3+C \longrightarrow UO_2+UC_2$ 4. Densification Argon + 10% CO (1800°C) *(D. A. Petti et al., June 2002)* INELL/EXT-02-00300 Report *(J. M. Saurwein et al., 2002) ORNL/TM-2002/262* Report	« UCO » kernel Ø =200 µm d=10.51 g/cm^3 *(Petti, D.A, et al., Oct. 2002)* INELL/EXT-02-01268 Report
« UCO»	1. Calcination under Argon (?) (550°C) 2. Sintering under Argon + 1% CO (1550°C, 4H) $UO_2+UC_xOy \longrightarrow$ (highly densified kernel) 3. Sintering under Argon + 3% CO (1550°C, 4H) $UO_2+UC_xOy \longrightarrow UO_2+UC_2$ *(D. P. Stinton, et al., 1981) ORNL/TM-7651 Report*	Dense « UCO » kernel No characteristics Ø and d data

Table 2: Summary of the obtainment routes according to imposed temperature and gases used during calcination and sintering steps (HMTA process)

2.5 Predictable experimental difficulties during « UCO » manufacturing using the sol-gel route and the main characteristics of the obtained kernels

From an experimental point of view, attention must be drawn to the **modification of the first step**, i.e. the step corresponding to the introduction of carbon black in the initial solution. Based on the knowledge of the LCU relating to the fabrication of kernels with the external sol-gel process, the possible trouble points are the following:

- the **quality of the mixture** between the initial solution containing uranyl nitrate, the PVA (organic polymer) and the THFA with the carbon black,
- and the **quality of the carbon black** used.

The dispersion quality of the mixture (initial solution + carbon black) and of the carbon black itself are indeed important parameters. A poor dispersion quality or a poorly adapted carbon black quality can block the injection nozzle at the drop formation step, impact on the subsequent stages of the external gelling process (ageing, washing, drying) and on the homogeneity of the final product obtained. On the latter point, the homogeneity of the injected initial solution can influence the homogeneity of the final product: since the percentage in carbon present in the kernel can be different within the same kernel or in another kernel and lead to different phases after sintering.

The types of mixers used (rotor, ultrasonic bath, sonotrode…) as well as the adding of a dispersant [21] (type of dispersant to be defined) are parameters that will influence the quality of the mixture. In the existing documentation, information given on the type of mixers and dispersants used is rare and not very precise: the

[21] investigation was performed on the possible addition of a dispersant type tensio-active in order to facilitate the dispersion of carbon black.

use of an ultrasonic bath (*D. P. Stinton et al., March 1981*), of a sonotrode (*G. Ledergerger, et al., 1992*) and the introduction of a "Tamol"-type dispersing agent (*Caldwell, 1993*).

The type of carbon black used is also an important parameter. Commercialized carbon black can be synthesized according to different routes that, among other things, will influence the specific surface (m^2/g) and the state of the surface of the carbon black itself (cf. Appendix 4). A chemical treatment performed on the carbon black beforehand allows us to render the surface more hydrophilic or on the contrary, more hydrophobic. The specific surface and state of the carbon black surface have a considerable influence on the dispersion of the carbon black in the initial solution. The choice of carbon black to be used for the mixture is consequently an important matter that must be taken into account.

The amount of carbon that we try to incorporate into the kernel is also a point to be taken into consideration from the viewpoint of an experimental realisation. The great C/U ratios have been reached on the order of 4 to 6 (80 to 85% molar of carbon) to obtain porous "UCO" kernels (*M. Kadner, Jürgen Baier, 1976*). However, it is reasonable to think that we might be limited by the quantity of carbon black introduced into the initial solution even though this point may be improved by the type of mixer used, by the presence of a dispersant and by the quality of the carbon black used (specific surface). We might indeed suppose that the high C/U ratios will generate a black particle aggregation and consequently poor homogenisation of the initial solution.
An other point that has retained our attention is the calcination step. Few papers develop that step. The main goal of this step, for the external process, is the decomposition of the organic polymer[22]. This decomposition is considerated as midely exothermic and happens between 280 and 300°C (*R.L. Develasco and al., 1988*). A higher temperature of decomposition has also been evocated at 400°C (*E. Zimmer and al., 1978*). According to some authors, that temperature can go up to 700°C under an oxidizing atmosphere as air and 900°C under a reductive atmosphere (*T. Kazutoshi and al., 1995*). A last author indicates different states of the decomposition of PVA as following (*Gilman and al., 1994*):

left Matter	Appearance	Ratio C/H	Yield (%)
PVA	Solid white powder	0,5	NA
Polymer residue 250°C (30 min)	Yellow-orange foam	0,52	82
Polymer residue 300°C (30 min)	Brown rigid foam	0,71	47
Polymer residue 350°C (30 min)	Black-Brown foam	0,83	18
Polymer residue 400°C (30 min)	Black powder	1,00	5

Table 3: PVA and its residues: Appearance, ratio C/H and yield

(Gilman and al, 1994)

The calcining atmosphere is an important parameter. During this step, it has been shown that a main part of the carbon introduced in the kernels is lost. A variation of the carbon weight loss of 15 to 37 % is due to the type of atmosphere used. Most authors mention the use of an inert argon atmosphere as shown in the following table.

Calcining atmosphere	Ration C/U after the sintering step	Carbon left (% weight)
Ar – 0,5% CO	0,0335	62,9
Ar – 1% CO	0,0414	77,7
Ar – 2% CO	0,0451	84,6
Ar – 4% H2	0,0432	81,1

[22] Polyvinyl alcool

Tableau 4 : Carbon weight loss / type of atmosphere used (*Stinton et al*, 1982)

A last important parameter is the type of crucible used during the calcining step. A graphite crucible reacts chemically from 1200°C and above whereas a tungsten crucible stays inert (*G. Danger, and al., 1974*). Others authors give precisions concerning the type of crucible used as molybdenum carbide (*D.P. Sinton and al., 1983*) or tantalum (*J. Lee and al., 1993*).

The characteristics of the kernel obtained by the sol-gel process of pseudo external gelling (*Kadner, M. et al., 1976*) are listed in Table 3.
The porous UC_XO_Y kernel have a 300 µm diameter for a low density (d=3.5 g/cm^3). The carbon mass percentage in these kernel is high (more than 12%) to be linked to the high amount of carbon introduced in the initial solution (for an initial C/U ratio of 4 to 6).
The dense UC_XO_Y kernel have a diameter of 200 ± 10 µm for densities much higher, equivalent to those of the UO_2 (higher than 10.5 g/cm^3). These kernel contain less than 2% mass of the carbon (for an initial C/U of 1 to 2).

External gelling process (GSP)									
Type of kernels	Diameter (µm)	Density (g/cm3)	Ratio C/U (in the broth)	[U] weight %	[O2] weight %	[C] weight %	Sphericity ∅max/∅min>1,2%	quantity	Biblio graphic references
Firm	**- HOBEG -**								
UO2	200 ± 10	10,5 (>95% dthéo.)						lab.	
UC2 melted	200 ± 10	>10,3 (>90% dthéo.)	4 :1 UO2 + 4C	90 (Huschka, H. et al., 1977)	< 0,1 %	> 9,3 %	< 25 (Huschka, H. et al., 1977)	100 kg	Kadner, M. et al., 1976
UC2 sintered	215 - 220	9 (>80% dthéo.)	4 :1 UO2 + 4C		0,2 – 0,5 %			lab.	
UCxOy porous	300	3,5	4 à 6:1 UO2 + 4 à 6C			> 12 %		lab.	
UCxOy denses	200 ± 10	> 10,5	1 à 2 :1 UO2 + 1 à 2C	92 (Huschka, H. et al., 1977)	6	2	< 25 (Huschka, H. et al., 1977)		
Firm	**- General Atomics -**								
UCO	≤360	>10,5		87				5,5 kg	Develasco, R.L. et al., 1988

Table 5: Characteristics of kernel obtained with the external gelling process (GSP)

The characteristics of the kernel obtained using the internal gelling sol-gel process are given in the following table. The diameters of the UC_xO_y kernel are high; 350 and 500 µm, (*"Fuel design and fabrication", IAEA TECDOC 978*). Lower diameters, 200 µm were also obtained (*D. A. Petti et al., Oct. 2002*).

Internal Gelling Process			
Particle type	**UCO**	**UCO (UO_2 + UC_2) US Program**	
		Fissile 19.9% enriched	Natural Fertile (0.7%)
Diameter (µm)	200	350	500
Density (g/cm^3)	10.51 (>90% $d_{théo.}$)	-	-
Biblio reference.	D.A. Petti et al., NP-MHTGR Fuel development-Program Results, Oct. 2002 Ineel/EXT-2002-1268 Report	IAEA TECDOC 978/HTGR 2 "Fuel design and fabrication"	

Table 6: Characteristics of kernel obtained with the internal gelling process (HMTA)

Information in the current literature is decidedly lacking concerning the microstructure of the "UCO" kernel obtained using the GSP and HMTA processes (UO_2 phase distribution, porosity distribution, grain size…) Only the study carried out by the Stinton team (*D.P. Stinton et al, July 1982*) on the elaboration of "UCO" kernel through the internal sol-gel route reveals the existence of 2 phases, i.e. UC_2 and UO_2 (cf. Appendix 3).

2.6 Conclusion on the manufacturing of "UCO" kernels using the sol-gel route

According to the bibliographic study carried out on sol-gel route processes of UCO kernel fabrication (though there are few pertinent documents found on the subject), the elaboration of these kernels appears to be possible through either internal or external gelling processes. Modifications intervening in the preparation stage of the broth (introduction of carbon black) and in the last steps of the thermal treatments of calcination and sintering through a choice of temperature and gases enable us to obtain this type of kernel.

The first stage of modification is delicate matter given the possible trouble points that may occur and these involve the quality of the mixture between the initial solution containing uranyl nitrate, PVA (organic polymer) and the THFA with the carbon black and the quality of the carbon black that is used.

As for the final stages of thermal treatments involving calcination and sintering, the lack of any precise information available in existing literature concerning thermal cycles of reactional sintering clearly indicates the need to develop an experimental test programme.

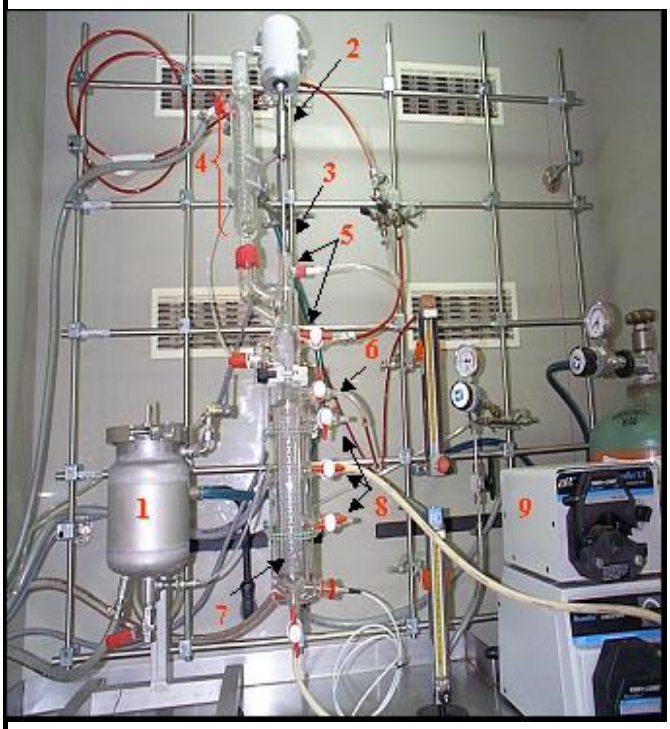
3 EXPERIMENTAL INVESTIGATIONS IN ORDER TO MANUFACTURE « UCO » KERNELS

This chapter describes the experimental protocol we have followed to produce a batch of dried kernels made of uranyl nitrate and carbon black to will then go through calcining and sintering steps in order to obtain "UCO" kernels.
The description includes the experimental device and the reagents we have used, the stages of preparation of the uranyl nitrate solution as well as the broth, the injection, the dispersion and the precipitation of the particles in ammonia solutions of precipitation and ageing, followed by the stages of washing with water and dehydration of the cores with an alcoholic solution, followed by the drying stage. The calcining, reduction and sintering steps are developed in a specific paragraph because of the impact of the experimental parameters on the microstructure and the compositions of the final kernels.

3.1 Manufacturing of dried kernels made of ADU (ammonium di-uranate) and carbon black

3.1.1 Facilities description

A UO_2 GSP particule production facility has been conceived at the LCU in our laboratory, in order to produce lab-scale UO_2 kernels of about 15 to 20 000 kernels by campaign, that is to say batches of about 20 grammes. We used the same device in order to produce our kernels containing uranyl nitrate and carbon black. The experimental device we worked on is represented in the following figure.



(1) Pressurized vessel bringing the broth to the top of the column,
(2) Arrival of the broth,
(3) Injection nozzle of the broth,
(4) Cooling system,
(5) Air arrival,
(6) Ammoniac gas arrival,
(7) single glass reactor in which is performed the gelification, the ageing and the washing steps
(8) Fluidization system for the different baths,
(9) Peristaltic pumps.

Figure 4 : Lab-scale GSP particule production facility

The feed material containing a uranyl nitrate solution, a polyvinyl alcohol dispersion, further additives and carbon black is introduced in the pressurized vessel in order to conduct the broth at the top the device through a vibrating nozzle. The spheres are formed by breaking up the liquid microspheres by the vibrating noozle located at the top of the ammonia column. The droplets react with air or gaseous ammonia to partially gel the spheres. The microspheres are then gelled through baths of liquid ammonia in order to give a precipation of ammonia uranate. Excess of ammonia, THFA and nitrates are extracted by a step of washing with water. Isopropyl alcohol is then used to remove water, ammonia, THFA and the nitrates. The kernels drying step is performed to remove alcohol and a significant amount of water from the kernels.

The main manufacturing steps that will be developed in the following paragraphs consists of the following :

- Step1: preparation of the uranyl nitrate solution,
- Step 2: preparation of the broth,
- Step 3: Injection and dispersion of the initial solution,
- Step 4: Precipitation and ageing in a solution of ammonia,
- Step 6: Washing of the kernels with water,
- Step 7: Dehydration of the kernels with isopropyl alcohol,
- Step 8: Drying of the kernels.

3.1.2 Details on the steps 1 to 8: from the preparation of the broth to the drying of the kernels

3.1.2.1 Preparation of the uranyl nitrate solution (with a previous under-stage of preneutralisation of the uranyl nitrate solution).

A uranyl nitrate solution[23], is prepared starting from a solid powder of U_3O_8 introduce in a solution with the nitric acid. The nitric acid is in very light excess in order to allow the total dissolution in solution and to avoid the presence of a too large quantity of free acidity in the uranyl nitrate solution which slows up its precipitation. Indeed, ammonia reacts preferentially with the free H+ ions and can thus slow down and limit the reaction of precipitation. To minimize to the maximum free acidity, the uranyl nitrate is neutralized beforehand by a concentrated ammonia solution.
The neutralization of free acidity can generate a second interest by forming ammonium nitrate. Indeed, NH_4NO_3 is quoted in the literature like "agent plug" of the acid uranyl nitrate solution. This parameter seems important because in the literature is mentioned processes in which NH_4NO_3 is voluntarily added to the initial solution (*Xu Zhichang and Al, 1990*).
The final concentration of the nitrate uranyl solution is of 450 g/L in uranium.

[23] $UO_2(NO_3)_2$

3.1.2.2 Preparation of the broth

The neutralized uranyl nitrate solution is added to polymer[24] and an alcohol. The polymer that supports the precipitation, is soluble in aqueous mediums. It should be noted that there are several classes of PVA. The latter are indexed according to their degree of hydrolysis. PVA can contain a certain number of acetate functions, sensitive to hydrolysis in acid medium. To limit this dehydration phenomenon of the PVA chains, the alcohol is added to the mixture. This alcohol also has the property to protect the polymeric chains from the radiolysis generated by the presence of radioactive uranium.
According to the uranium concentration aimed, the volume of the broth is adjusted with distilled water. The concentration of polymer as well as the alcohol (per volume) are fixed according to the spherical shape of the precipitated drops observed with a stroboscopic lamp whose frequency is connected to the frequency of the vibrating nozzle.

The carbon black powder is then added to the broth. Two types of carbon black were tested, both coming from a furnace black process, a low specific area of 20 m^2/g and a high specific area of 350 m^2/g. The dispersion of the mixture was performed using an adapted sonotrod (dispersive probe using ultrasounds) during ¼ of an hour. The quality of the dispersion is an important factor because it can block the injection nozzle and also the homogeneity of the initial mixture influences the homogeneity of the final kernel. Carbon black was added to the broth in order to obtain a ratio of C/U of 2.2. After testing both type of carbon black, the highest specific area was selected because of the absorbent behaviour obtained by a preliminary surface treatment increasing its "solubility" in the aqueous phase and the quality of the homogeneity of the broth.
No further dispersant (type Tamol) was added to the final mixture because it was not needed.

3.1.2.3 Injection, dispersion and precipitation of the broth into a ammonia solution (higher concentration)

The broth is introduced into a pressurized vessel. The pressure, constant, maintained on the surface of the solution in the pressurized vessel, propels the broth til the vibrating nozzle.
The liquid jet is divided into drops that generate liquid spheres. Tests were made using a nozzle which lead to a diameter of 750 µm for the dried kernels obtained. No optimisation of the size of the kernel have been done. It was not the purpose of this study.
The flow of the liquid broth, the frequency of the vibrator, the amplitude of the vibration and the diameter of the nozzle condition the quality of the drops obtained. Those parameters were tested and then fixed.
The formed drops cross a layer of ammonia gas present in the top part of the column. In order to form a shell, protecting the kernels from smashing on the liquid ammonia beneath. The mixture is then agitated. This step of the process is the determinant because it conditions the shape and the final size of the future oxy-carbide kernels.
The reaction of precipitation initially takes place on the surface in contact with gas ammonia (NH_3) then during the stage of gelation in contact with liquid ammonia (NH_4OH) (see appendix 6).

3.1.2.4 Ageing of the cores in an ammoniated solution of ageing (lower concentration)

The step of ageing of the kernels prolongs the preceding step by completing their precipitation. The kernels are in contact in the column with a weaker concentration of ammonia. The temperature as well as the duration of the step are set to be higher then those of the first ammonia solution in order to generate a longer contact between the kernels and the ammonia reagent and a better diffusion of ammonia in the kernels. The time of ageing of the kernels must be limited because a prolonged stay could cause a swelling phenomena or a decomposition of polymer.

[24] PVA : Polyvinyl alcohol

3.1.2.5 Washing of the kernels with demineralized water

The reactions of precipitation and ageing involves the formation of ammonium nitrate salts (formed during the reaction of precipitation).Their presence in the precipitated kernels is a cause of damage during calcining and sintering steps due to the decomposition of nitrates into gases that can be involved in the explosion of the kernels.
The kernels are washed with demineralized water to remove the ammonium nitrate salts. The number of washing cycles is fixed by the measure, after each washing step, of the conductivity and an evaluation of the concentration of the NO_3^- ions of the stripping solution. Values have been determined for both parameters and are obtained between 4 to 7 washing cycles.

3.1.2.6 Dehydration of the kernels using isopropyl alcohol solution

The isopropyl alcohol is used as a solvent for the dehydration of the final kernels. Several successive washings are necessary to eliminate free water still present within the kernels. The free water forms with the alcohol an azeotrope at room temperature, which will withdraw water out of the kernel. The advantage of such a type of drying compared to a thermal drying is to obtain a less important and brutal withdrawal of the kernels. Isopropyl alcohol is used for 3 to 5 dehydration steps until the concentration of water in the stripping solution is lower than 10 mg/L measure using a Karl Fisher method. The kernels are then left ½ hour at room temperature in order to superficially dry them.

3.1.2.7 Drying of the kernels

Following the dehydration step, the kernels were placed in an oven under a partial vacuum at 80°C to finish evaporating the azeotrope water/ isopropyl alcohol. At this stage of the process, the kernels still have an amorphous structure and the polymeric network is not yet degraded because the drying temperature is lower than the decomposition temperature of the organic material.
The final dried kernels have a diameter of approximately 750 µm and are illustrated in the following figure.

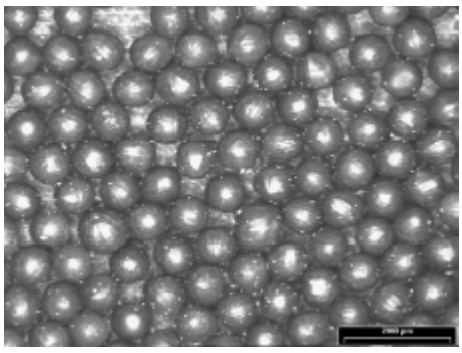


Figure 5 : Optical observation of the dried kernels made of ammonium di-uranate (ADU) and carbon black

3.2 The calcining thermal treatment step

The first part of this paragraph synthesizes the principal conclusions of the literature in order to establish an experimental grid relative to the calcining step applied to the kernels manufactured in our laboratory.
The second part of this paragraph is the application of the preceding thermal protocol to the non radioactive components taken one by one of the kernels of ADU+carbon black in order to evaluate the influence of gases, temperatures and times of the soaks on their reactivity.
A third and last part relates to the influence of the temperature and duration of the soak on the composition of the kernels.

3.2.1 Literature review applied to our experimental calcining step

Previously, we showed that various heat treatments exist. They all use argon in order to preserve the maximum of carbon within the kernels. Experiments conducted on UO_2 kernels showed that the calcining step under air helps to remove totally PVA and ammonium nitrates contained in the kernels. A calcining step under argon (5 ppm of O_2) does not remove totally the PVA and the ammonium nitrate, but allows a reduction of the uranium. After sintering, the kernels calcinated under argon contain two phases; UN and UN_2 other than the normal UO_2 phase, resulting from the carboreduction with nitrogen and the carbon traces within the kernels. Under air, only UO_2 is obtained (*F. Charollais, et al, 2004*).

According to a TGA carried out on carbon black (under air until 1000°C), it is shown that starting from 430°C, the carbon black is oxidized by oxygen.
A calcining step under air at 430°C, followed by a sintering step under argon till 1600°C, performed on ADU+carbon black kernels was carried out in our laboratory. With this treatment, no trace of carbon is measured in the kernels, we obtain only oxide kernels. A test of sintering to 1600°C (without the calcining step) shows the presence of two very porous phases of UC and UO_2. Consequently, we chose to test on our experimental kernels four different types of calcining steps:

- The first type of calcining cycle is drawn from the publication of Develasco (*Develasco, R.L. and Al, 1988*) which contains two soaks at different temperatures (Figure 6-a),
- the second type of calcining cycle drawn partly from HOBEG process (*M. Kadner and al., 1976*), which contains one soak (Figure 6-b),
- the third type of calcining cycle is drawn from the process of Develasco (Figure 6- a), but with an important modification on the level of the first soak which will be carried out partly under air (Figure 6-c),
- The last type of calcining cycle has a first soak at 340°C broken up into two parts, the first under air, the second under vacuum in order to eliminate all the residual oxygen. The end of the cycle will be carried out under argon 6.0 as for the other cycles (Figure 6-d).

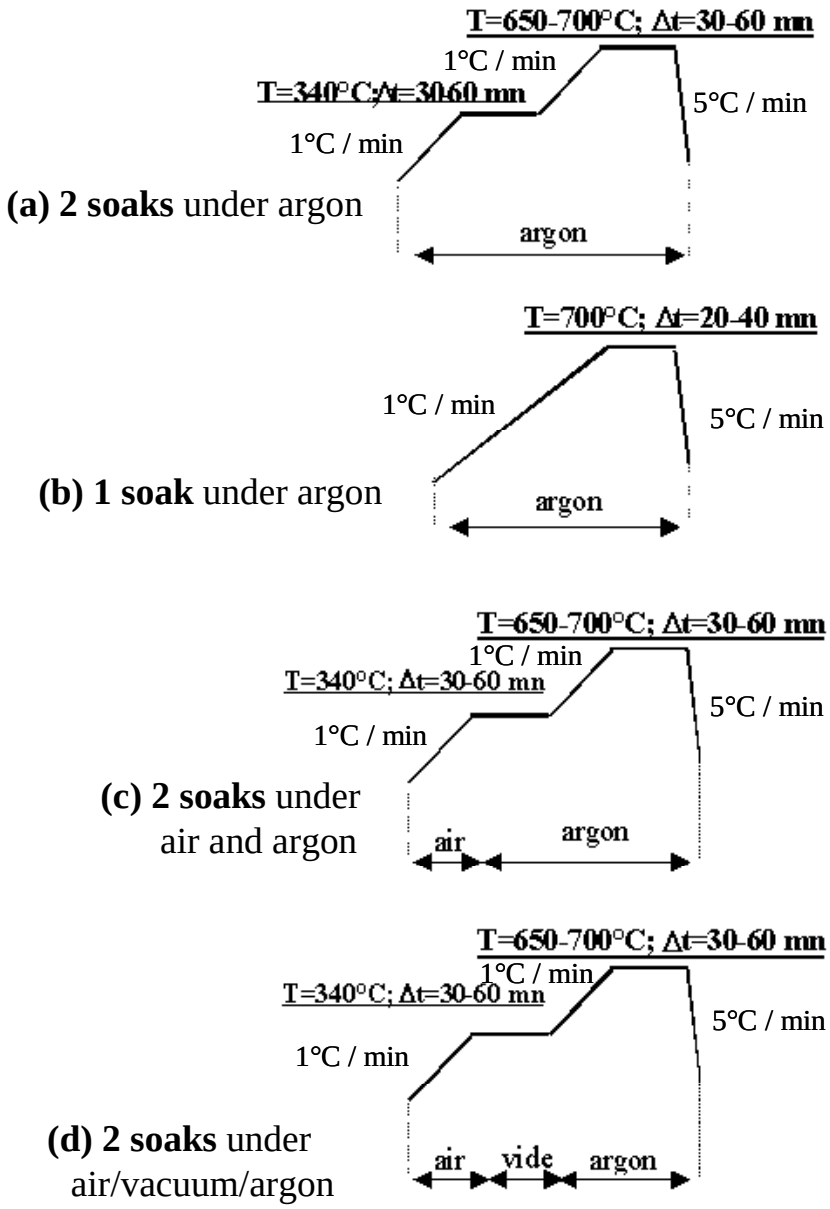


Figure 6 : Scheme of the four different types of calcining step considered

In order to observe the influence of the soak at 340°C on the PVA, various thermogravimetric analyses were carried out with durations of soaking stages ranging from 0 to 120 minutes.

3.2.2 Elaboration of a calcining protocole for the U-kernels based on thermogravimetric results obtained on raw materials

The heat treatment of the calcining step was defined starting from the TGA results carried out on raw materials introduced in the broth with the uranyl nitrate that is; Polyvinyl alcohol (PVA), ammonium nitrate and carbon black (see table 7).
Table 7 recapitulates the four main thermal treatments described in Figure 6.
Treatments 1-a, 1-b and 1c corresponds to modifications of the heat treatment number 1 that is to say: the quality of argon (passing from argon 6.0 to argon 5.5 (1-a)), and the lengths of the first soak ranging from 0 to 120 minutes (heat treatment number 2 (0 min), 1-b (30 min), 1 (60 min) and 1c (120 min)).

Type of treatment	**1**	**1-a**	**1-b**	**1-c**	**2**	**3**	**4**
Temperature of the first soak	**340°C**	340°C	340°C	340°C		**340°C**	340°C
Duration of the first soak	60 min	60 min	30 min	120 min		60 min	60 min
Temperature of the second soak	650°C	650°C	650°C	650°C	650°C	650°C	650°C
Duration of the first soak	60 min	60 min	60 min	60 min	60 min	60 min	60 min
Air between 20°C and 340°C						**X**	X
Vacuum at 340°C							X
Argon 6.0	**X**		X	X	X	X	X
Argon 5.5		X					
PVA	X	X	X	X	X	X	X
NH4NO3	X					X	
Carbon black	X					X	X
4% of carbon black+ 96% of PVA	X					X	X

Table 7 : Summary of the different thermal treatments performed on non-radioactive material

The observations on the TGA results performed on NH_4NO_3 for the treatments 1 and 3 showing the influence of the presence of argon 6.0 or air in the first soaking step (at 340°C) are the following (see. TGA curves Figure 7) :

- Indifferently, total disappearance of ammonium nitrate at 290°C,
- the elimination of ammonium nitrate is carried out using a heat treatment including a slow rise of temperature of 1°C/min exceeding 290°C under air or argon 6.0.

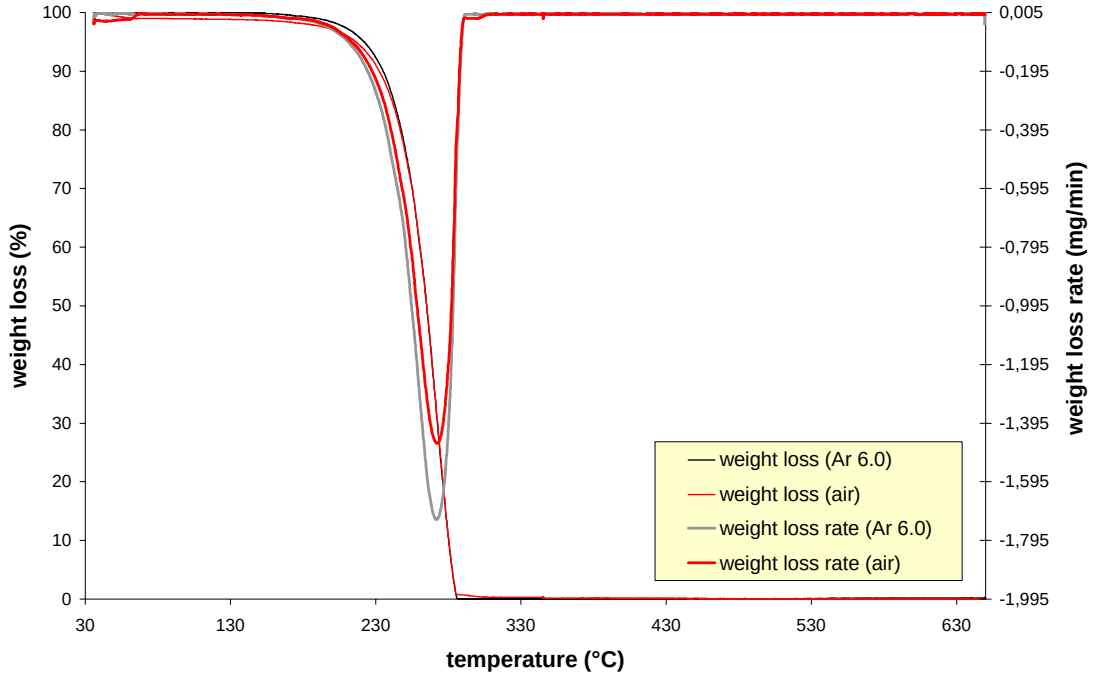


Figure 7 : Comparison between TGA curves for NH_4NO_3 (air/argon 6.0)

The observations on the TGA results performed on carbon black using for the first soak, argon 6.0 (thermal treatment n°1), air (thermal treatment n° 3) or air followed by a vacuum (thermal treatment n°4) are the following (see. Figure 8):

➡ let's note the weight loss before 50°C, due to the evaporation of water,

➡ the TGA curve under argon 6.0 shows a low weight loss during all the thermal treatment coming up to a total weight loss of 6%,

➡ the presence of air at the beginning of the heat treatment generates the consumption of carbon starting from 440°C till 600°C, at this temperature no carbon remains in spite of the treatment under argon performed at half of the soaking step at 340°C,

➡ the vacuum performed at half of the soaking step at 340°C limits the weight loss, at the end of the cycle 80% of the compounds is still present. This value is more important than the treatment carried out entirely under argon 6.0,

➡ only the treatment carried out entirely under argon 6.0 preserves the carbon black.

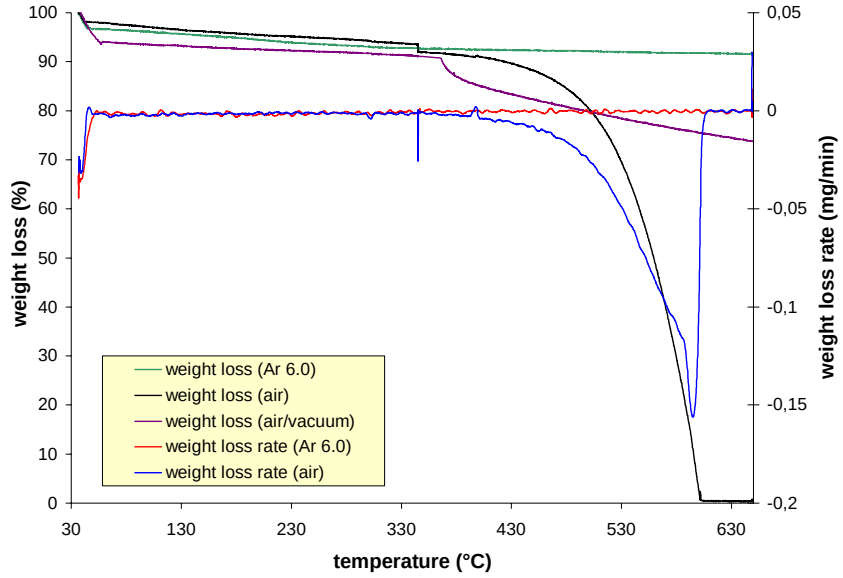


Figure 8 : Comparison between TGA curves for carbon black

The observations on the TGA results performed on the polymer using for the first soak argon 6.0, followed by a second soak also under argon 6.0 (thermal treatment n°1) are the following (see **Figure 9**): Two main steps of decomposition are observed :

➡ the first occurs at 340°C where the PVA breaks up partially by scissions of the organic chains to produce polyene (*Gilman and Al, 1994*) (appendix 7). This decomposition can generate up to 70% of the loss of the initial weight as seen in the following figure,

➡ the second decomposition occurs at 420°C where PVA goes on breaking up to form short aliphatic chains (*Gilman and Al, 1994*) (appendix 7, see Figure 22).

The same type of curve has been observed under air/vacuum/argon 6.0 (thermal treatment n° 4) with the same decomposition steps.

The presence of a soak at 340°C increases the first decomposition of PVA. The quantity of oxygen seems to changes the effectiveness of the first decomposition of the PVA. When the treatment is carried out under argon 6.0, the soak at 340°C generates a weight loss of 70% of the polymer whereas a treatment under air generates 50%, in the same conditions, of the weight loss. The presence of oxygen could modify and slow down the mechanism of decomposition of PVA.

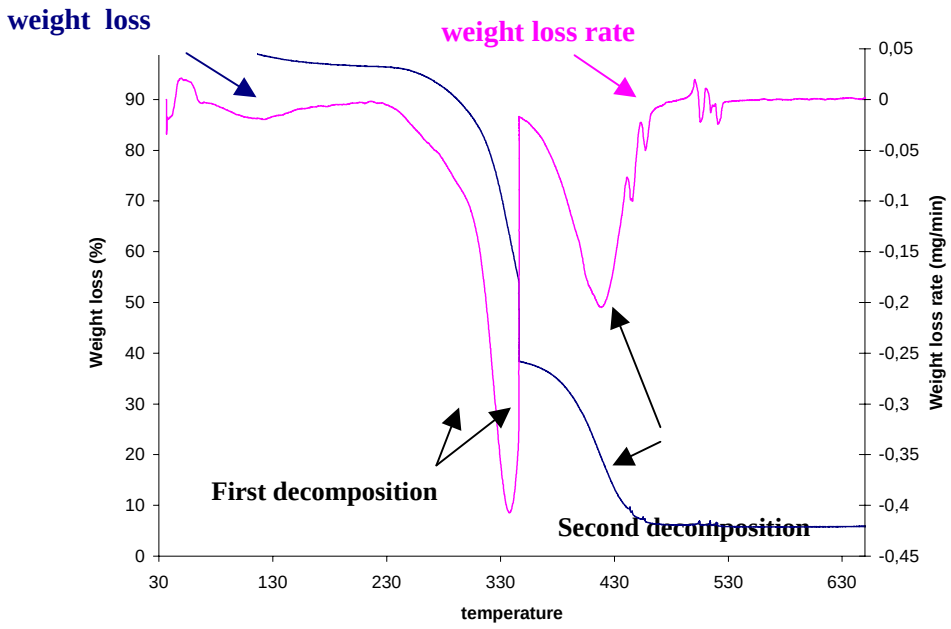


Figure 9 : TGA curves for the polymer under argon 6.0 at 340°C then 650°C during 60 minutes

To conclude, in regard to the results obtained by TGA on the compounds taken one by one, we selected for our experimental kernels the following thermal treatment:

- 2 soaks under argon, one at 340°C during 60 minutes in order to break up correctly the polymer followed by a soak at 650-700°C during 60 minutes in order to reduce the uranium present in the kernels (valence 6 form) into a UO_2 phase (valence 4 form) (*DeVelasco et al., 1988*) and avoiding the carbonitruration phenomena (Charollais and al., 2004).

This thermal treatment generates the most revealing decomposition of PVA with the lowest carbon consumption.
We will now consider the influence of slight modifications of this efficient protocol on the final composition of the kernels made of ammonium di-uranate and carbon black in terms of the length of the soaks and the temperature of the second soak (600 to 700°C).

3.2.3 Effect of the calcining protocol on the composition of the kernels made of ADU and carbon black

This paragraph develops the effect of the calcining protocol on the composition of the kernels in terms of:
- the length of the soaks,
- the temperature of the soaks.

Knowing that under air (*F. Charollais and al, 2004)*, the elimination of the sub-product is the most efficient, a comparison will be made between the treatment under air and the most optimized calcining treatment we will have found for our kernels in terms of weight loss.
Theses effects were evaluated using the identification of phases formed during the treatments by X-ray diffraction analysis and weight loss results.

The calcining treatments, under flowing argon 6.0 (as concluded above), described in the following table were carried out on ADU + carbon black kernels and for the thermal treatments 1 and 2, also on kernels containing only ADU. Two soaks were performed, one at 340°C and the second one between 650°C and 700°C. The length and the temperature of the soaks were varied.
The following table describes the different treatments performed.

Type of treatment	**1**	**2 ***	**3***	**4**	**5**
Temperature of the first soak	340°C	340°C	340°C	340°C	340°C
Duration of the first soak	60 min	60min	300 min	60 min	120 min
Temperature of the second soak	650°C	700°C	700°C	700°C	700°C
Duration of the second soak	60 min	60 min	300 min	6 min	10 min
Argon 6.0	X	X	X	X	X
ADU + Carbon black	X	X	X	X	X
ADU	X	X			
TGA		X	X		

Tableau 8 : Summary of the different thermal treatments

** treatments carried out in a TGA, the rest were carried out in an alumina furnace.*

X-ray diffraction analysis performed on the samples show that, whatever type of calcining treatment applied, a UO_{2+x} type phase is obtained. (see **Figure 10**).

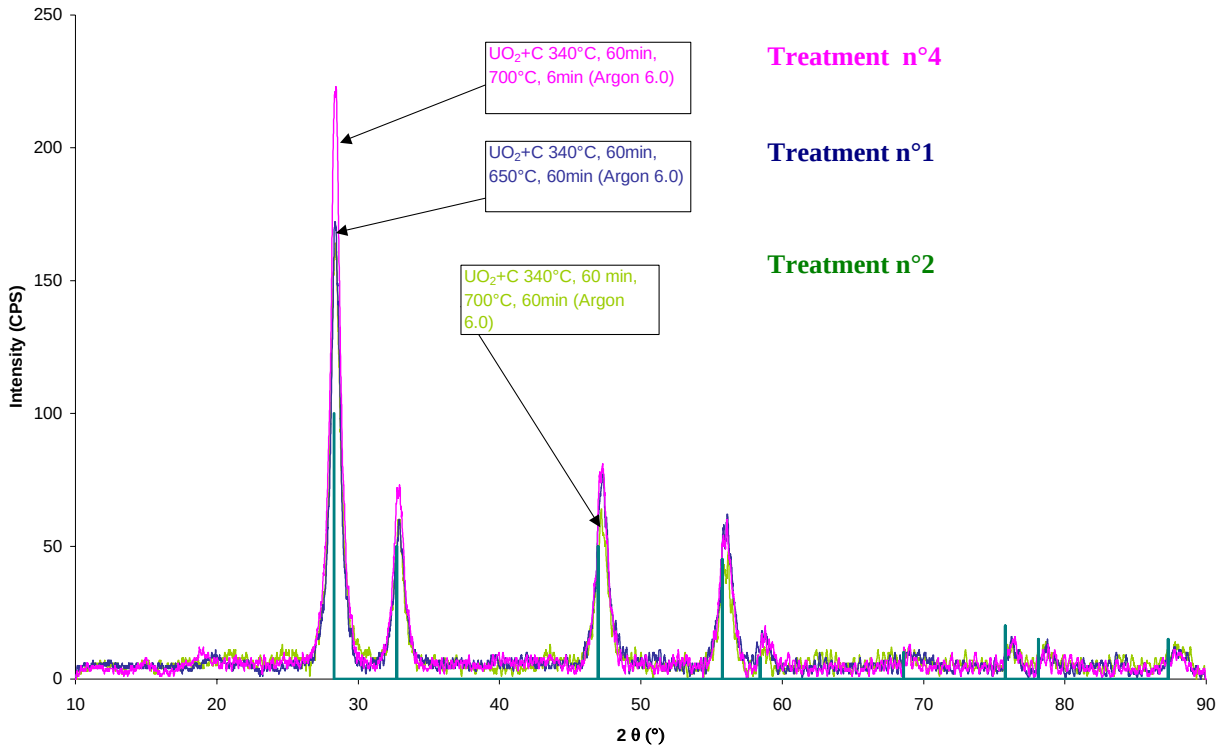


Figure 10 : Diffractogram of the kernels after the calcining treatments / JCPDS No. 41-1422 (UO2)

Only treatments 4, 1 and 2 were represented because the other treatments did not show revealing differences. One can notice the strongest intensity peak, for the treatment n°4, corresponding to the shortest second soaking period. At 700°C, a length of 60 minutes is not needed, 6 minutes are sufficient. The second soaking period (650°C or 700°C) does not generate a variation of the kernel's composition but influences the intensity of the peak which depends on the quantity of the product analyzed and measurment parameters (not quantitative analysis). Consequently, we will retain for the second soak, 700°C during 6 minutes.

The observations on the TGA results performed on kernels containing ADU+carbon black are the following (see **Figure 11**):

- several important weight losses, the first starting from 100°C and until 150°C (disappearance of the water contained in the kernel) and the second around 190°C corresponding probably to the reduction of the UO_3 into U_3O_8. The disappearance of ammonium nitrate at 290°C is notable. The weight loss due to the decomposition of the PVA is lower than expected. After 450°C, the slow decreassing of the weight loss could be attributed to the end of the PVA's decomposition and the slow reduction of the U_3O_8 into UO_{2+x}. No peaks can be attributed to a carbon black loss.

The conclusions on the TGA results are the following:

- a carbon conservation inside the kernel seems to appear,
- sub-products such as ammonium nitrate and the PVA seem to be broken up.

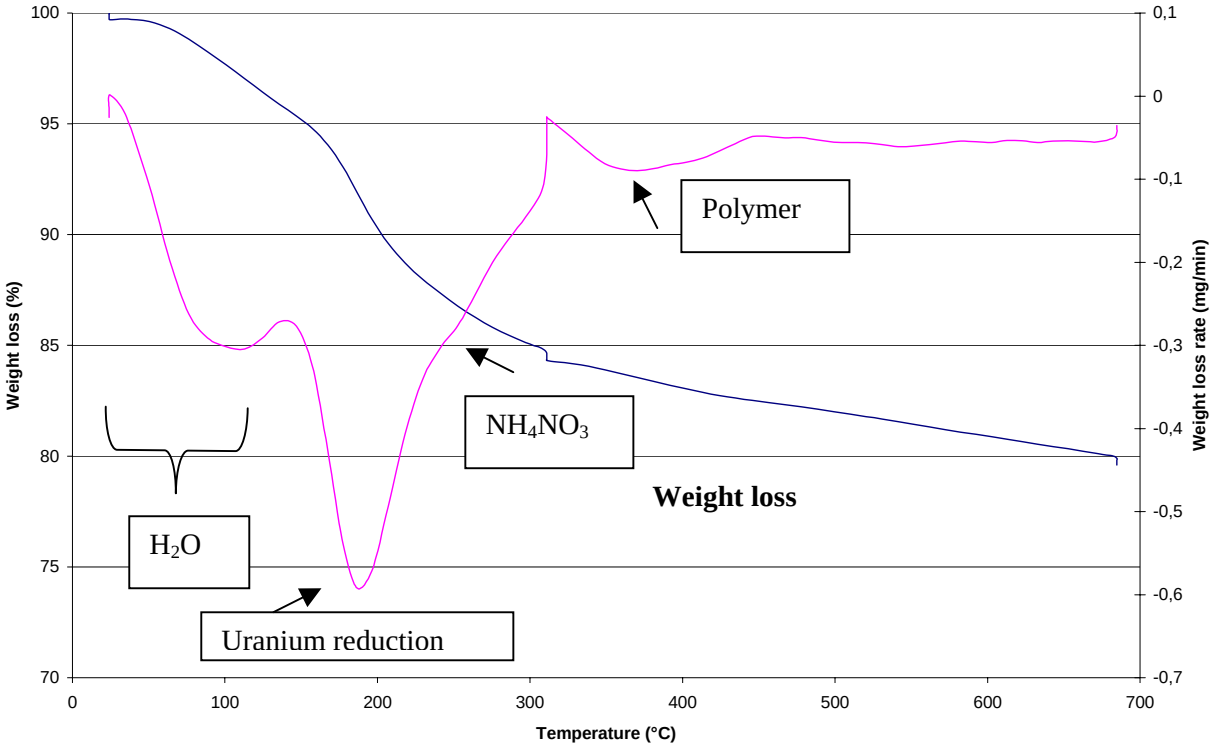


Figure 11 : TGA curves for kernels containing ADU+carbon black (under argon 6.0)

To conclude, the most optimized calcining thermal treatment leading to a uranium dioxide phase + carbon black, preserving the carbon black and eliminating the additives resulting from the GSP process, could be the following:

- 2 soaking periods, 340°C during one hour, followed by 700°C during 6 minutes, under argon 6.0.

3.3 The sintering thermal treatment step

The first part of this paragraph synthesizes the principal conclusions of the literature in order to elaborate a protocol for our sintering step. A second part develops the application of this thermal protocol to the ADU + carbon black kernels in order to evaluate the influence of gases, the temperatures of the soaks and the presence of carbon as an additive (comparison between kernels with or without carbon) on the microstructure and the kernel's final composition.

3.3.1 Literature review applied to our experimental sintering step

In the literature, there are a certain number of thermal treatments which allow the manufacturing of uranium oxycarbide starting from calcined kernels containing only uranium, oxygen and carbon. This using the external process (cf table 1, *Develasco and Al, 1988* and *Kadner and Al, 1976*) or by the internal process (cf table 2, *Petti and Al, 1993*, *Stinton et al., 1983*). All treatments using carbon monoxide were eliminated because this gas cannot be used within the laboratory and those treatments were consequently, not applied.

To carry out the sintering of the kernels after the calcination, we applied two types of thermal treatments:

- The first is drawn from the American process "General Atomics" (*R.L. Develasco et al., 1988*). This process is characterized by two soaking steps: the first is carried out at 1600°C, during at least half an hour, followed by a second one at 1800°C, of at least half an hour. The rises and descents in temperature are not defined in the publication. We applied this treatment by fixing a slow rise at 3°C per min to avoid a kernel deterioration,
- The second process is drawn partly from the German process "of HOBEG" (*Mr. Kadner, and Al, 1976*). This thermal treatment only has one soaking step between 1750 and 1850°C. In our experiments, we fixed this temperature at 1800°C, during 60 minutes with a slow rise in temperature of 3°C per min.

Except for these two processes directly drawn from the literature, we also tested other types of thermal treatments varying the length of the soaking period, the temperature and the type of gas used. The details of these thermal treatments are given in the following table.

3.3.2 Effect of the sintering thermal treatment on the microstructure and the composition of the calcinated kernels

The following sintering treatments (see table 9) were carried out on ADU kernels + carbon black and on kernels containing only ADU which were calcined beforehand.

Sintering thermal treatment	A	B	C	D	E	F	G
Temperature of the first soak	1600°C	1800°C	1800°C	**1850°C**	1600°C	1800°C	1600°C
Duration of the first soak	30 min	60 min	**240 min**	**240 min**	**240 min**	**240 min**	30 min
Temperature of the second soak	1800°C	-	-	-	1800°C	-	-
Duration of the second soak	30 min	-	-	-	**240 min**	-	-
Gas	Argon U	Argon U	Argon U	Argon U	**Hydrogen**	**Hydrogen**	Argon U
Calcining thermal treatment previously applied (see table 8)	2	1 ou 2	1 ; 2 ou 5	1 ou 5	5	1	4
Type of process	GSP	GSP	GSP	GSP	GSP	GSP	GSP
Authors	Develasco	Kadner	Drawn from Kadner	Drawn from Kadner	Drawn from Develasco	Drawn from Kadner	Drawn from Develasco

Tableau 9 : Summary of the different sintering thermal treatments

The treatments A and B are adapted from the literature, the treatments C and D are a modification of the thermal treatment B in order to determine the effect of the time and temperature of the soaking step. The treatments E and F modified starting from treatment A (for the treatment E) and from B (for the treatment F) were applied to decrease the quantity of oxygen within the kernels thanks to a reductive hydrogen atmosphere. The aim is to

facilitate the reaction between carbon and uranium. The purpose of treatment G, derived from treatment A, is to observe the utility of the step at 1600°C determined by Develasco (R.L. Develasco and Al, 1988).

The raw observations on the TGA result for E treatment performed on kernels containing carbon black show four different weight losses (see figure Figure 12):

➧ the three first peaks could be due to the decomposition of some residual PVA or NH_4NO3 remaining in the kernels after the calcining treatment and to the end of the reduction of UO_2+x (see figures 10 and 11) ;

➧ the last most important peak, could be attributed both to the reduction of oxide to form a sub-stoechiometric uranium dioxide ($UO_{1,96}$) and the formation of a carbide phase within the kernels.

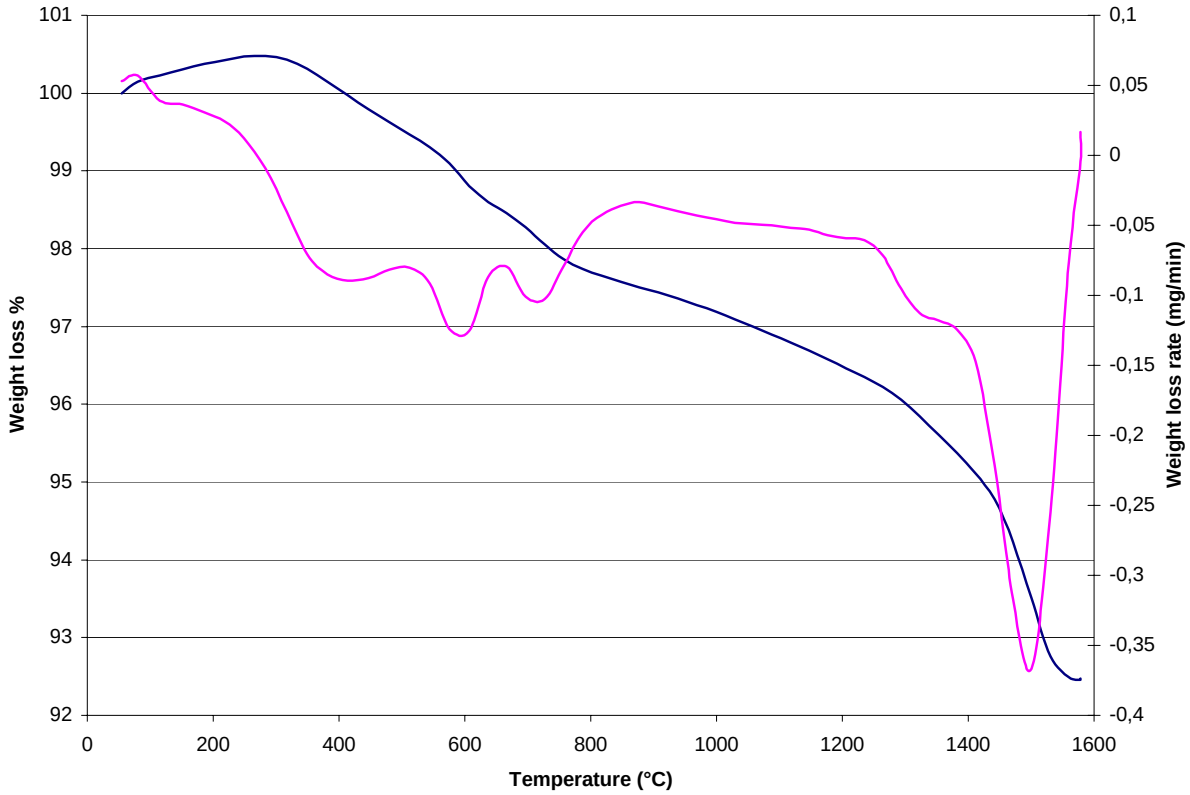


Figure 12 : TGA curves of sintered kernels containing carbon black till 1600°C

Further information can be gathered by comparing X-ray diffraction patterns for kernels containing carbon as an additive in order to evaluate the influence of our thermal treatments on the kernel's final composition (see **Figure 13**).

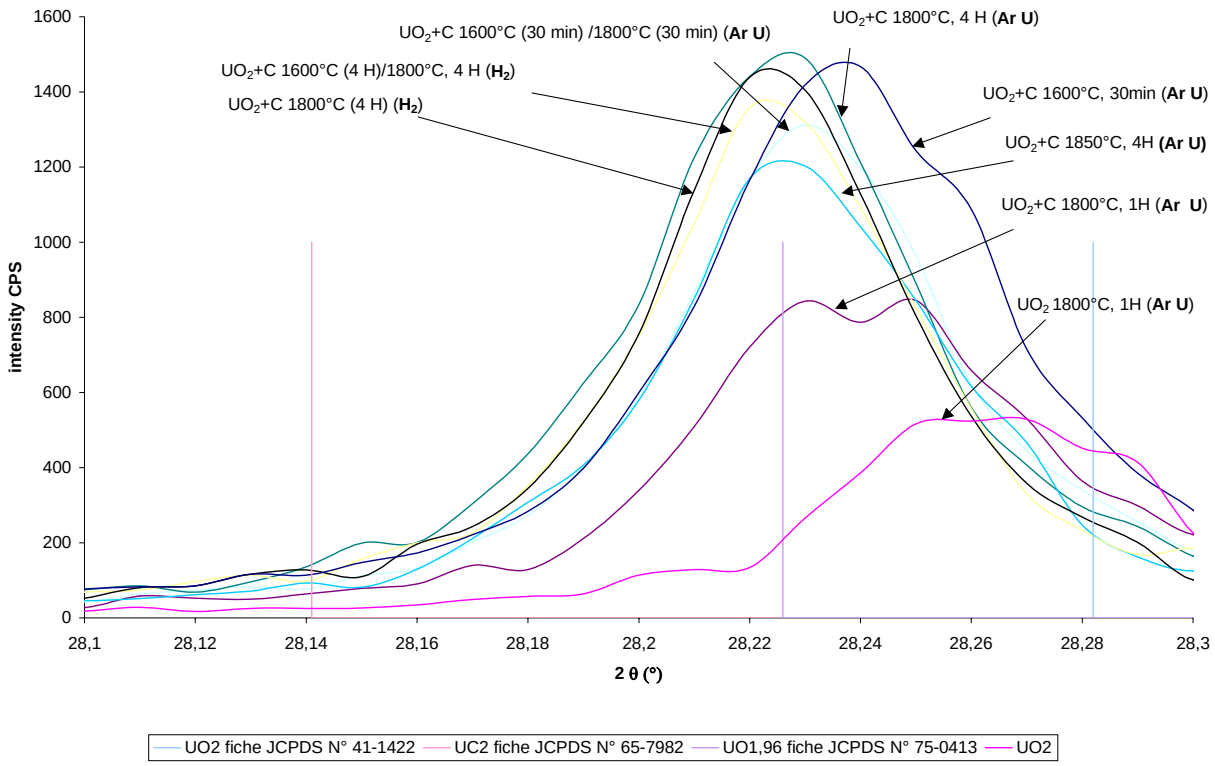


Figure 13 : Comparison of the X-Ray diffraction patterns for sintered UO2+C kernels

In order to help us analyze these results, let's note that the UC_2 phase comprises two types of crystal lattices: a face-centered quadratic structure (standard CaC_2) and a face-centered cubic structure (standard CaF2). These phases were defined for a binary system UC (*C. Guéneau and al, 2003*).

The preferential formation of a quadratic UC_2 structure is carried out between 1480 and 1760°C, in binary diagram UC. In the case of a ternary diagram, the temperatures of the crystallographic structure changements are very unsure. The face-centered cubic UC_2 phase is formed at a higher temperature, above 1760°C (*P.Y. Chevalier and al, 2001*).

In the temperature range in which we are located (up to 1800°C), the phase obtained would be of face-centered cubic structure. This is what appears in the previous diffractogram tracing the thermal treatments carried out up to 1800°C, the theoretical peaks of the UC_2 corresponding to card JCPDS 65-7982 (UC_2 CFC).

The solubilization of oxygen in the UC lattices is a known information in the literature (*Besmann T. M., 1983 and Heiss A., 1975*). When the quantity of O increases in UC lattice (CFC), the lattice parameter decreases (*P. E. Potter, 1972*).

Concerning the UC_2 phase which is the compound which seems to exist in our diffractograms, a parallel can be established knowing that UC_2, having the same structure than UC (face-centered cubic structure), can also see its lattice parameter decrease with an increase in the oxygen content. It is what could be observed in these diffractograms (see Figure 13). One observes a shift of the peaks towards the higher angles, leading to lower lattice parameters (*C Guéneau and al, 2003*).

No notable difference can be observed between all treatments but the treatments leading to the peaks the most left handed (going towards the UC_2 phase) seems to be those with one soak 1800°C, under hydrogen or argon U.

X-ray diffraction analysis performed can give us explanations on the influence of the different gases (argon U or hydrogen) and the presence of carbon as an additive in the kernels on the kernel's final composition (see **Figure 14**).

The following X-ray diffraction patterns show an uranium dioxyde phase reduced by the presence of carbon, for the treatments under argon U and even more reduced by the presence of carbon and hydrogen for the treatments under hydrogen (all curves are on the left of the theoretical UO_2 ray). Consequently, this explains a stronger reduction of kernels treated under hydrogen than under argon. The presence of supplementary carbon in the kernel containing carbon black as an additive, allows a reduction a little much higher than the kernels with no carbon. In order to improve the results, a higher amount of carbon introduced in the initial broth would be recommended. In these kernels, the residual carbon issued from the decomposition of PVA is sufficient to go towards the UC2 phase. This can be observed for both types of kernels by the presence of identified shoulders on the left hand of the broad peaks ($UO_{1,96}$) allowing us to propose as an hypothesis the existence of smaller intensity peaks going toward the UC_2 phases. They are identified as a possible $UC_{2-x}O_x$ phase, which is the same thing, at this temperature (1800°C) then a UC_2 phase including oxygen by solubilisation in it's lattice (*C. Guéneau and al., 2003*). This is observed for both treatment atmospheres, slightly more on the left hand for the hydrogen treatments that are more reducing. Let's note that a LaB_6 reference sample was previously passed and no shoulders appeared. To corroborate our hypothesis, in the literature, it is indicated that the carbide phase starts forming from 1530°C when the ratio O/U is lower then 1,99 (*S. Gossé and al. 2006; V.L. Weeler, 1971*). We could be in this case.

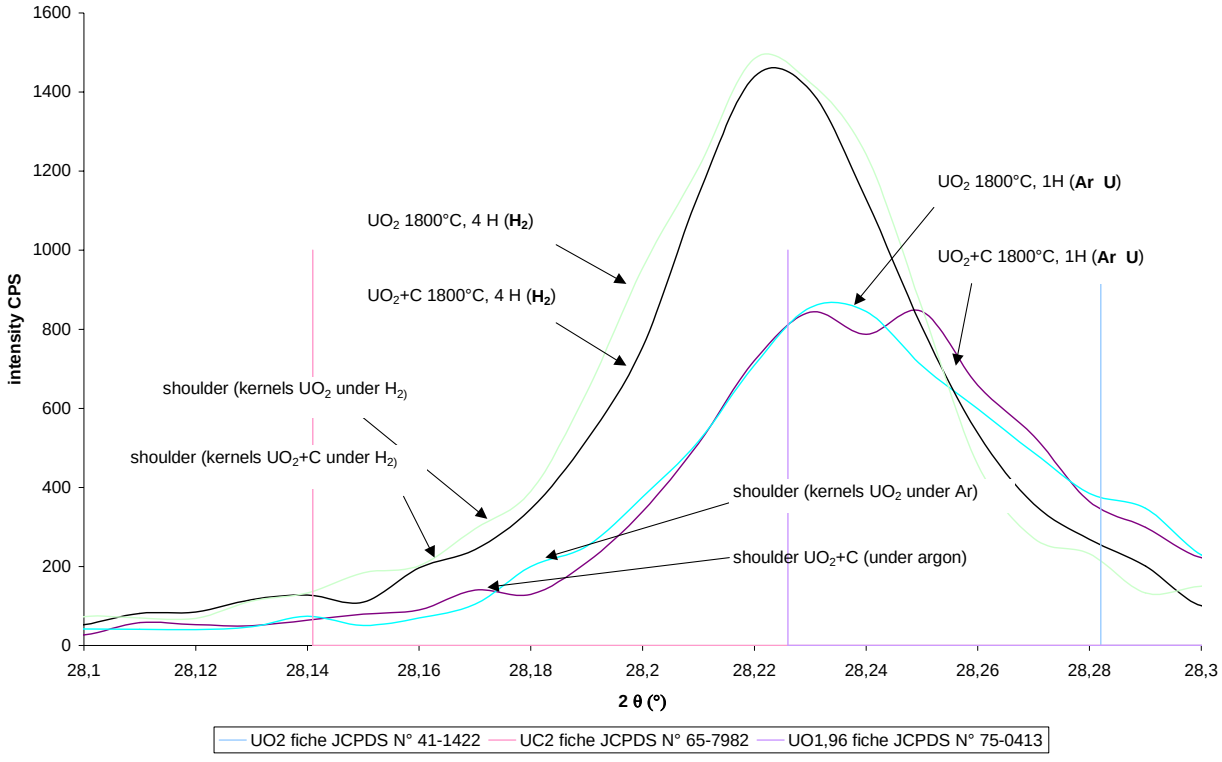


Figure 14 : Comparison of the X-Ray diffraction patterns between UO2+C and UO2 kernels for different sintering gases

We can conclude that for all treatments, a UC_xO_{2-x} phase could be present for both treatment atmospheres under argon and hydrogen. The thermal treatment under hydrogen tends to give better results. Under hydrogen, the soak at 1600°C does not seem necessary. We will retain a sintering treatment at 1800°C during 4 hours, under flowing hydrogen. To corroborate our conclusions, an electron microscope observation of a polished face of our sintered kernel under hydrogen (previous treatment), shows the presence of only one white phase with small porosities. The EDS analysis shows, in several places and on several kernels, 14% of uranium atoms, 56% of oxygen atoms and 30% of carbon atoms. It is nevertheless, an account comprised of great inaccuracy due to this method of characterization (the carbon and oxygen atomic number are very close and are very light elements compared to uranium). We can however deduce that it left in the kernels uranium, oxygen and carbon. The retrodiffused electrons show the presence of only one homogeneous phase in the kernels (see Figure 15). The comparison between kernels with carbon as an additive and kernels with no carbon, calcinated and sintered under hydrogen in the same conditions (calcining treatment 1+sintering treatment F) added shows a greater porosity in the kernels manufactured with carbon black. The added carbon can act like a porogene in the kernels.

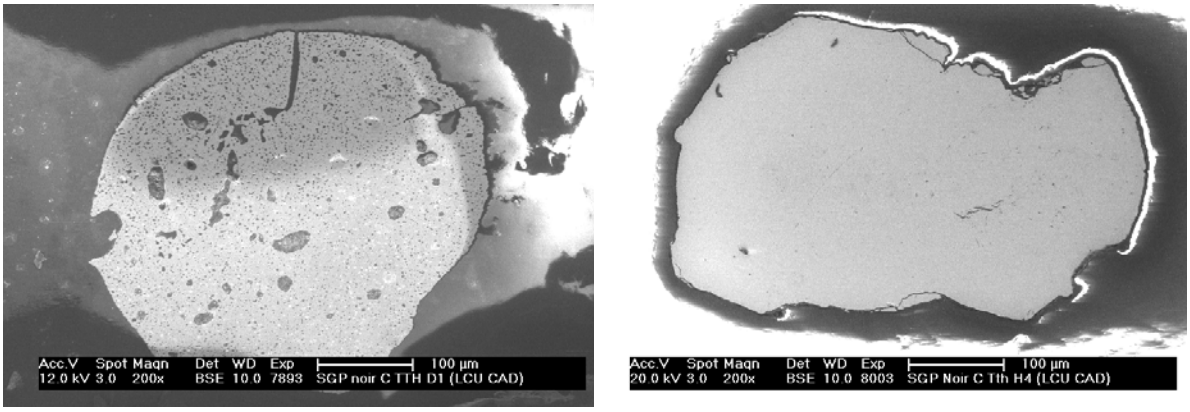


Figure 15 : Micrograph of kernels containing ADU+carbon black (left) and without carbon black (right)

4 CONCLUSION ON THE MANUFACTURING OF UCO KERNELS

The purpose of our experimental research was to manufacture UCO kernels by an external sol-gel process. The first step was to manufacture the dried kernels mainly constituted by ADU and carbon black.

The manufacturing process used was detailed from the preparation of the solution, formation of the droplets, gelation, ageing and washing until the step of the drying of the kernels.

The calcining and sintering steps were particularly developed, based on specific data extracted from the literature because of the impact of the thermal treatment (the temperature, gas nature) on the microstructure and the composition of the kernels. It was shown, following an experimental grid concerning the calcining step while modifying the following parameters; the temperature, the time and the number of soaking periods and the type of gas used, that all the starting components are eliminated except carbon and uranium oxide.
The most optimized calcining thermal treatment leading to a uranium dioxide phase with the presence of carbon black, preserving the carbon black and eliminating the additives resulting from the sol-gel external process, is the following: 2 soaking periods, 340°C during one hour, followed by 700°C during 6 minutes, under argon 6.0.
The sintering thermal treatment was also developed in order to obtain an uranium dioxide sub- stoechiometric that favors the formation of a oxycarbide uranium phase. The kernels obtained by the calcining-sintering thermal treatment could be mainly a $UO_{1,96}$ phase containing a little UC_2 including oxygen or, in an other term, a $UC_{2-x}O_x$ phase. This treatment is the following: 1 soaking period at 1800°C during 4 hours under pure hydrogen. More experimental analysis should be added to our panel of X-ray diffraction, EDS analysis and electron microscope observations in order to confirm the phase obtained.

Additional tests are recommended in order to:
- obtain kernels with a sufficient amount of oxy-carbide phase that could be characterised with certainty
- and also to form a phase, after calcination of the kernels, richer in carbon to obtain a oxycarbide phase richer in carbon ($UC_{2-x}O_x$) to tend, in the long term, towards 2 phases UC_2+UO_2.

Obtaining a carbon richer phase can be carried out:

- by the addition, of more carbon black powder at the time of the preparation of the initial solution;
- by specific thermal treatments of the kernels placed in a supplementary amount of a carbon black bed, during heat treatment ;
- or by treatments at temperatures under 1600°C, with flowing hydrogen, in order to obtain a quadratic UC2 phase or, treatments at 1600°, under vacuum to withdraw carbon monoxide gas formed in the kernels in order to displace the reaction towards the formation of a UC_2.

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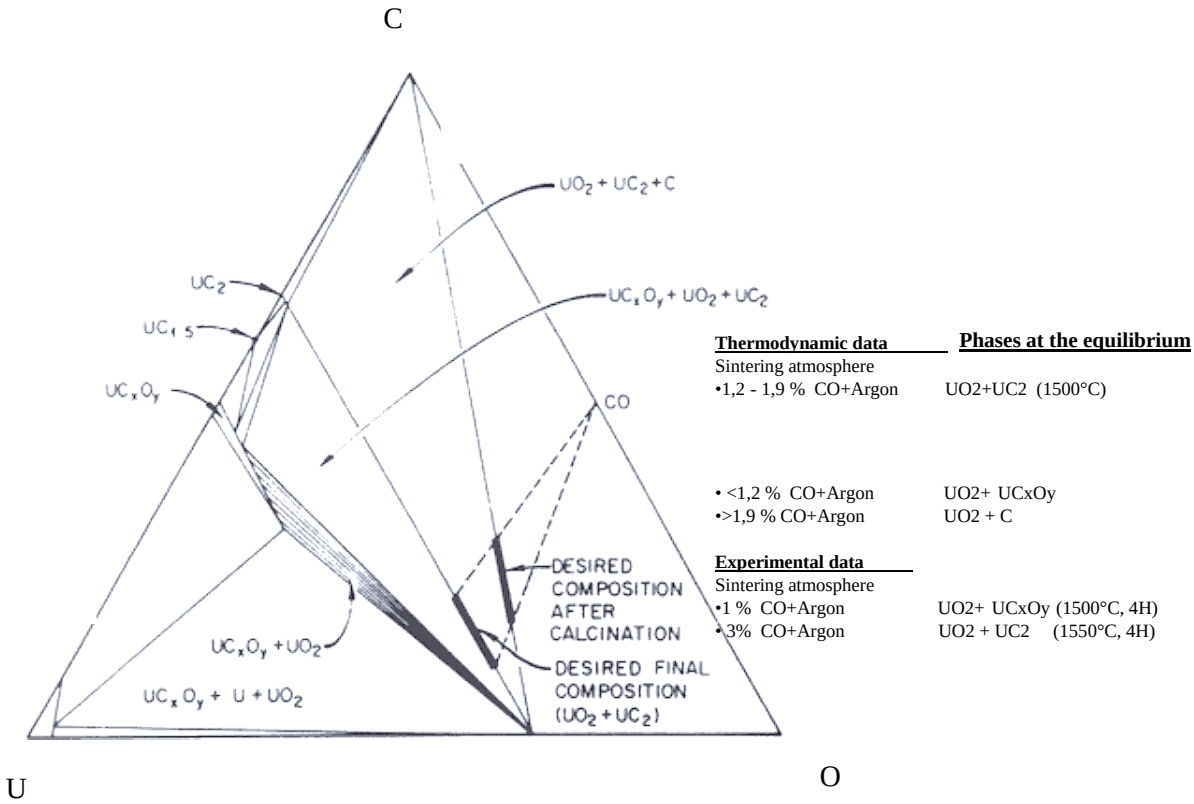
6 APPENDIXES

Appendix 1: **Diagram of the Uranium-carbon-oxygen equilibrium *(Stinton et al., 1982)***



Equilibrium Diagram Uranium-carbon -oxygen

(desired compound after calcination and final composition)

Stinton and al., 1982

Figure 16 : Equilibrium diagram uranium-carbon-oxygen

Appendix 2:

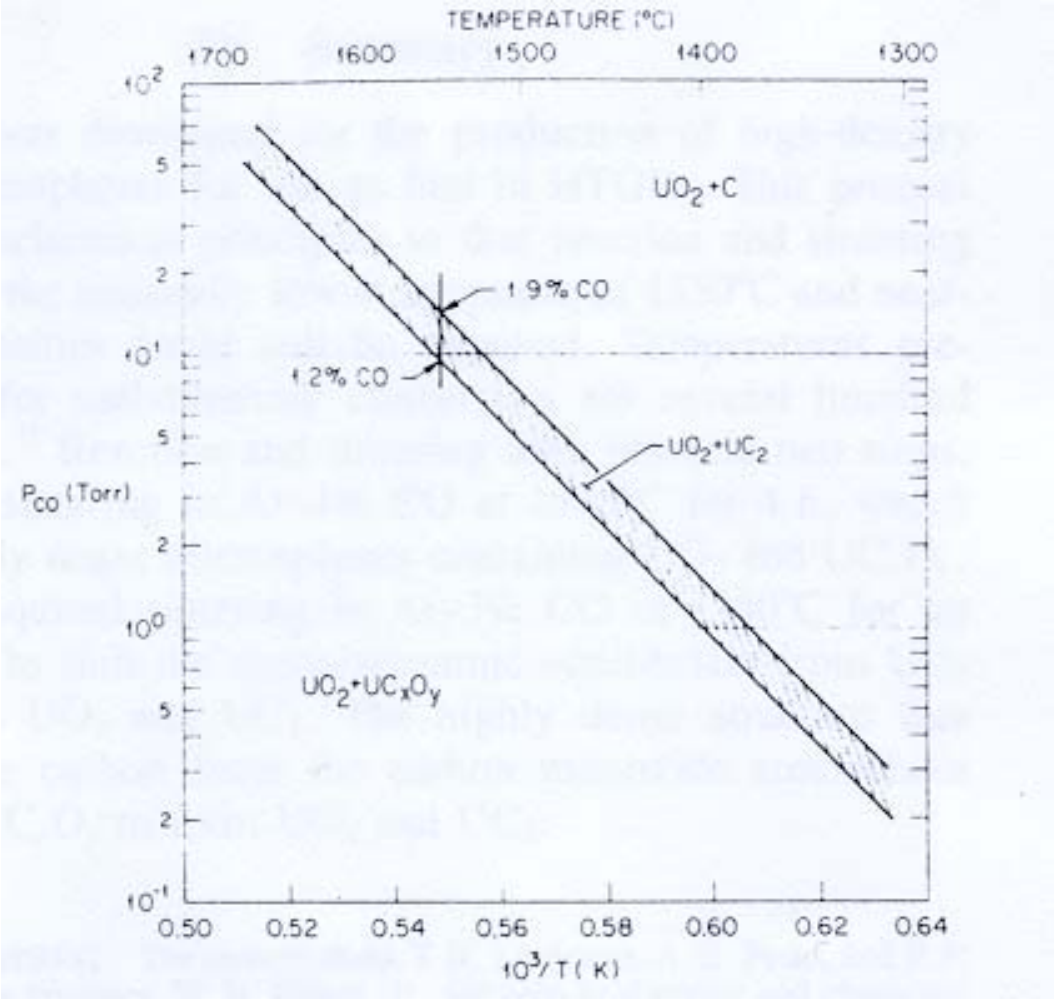
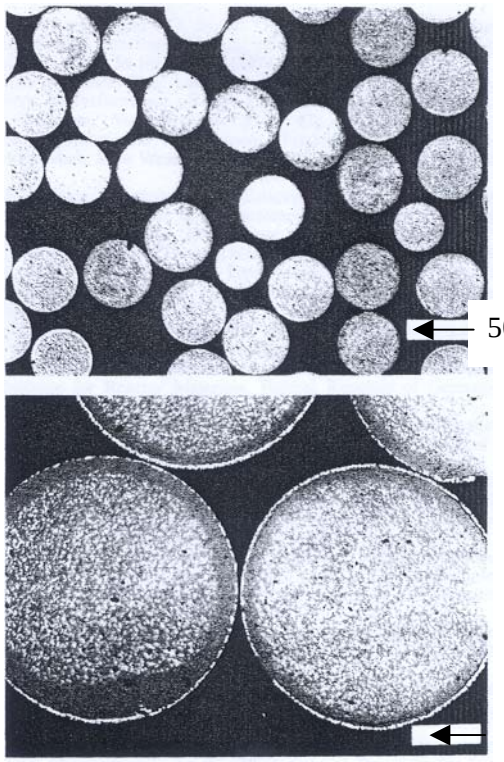


Figure 17: Curves showing that the UO_2 and UC_2 phases are in equilibrium for the a initial molar concentration of CO ranging between 1.2 and 1.9 %, at 1550°C *(D.P. Stinton et al., July, 1982)*

Appendix 3: **Sintered microspheres obtained through the internal sol-gel route (*D.P. Stinton et al., July, 1982*)**



Sintering conditions: Ar – 1 % CO (4H) then Ar – 3 % CO (4H) UO_2-UC_xO_y → UO_2-UC_2

Figure 18: Photograph MEB obtained by «UCO» kernel showing 2 UO_2 phases: UO_2 (grey coloured phase) and UC_2 (white coloured phase)

Appendix 4: **Complementary information on "carbon black"**

Carbon black is elementary carbon in the form of highly dispersed powders that are produced through controlled pyrolysis of hydro-carbides in the vapour phase.

Carbon black is also known under various names such as **acetylene black**, **tunnel black, oven black, lamp black, flame black, thermal black** and under its English name of **"carbon black"**. The CAS registration number of carbon black is 1333-86-4. The Chemical Abstracts Service of the United States has attributed this number to designate carbon black and it is the **sole identification number** in the entire world.

Various industrial processes can produce different types of carbon black, including **acetylene black**, **tunnel black, oven black, lamp black, flame black, thermal black.** The mean diameter of the particles of several commercialised carbon blacks is somewhere between 0.01 to 0.4 micrometers whereas the mean diameter of the aggregates varies from 0.1 to 0.8 micrometers. The elementary carbon content of most carbon blacks ranges between 97 and 99%.

Carbon blacks may also contain hydrogen, oxygen, nitrogen and sulphur atoms that are chemically linked. Their oxygen content is of the highest importance for the applications of these products. Oxygen is linked to their surface especially in the form of either acid or basic functional groups. Given the nature of the departure materials, their production methods, their high surface area and the properties of their surface, the commercial carbon blacks typically contain variable quantities of adsorbed by-products, particularly aromatic compounds.

Appendix 5: **Details on the Polyvinyl alcohol compound**

Several polyvinyl alcohol classes exists. The latter are indexed according to the degree of hydrolysis (cf Figure Figure 19). The polyvinyl alcohol can contain a certain number of groupings acetates, sensitive to the hydrolysis in an acid medium. While being hydrolyzed, the chemical structure changes generating a change of viscosity of the solution and making the solution very instable.

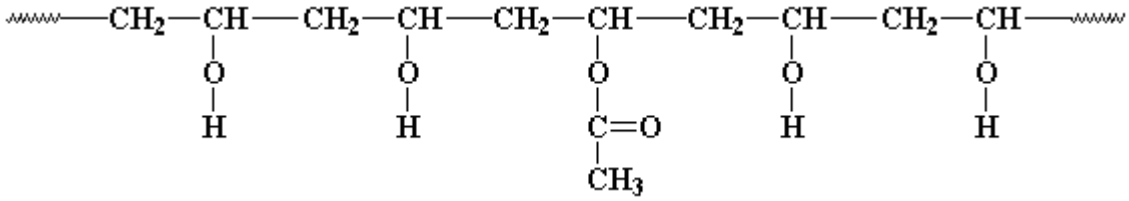


Figure 19 : Representation of the PVA polymer with it's residual acetate groups

In an acid medium, there is a certain instability of the alcohol functions. To limit this dehydration phenomenon of the PVA chains, an alcohol like type tetrahydrofurfurylic alcohol (THFA) is added to the mixture. This alcohol has also the property to protect the chains of polymer from radiolysis generated by the presence of uranium[235].

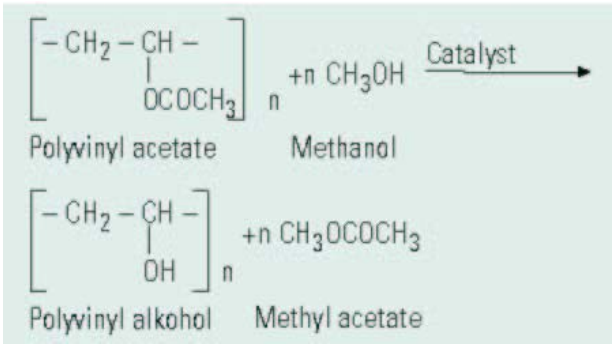


Figure 20 : Hydrolysis reaction of the polyvinylic acetate group

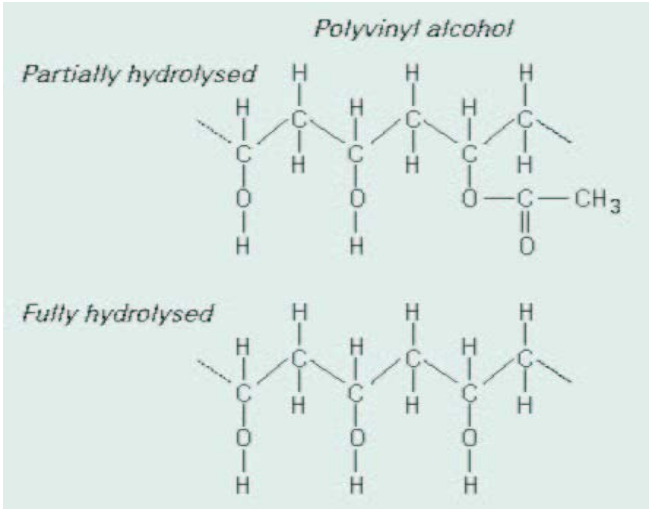


Figure 21 : Simplified formula of partially and completely hydrolysed PVA

Appendix 6: **Details on the Polyvinyl alcohol compound**

The litterature gives the following precipitation reaction :

(uranyl nitrate) $2\ UO_2(NO_3)_2 + 6\ NH_3\ (g) \longrightarrow U_2O_7(NH_4)_2$ (ADU25)$+ 4\ NH_4NO_3$

equation 1 : precipitation reaction of uranyl nitrate in presence of ammonia gas

$(3<pH<7)\ 2\ UO_2(NO_3)_2 + 4\ NH_4OH \longrightarrow 2UO_2(OH)_2 + 4\ NH_4NO_3$

$(pH>8\text{-}9)\ 2\ UO_2(OH)_2 + 2\ NH_4OH \longrightarrow U_2O_7\ (NH_4)_2 + 3\ H_2O$

equation 2 : Evolution of the precipitation reaction of uranyl nitrate in presence of liquid ammonia versus growing values of the pH of the solution

$2\ UO_2(NO_3)_2 + 6\ NH_4OH \longrightarrow U_2O_7(NH_4)_2 + 4\ NH_4NO_3 + 3\ H_2O$

equation 3 : precipitation of uranyl nitrate in presence of liquid ammonia (if the final pH of the internal part of the drop is > 8-9)

[25] ADU : ammonia diuranate

Appendix 7 : **Possible reactions of PVA during a calcining treatment under an inert gas (Gilman et al, 1994)**

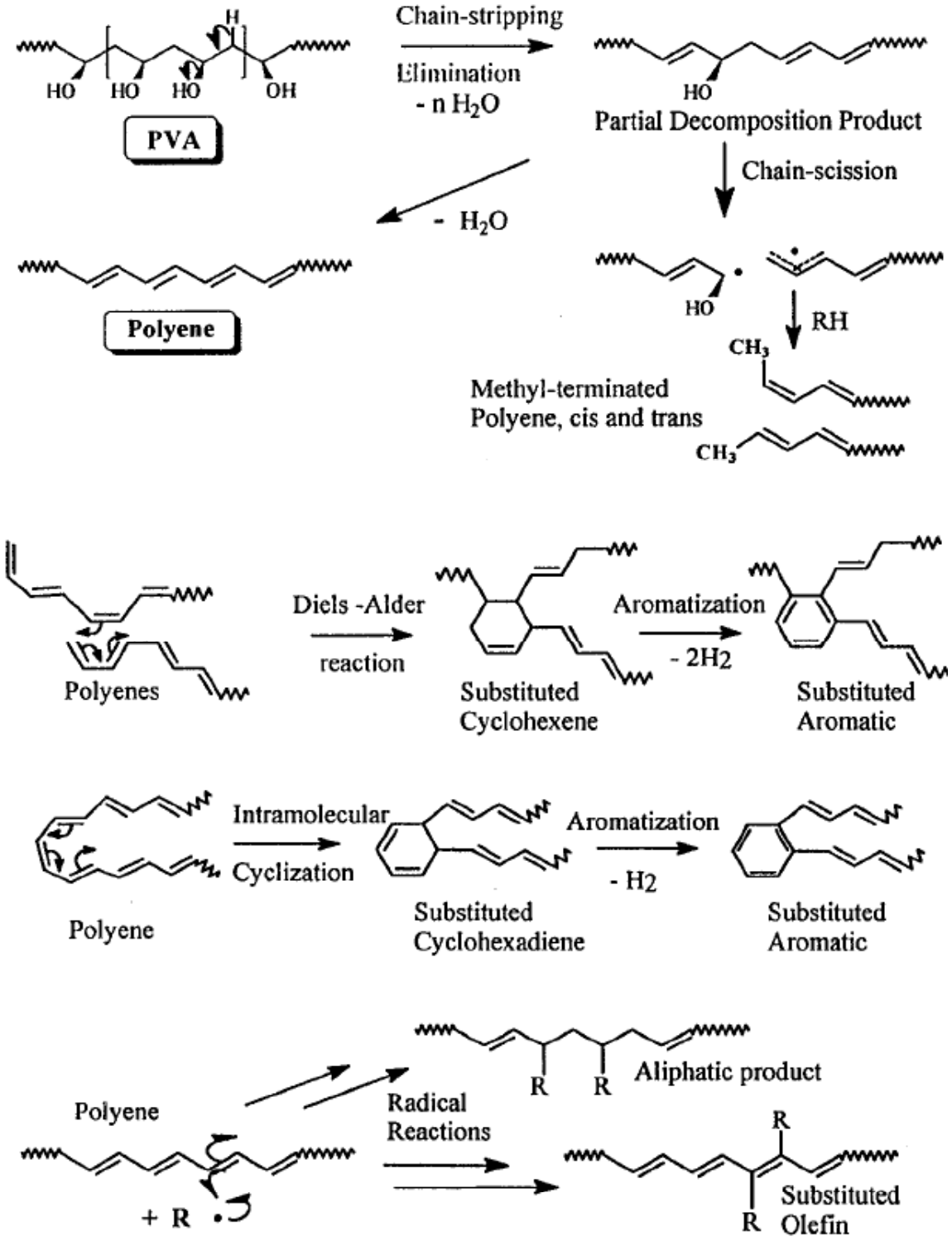


Figure 22 : Possible reactions of PVA during a calcining treatment under a inert gas

Appendix 8 : **TGA diagram on UO2 kernels under 2 different gases extracted from the following paper:** ***Charollais,*** *F., Duhart, A., Felines, P., Guillermier, P., Perrais, C., "Effect of thermal treatment conditions on microstructure and composition of high temperature reactor fuel kernel " , april 2004*

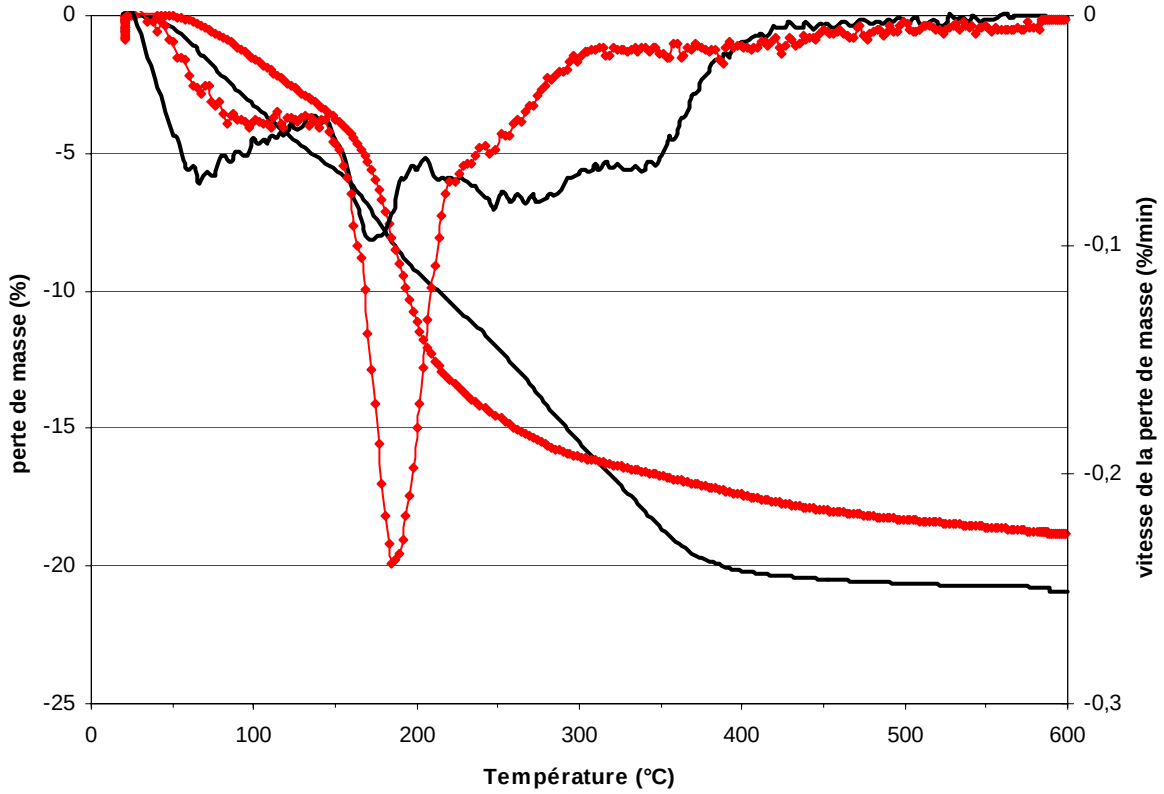


Figure 23 : TGA diagram on UO2 kernels under 2 different gases: air (in black) and argon (5 ppm of O2) (in red)