EUROPEAN COMMISSION

Community Research

RAPHAEL

Contract Number: 516508 (FI6O)

DELIVERABLE (D-FT1.2)

ZrC Innovative coating

Author(s): **Marc PEREZ**

.....

L. OBRINGER, C. MOLLARD, O. DUGNE (Technical Support)

Reporting period: 15/04/2005– 15/10/2006

Date of issue of this report : 15/11/2006

Start date of project : **15/04/2005** Duration : **48 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**

Distribution list

Person and organisation name and/or group	Comments
See the distribution list in the document	To comply with CEA QA

ReActor for Process heat, Hydrogen And ELectricity generation (RAPHAEL)		
Sub-project: SP-FT **Work package:** 1	**RAPHAEL document no:** RAPHAEL-0611-D-FT1-2	**Document type:** Deliverable
Issued by: CEA (FR) **Internal no.:** DTH/DR/2006/103		**Document status:** Final

Document title

Sub-project Fuel Technology (SP-FT)

ZrC Innovative coating

Executive summary

The technical problems raised during the first chlorination tests were partly solved thanks to a new smaller reactor located closer to the furnace.
Again, thermalisation tests showed how chlorination temperature control is tricky in the process. Automatic temperature control and monitoring allowed possible recondensation points to be identified. Modifications were embodied so as to accurately heat and control temperatures in the reactor. Finally, an injection test was successfully performed.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	15/11/2006	First issue	M. Pérez CEA	F. Charollais CEA	M. Phélip CEA S. Lansiart	E. Bogush ANP

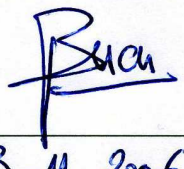
Direction de la recherche technologique - DRT
Laboratoire d'Innovation pour les Technologies des énergies nouvelles et les Nanomatériaux - LITEN
Département des Technologies de l'Hydrogène – DTH
Laboratoire des Technologies de l'Hydrogène - LTH

Rapport technique DTH/DR/2006/103

ZrC Innovative coating

M. PEREZ - L. OBRINGER – C. MOLLARD - O. DUGNE

Référence du contrat	A CDHTR 03-01-05
Référence PRODEM	04-01271
Domaine/Projet	Projet RAPHAEL
Clés financement	CEE (via DEN/DDIN)
Nature du rapport	Avancement
Confidentialité	Les informations contenues dans le présent document sont régies par les clauses de confidentialité de l'accord Tripartite, elles sont à l'usage des seuls destinataires désignés et ne doivent en aucun cas être transmises à des personnes ou organismes extérieurs à cet accord.

	Rédacteur	Vérificateur	Approbateur
Nom	Marc PEREZ	Emmanuel RIGAL	Philippe BUCCI
Fonction	Chef de projet	Ingénieur	Chef de laboratoire
Signature			
Date	10/11/2006	13/11/2006	13-11 2006

LISTE DE DIFFUSION

Rapport complet à:

CLIENT	**AREVA NP**	
	D. HITTNER	5 ex.
	M. PASQUET	1 ex.
	F. CELLIER	1 ex.
	P. GUILLERMIER	1 ex.
	EDF/R&D	
	F. VASSEUR	5 ex.
DEN/SAC/DDIN/SF	Ph. BROSSARD	1 ex.
	F. STORRER	1 ex.
DEN/CAD/DER/SESI	D. BARBIER	1 ex.
DEN/CAD/DEC/SESC	M. PHELIP	1 ex.
	S. LANSIART	1 ex.
DEN/CAD/DEC/SPUA/LCU	F. CHAROLLAIS	1 ex.
LITEN	D. MARSACQ	1 ex.
	B. VINET	1 ex.
DTH/Dir	Ph. BACLET	1 ex.
	H. BURLET	1 ex.
LABORATOIRE	Ph. BUCCI	1 ex.
	Auteur (s)	1 ex.
	Archivage	Original + 1 ex.
BASE HTREX	htrex@cea.fr	1 ex. Format pdf

Page de garde + résumé + Liste de diffusion à :

Chefs des autres Laboratoires du DTH :

- LEV : LEFEBRE-JOUD Florence
- LPAC : ANTONI Laurent
- UTIAC : DE DINECHIN Guillaume

DEN/SAC/DDIN/SF	F. CARRE
	C. RENAULT
	M. DELPECH
	Ph. BILLOT
	P. ANZIEU
DEN/SAC/DRSN/DIR	D. CARAMELLE
DEN/SAC/DANS/DMN/DIR	Ph. BILLOT
DEN/CAD/DTN/DIR	JM. MOREY
DEN/CAD/DEC/DIR	JPh. NABOT
DEN/SACDRSN	G. BAYON
DEN/VAL/DTEC/DIR	M. BOIDRON
DEN/CAD/DTN	A. LYOUSSI

Page de garde + résumé + Liste de diffusion + Lettre d'envoi à :

Ingénieur Qualité : JF. NOWAK

Bureau financier (Ventes) : S. VERMET

Table of contents

Introduction

The 6°FP ensures the continuation of what has been done within the 5°FP.
The 5°FP actions relative to fabrication aimed mainly at recovering the fabrication know-how of UO_2/SiC reference particle and at launching the first studies on ZrC innovative coating on surrogated kernels.
The 6°FP will intend to continue the effort at a laboratory scale. This report is showing how ZrC technique has been improved.
Zirconium chloride ($ZrCl_4$), the precursor of zirconium in ZrC deposit, is synthesised further to attack of zirconium grit by hydrogen chloride HCl in a reactor referred to as chlorinator. The reaction must be performed in temperature but, above all, chloride must be maintained at a temperature that is high enough to avoid any cold point likely to result in a recondensation plug up to the coating furnace. Further to the manufacturing of the new chlorinator, highly reactive zirconium had to be unloaded first. Its storage and eventually its transfer to the new reactor were performed after making sure that no cold point remained.

1. Zirconium unloading

1.1. Purpose

The purpose of the operation was to recover Zr from the chlorinator used during the previous studies. Considering the various volumes, the transfer of a part of zirconium grit from one container to another was required.

1.2. Safety

In its powdery form, Zr violently reacts by spontaneous combustion in the presence of air.
It is therefore necessary to work in an inert environment. A glove box (Figure 1) was chosen for this operation. After being made compliant and further to related checks, removal and transfer operations were performed as per the implemented procedure [1]. A chlorinator supporting system (Figure 2) was specifically manufactured and introduced in the glove box.

Figure 1. Glove box used for Zr unloading.

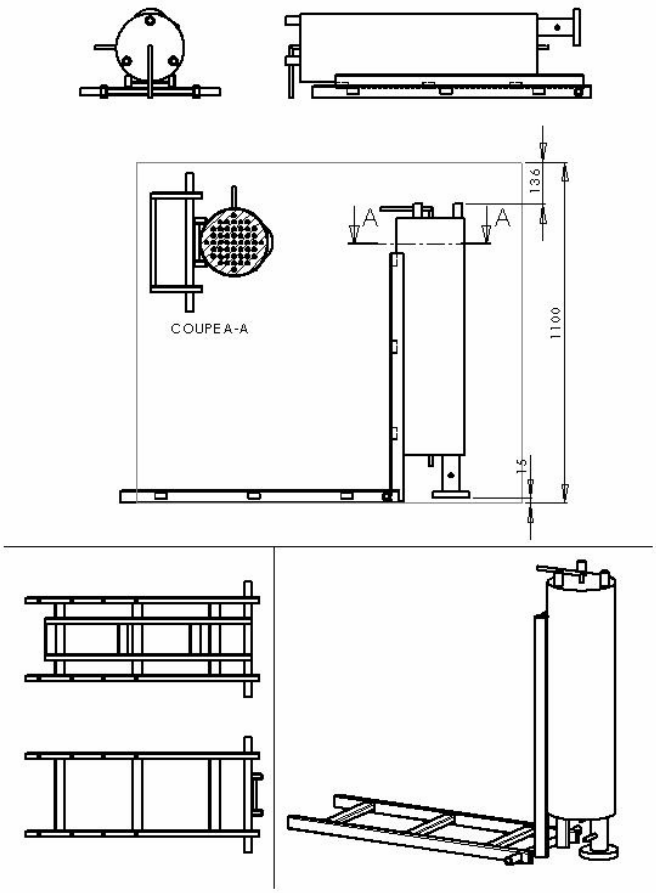


Figure 2. Supporting system for Zr unloading.

Therefore, a total of 28 kg of Zr were recovered without any particular problem, 4.6 kg of which were transferred to the new chlorinator. The remainder is stored in tight bottles for a future filling-up.

2. Chlorinator

The significant modification to the process consisted of the manufacturing and setting-up of the chlorinator underneath the coating furnace. The chlorinator (Figure 3) fitted with a reheater is secured on the gas injection probe. The chlorinator is fitted with temperature sensors so as to perform a thermal profile that is as complete as possible. Temperature measurements are performed at several points of the chlorinator up to the inlet union of the gas injection pipe.

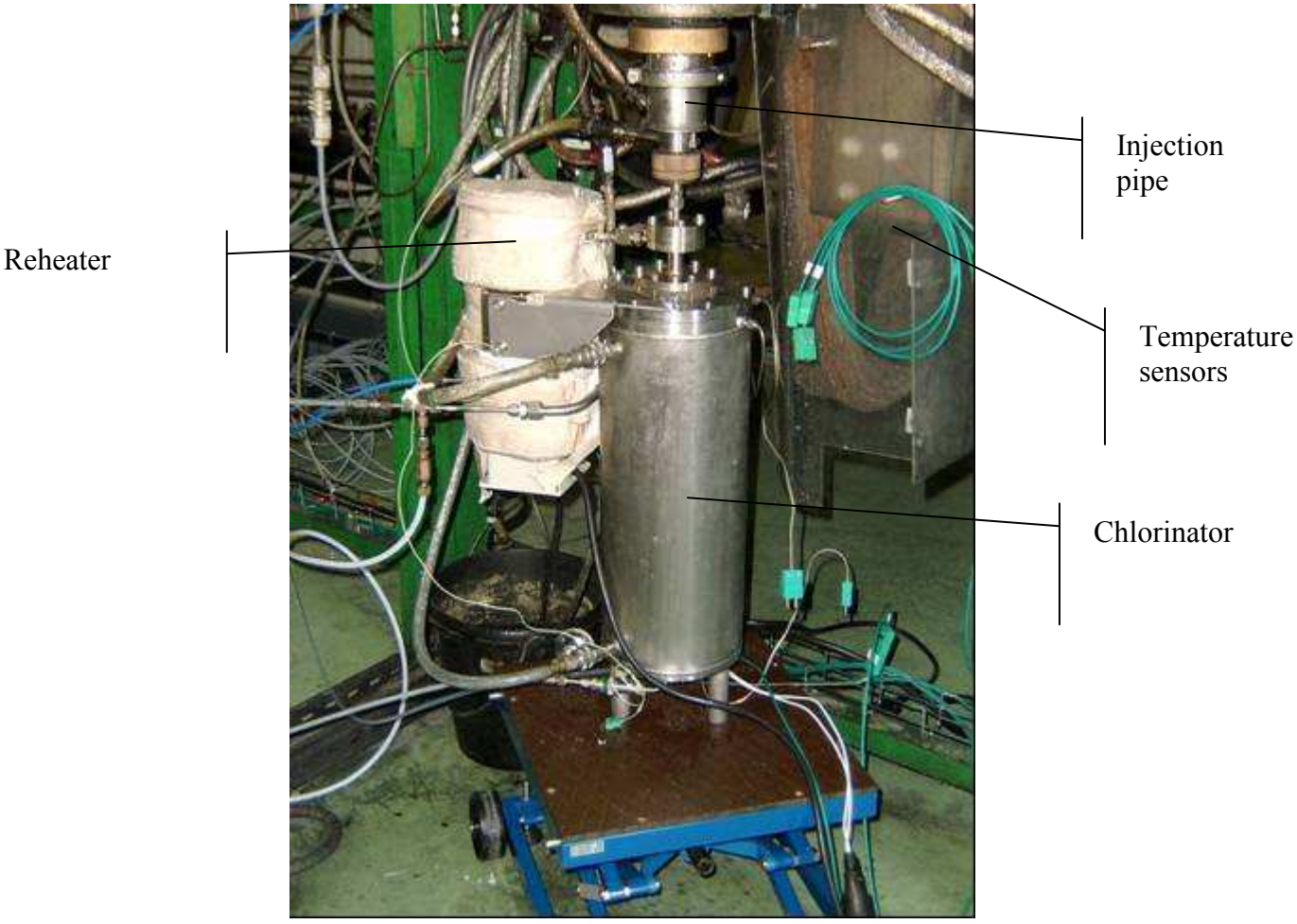


Figure 3. Setting-up of the chlorinator.

3. Chlorinator thermalisation tests

3.1. Test data

The chlorinator is fitted with an internal resistor. The chlorinator outlet is correctly insulated by means of a flexible mat. The reheater fitted on the chlorinator is also insulated with its flexible sleeve. The outlet between the reheater and the chlorinator is isolated with ceramic wool.

The temperatures are measured in various zones:

- reheater body temperature
- union temperature at reheater outlet
- chlorinator temperature in the crucible
- temperature at the top of chlorinator crucible:
    - either in the crucible graphite cover
    - or in the graphite outlet sliding coupling
- outside temperatures:
    - either in the graphite sliding coupling
    - or in the stainless steel sliding coupling tightening flange
- temperature of the junction flange for gas injected in the pipe.

3.2. Observations (refer to Figure 4)

Test No.1:

Further to heating the reheater and the chlorinator up to 400 °C, the following temperatures can be observed (further to being maintained for 30 min.):

- reheater gas outlet 315 °C (a)
- gas junction flange 270 °C (b)
- stainless steel sliding coupling tightening flange 225 °C (c)
- graphite outlet sliding flange: 250 °C (d)
- crucible graphite cover 410 °C (greater than crucible T) (e)

Test No. 2:

Further to these observations, the felt insulator above the crucible cover is removed. After heating the reheater up to 450 °C and the chlorinator up to 500 °C the following temperatures can be observed (further to being maintained for 10 min.):

- reheater gas outlet 330 °C (a')

● gas junction flange 280 °C (b')

● stainless steel sliding coupling tightening flange 245 °C (c')

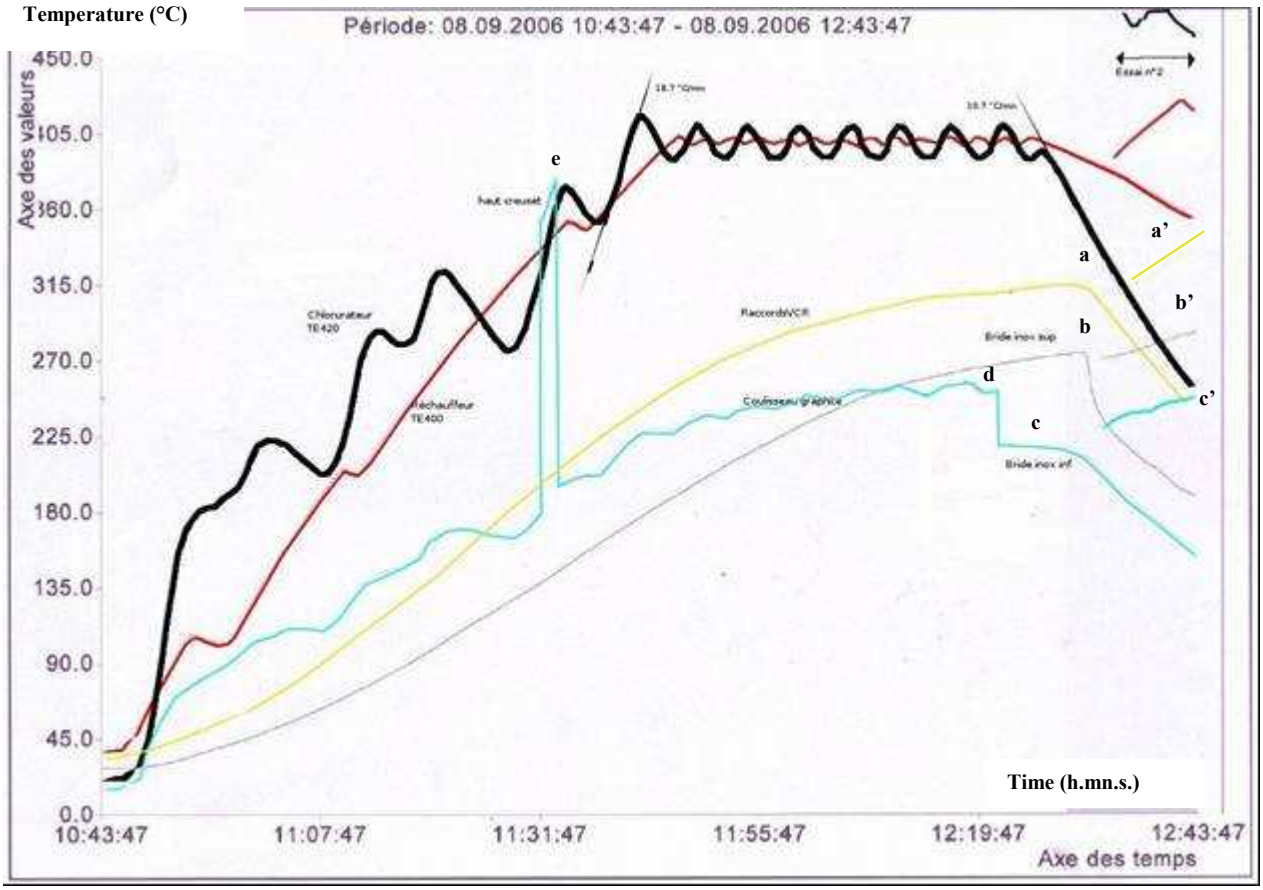


Figure 4. Temperature/time curves measured during tests 1 and 2.

3.3. Discussion

Reheater:

The reheater gas output temperature is approximately 130 °C below the reheater set point. Considering the melting point of aluminium (660 °C), it was deemed wiser to define a set point of 450 °C considering that the electric resistor is necessarily greater (~ 600 °C). The gas output temperature is therefore 330 °C maximum, that is the temperature of the union that dissipates heat, which explains why gases are hotter. It should be noted that these tests are performed in argon (15 l/min.) and that the exchange will probably be better with hydrogen.

Chlorinator:

● The chlorinator thermocouple was installed at 50 mm from the top of the crucible, so as to avoid any disturbing overheating in the Zr/HCl reaction zone.

● The chlorinator behaves correctly at 500 °C, and may very likely withstand much higher temperatures.
● The heat-up slope to 400 °C is 18.7 °C/min. for 3,500 W. When heating is stopped at 400 °C, the cooling slope is 10.7 °C/min., that is 2,500/1.7 ~ 1,500 W, which corresponds to the injection of 4 l/min. of HCl, thermal losses excluded. Consequently, the chlorinator can absorb 5 l/min. of HCl, and maybe up to 10 l/min.

4. Chlorinator/injection pipe junction zone

This is the coolest zone, notably at the stainless steel tightening flange of the graphite sliding coupling.
It is only at 245 °C with a chlorinator at 500 °C – it is worth noting that the cover is not fitted with felt insulator – but even with this insulator fitted, the temperature would not exceed 265 °C.
Removing the insulator from the cover made the temperature of the flange decrease by approximately twenty degrees. It is therefore necessary to install the insulator and better insulate graphite from stainless steel by performing the following operations:

● reboring the stainless steel cover so as to decrease thermal transfer in the unit with the possibility of introducing an insulator (mica sheet),

● replacing the graphite seal with mica between the stainless steel cover and the graphite sliding coupling so as to reduce conduction.

Probe temperature tests [2] had shown that it was necessary to inject gases at 372 °C so as to reach a minimum temperature of 288 °C in the probe, which prevents any risk of condensation. Now, during this test, the temperatures measured were 280 °C at gas inlet flange and 245 °C at lower flange. The risk was to create condensation in the probe because of insufficient heat to make up for losses.
It was therefore necessary to heat the union zone so as to make up for thermal losses and keep the gas energy so as to heat the probe.
As a heating clamp was not satisfactory as was, a square-section shielding resistor was fitted on the sliding coupling tightening flange for the test. The purpose of the test was to reach a 400 °C temperature in this zone so as to avoid any recondensation of $ZrCl_4$.

4.1. Test data

In addition to the previous test, the chlorinator is fitted with an additional resistor secured on the lower flange (graphite sliding coupling support). Thanks to a thermocouple fitted in the resistor it is possible to know its temperature and a rheostat is used to limit its power.
The felt carbon insulator is reinstalled on the chlorinator crucible, up to the contact with the cooled shell. The graphite seal underneath the graphite sliding coupling is replaced with 3 mica seals for thermal insulation.
The temperatures are measured in the following zones:

● union temperature at reheater outlet

● temperature in the chlorinator crucible

● outside temperatures:
  ● in the graphite sliding coupling
  ● or in the stainless steel sliding coupling tightening flange

● temperature of the junction flange for injected gases.

4.2. Observations (refer to Figure 5)

Test No. 1 without additional resistor (curve at approximately ~ 3:00-3:44 pm)
Further to heating the reheater and the chlorinator up to 500 °C, the following temperatures can be observed (further to being maintained for 30min.):

● gas junction flange 380 °C

● stainless steel sliding coupling tightening flange 335 °C.

Test No. 2:
The power injected on the resistor progressively increases until ~ 5:05 pm.
The following temperatures can be observed:

● gas junction flange 415 °C

● stainless steel sliding coupling tightening flange 390 °C.

Test No. 3:
Injection of 15 l/min. of H_2 in addition to the argon, the resistor is no longer supplied by mistake for a few minutes at approximately 5:05 pm.

● gas junction flange 440 °C

● stainless steel sliding coupling tightening flange 410 °C.

Test No. 4 (~ 5:40 pm):

The reheater is too hot for the propylene gas, since there is a risk of decay with carbon deposit at this temperature. The new conditions are T= 450 °C, injection of 15 l/min. H_2 in addition to argon, resistor set to 70% of its power.

● gas junction flange 420 °C

● stainless steel sliding coupling tightening flange 420 °C.

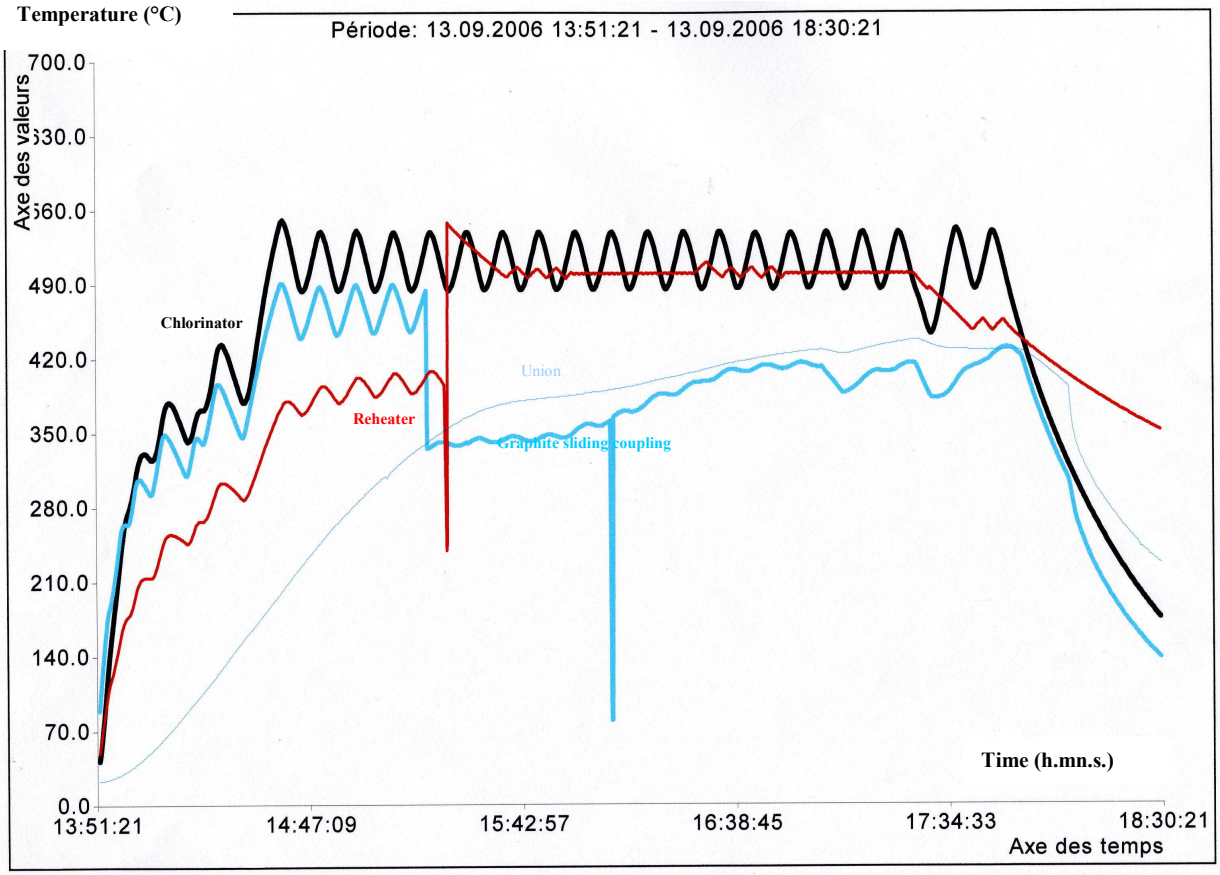


Figure 5. Temperature/time curves measured during tests 1, 2, 3 and 4.

The purpose of test No. 5 was to test correct thermalisation of the reactor with a Zr grit load of the order of 5 kg. As can be seen on the photo of Figure 6, the injection test was problematic. Leaks are noted at mica seals and characterised by recondensation of the chloride in the form of a white gel. Tightness was corrected and the test could be performed again.

Figure 6. Union between chlorinator outlet and injection pipe inlet.

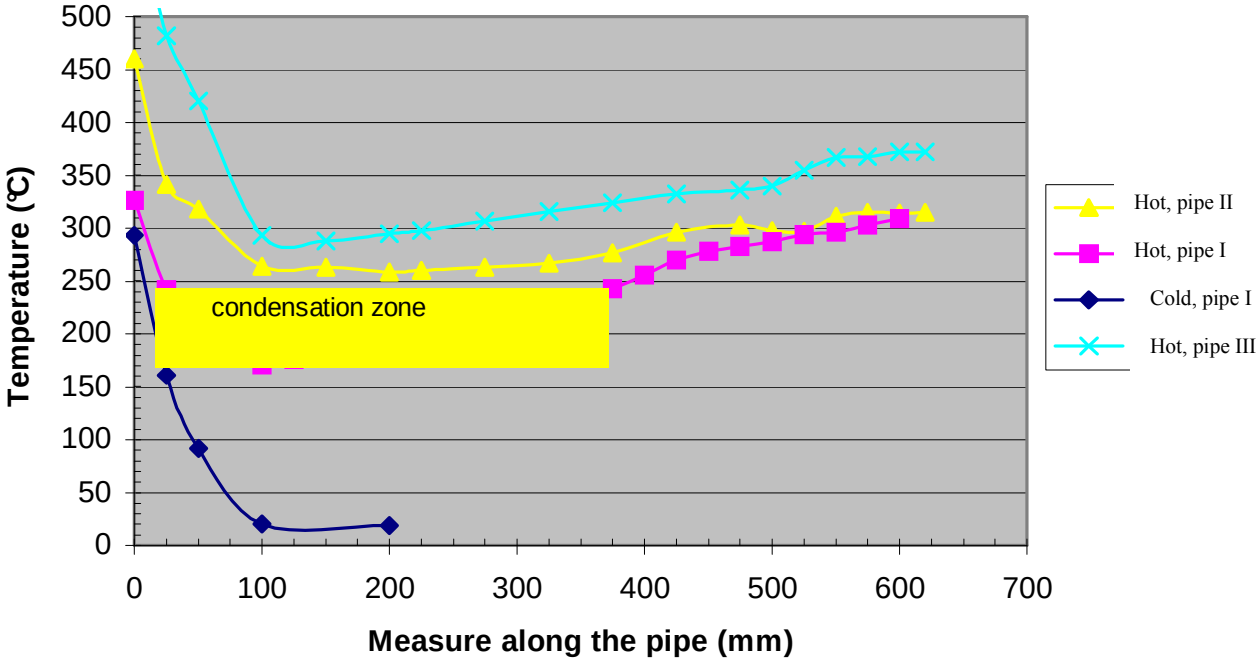
4.3. Test data

All temperatures are set to 420 °C with a resistor supplied at 70 % of 230 V.
The gases penetrate the probe at 420 °C minimum, in the test conditions. The following set points must therefore be defined:

- Reheater 450 °C
- Chlorinator 500 °C
- Additional resistor: 420 °C on stainless steel flange.

The mixture is supposed to condense at approximately 250 °C for a chloride diluted at less than 10%. The pressure or total flowrate variations have little influence (± 20 °C). For reference, Figure 7 below shows the thermal profile of the pipe of generation III (light blue), with an inlet temperature of 372 °C (right), minimum point at 280 °C, 100 mm before the injector. Therefore, with the inlet at 420 °C, the lower point should be limited at 300 °C.

Figure 7. Temperature profile in the injection pipe [2].



With these results, a new injection test was required to confirm the possibility of deposit on surrogated kernel.

5. Injection test in the coating furnace

5.1. Purpose

Its purpose was to test the behaviour of the chlorinator over a relatively long time (~3 hours): temperature rise due to attack reaction, plugging in the injection pipe or in the gas injector.

5.2. Test data

The coating furnace is loaded with zirconia kernels particles previously coated with 2 pyrolytic carbon layers. The particles bed is heated in argon up to approximately 1,550-1,600 °C, then the reactive (C_3H_6, $ZrCl_4$) and dilution (H_2, Argon) gases are injected in significant flowrate conditions, voluntarily conservative but properly controlled however.

5.3. Observations

A regular pressure increase has been observed during the deposit. This variation may be explained by a slight deposit at the injector hole related to its temperature. The diameter decrease is enough to explain the phenomenon. The upstream pressure varies from 1.3 bar absolute to 1.7 bar so as to obtain the required flowrate. Besides, a ± 0.1 bar variation is regularly observed on upstream pressure. A temperature variation of the order of 100 °C of the injection hole may explain this phenomenon and seems to be the exact copy of the periodic chlorinator variations (Figure 8). Without other significant consequences, deposit could be

carried on during the time planned. It should be noted that these variations may be smoothed thanks to a better control of heating unit settings.

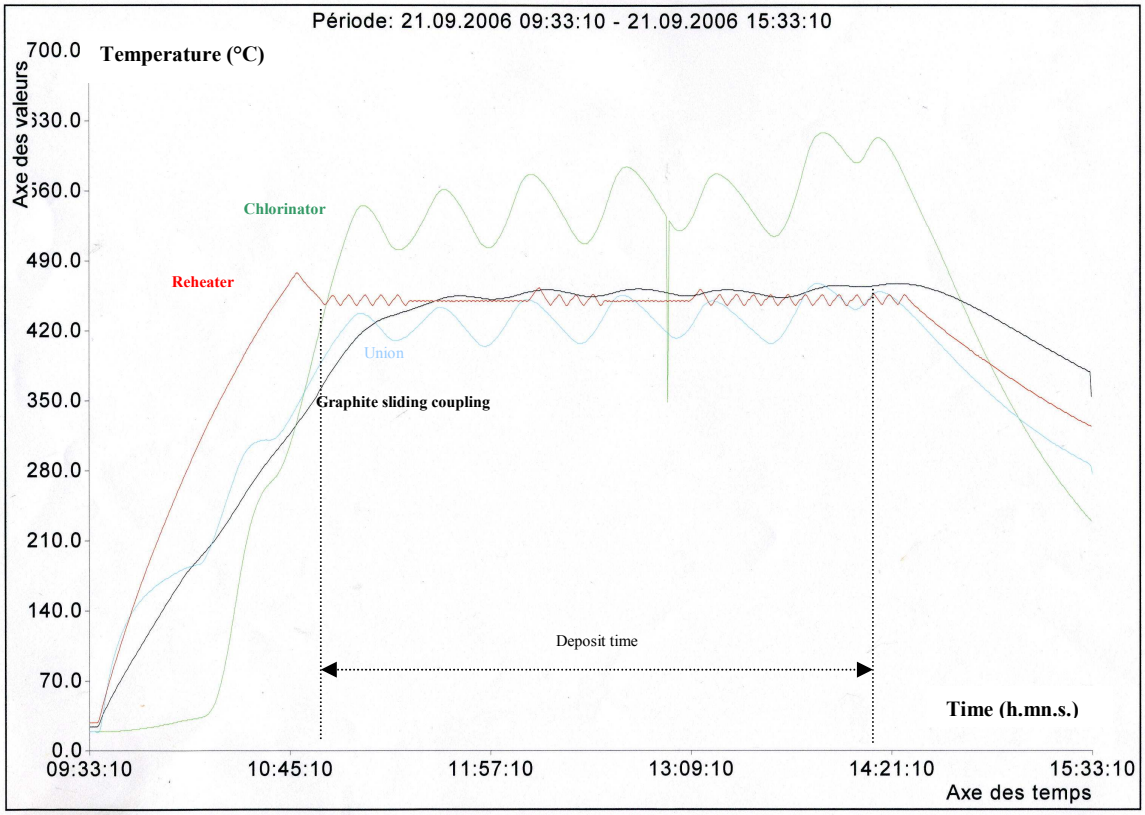


Figure 8. Temperature/time curves measured during deposit

5.4. Unloading

The weighing of particles shows that a significant deposit was performed. However, it was impossible to accurately calculate the zirconium consumption by weighing difference because of the modifications embodied on the chlorinator. Finally, examination of the injector confirms that a non-adhering deposit took place in the gas injection hole.
The particles are then scattered for various characterisations:

- Observation with optical microscope on polished section,
- Observation with scanning electron microscope on fracture,
- Analysis by X-ray diffraction.

6. Results of expert analysis of the deposited layer

The batch of particles was examined by the DTEC/STCF/LMAC of the CEA at Pierrelatte.

6.1. Microscope observation on polished section

Observations made by means of optical microscope on polished sections allow the thicknesses of the various layers to be measured (refer to Figures 9 and 10). Since the particles are not

totally spherical, measurement is given from the average of 10 measurements proper to each zone:

- the ZrC cladding layer is of the order of 133 µm,
- the dense PyC layer is of the order of 41 µm,
- the porous PyC layer is of the order of 85 µm,
- the particle diameter is of the order of 982 µm.

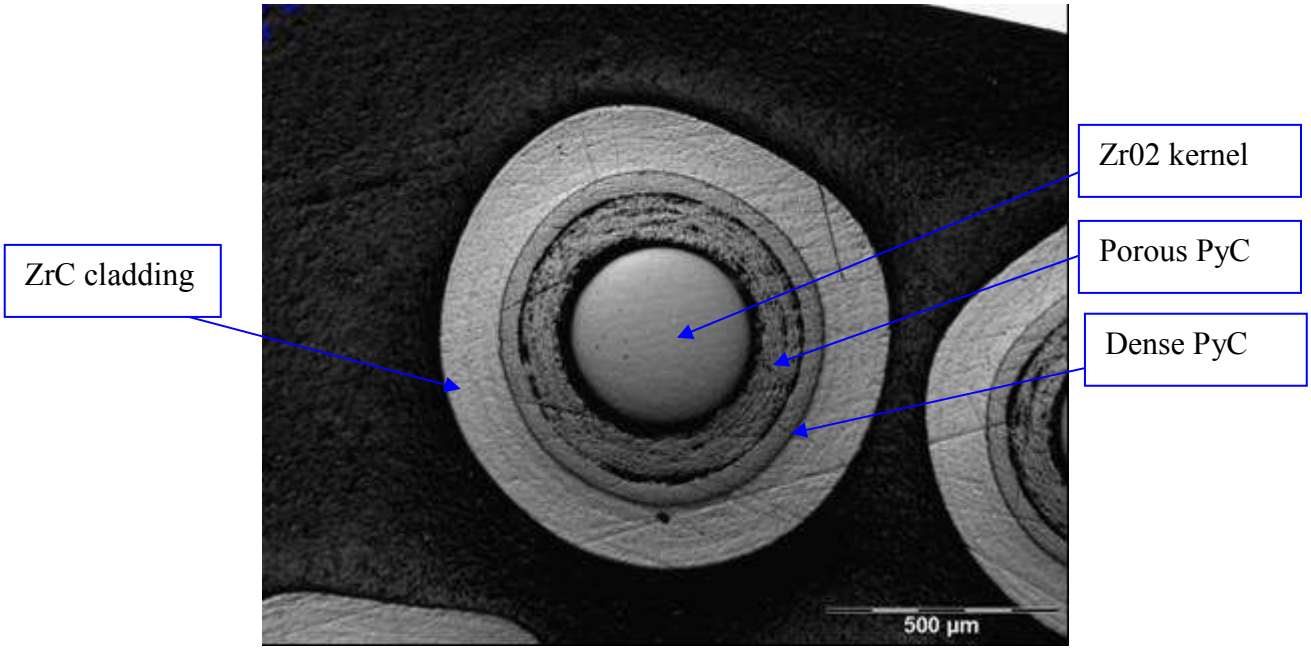


Figure 9. Observation with optical microscope on polished section (scale: 500 µm).

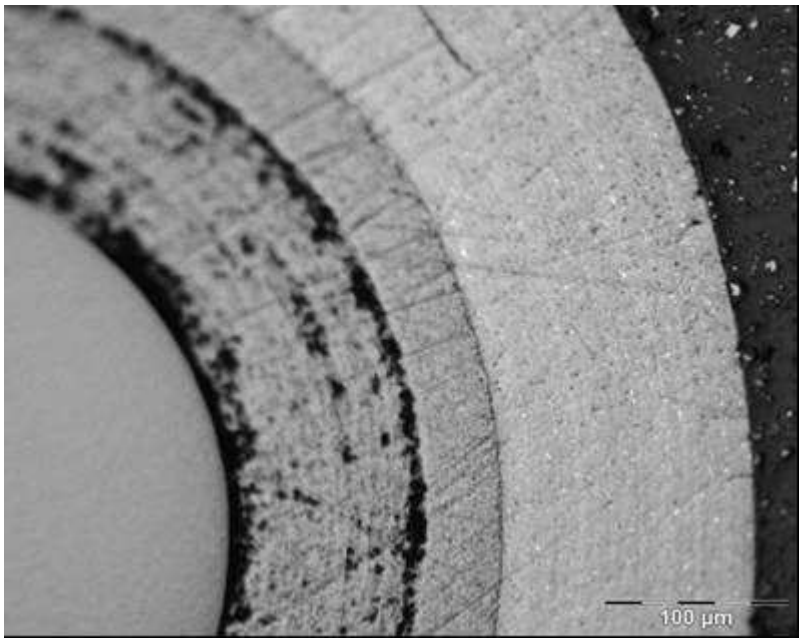


Figure 10. Observation with optical microscope on polished section (scale: 100 µm).

6.2. Fractography observation with scanning electron microscope (SEM)

Observations by means of scanning electron microscope (SEM) were performed on particle fractographies.
A first observation performed in secondary electron detection mode reveals the topography contrast for the various zones of the particle structure.
The zones of the ZrC cladding layer and the ZrO_2 kernel can be clearly distinguished in clear contrast. PyC layers appear in dark grey contrast (refer to Figure 11).
A second observation performed in backscattered electron detection mode reveals the particle's chemical composition contrast (refer to Figure 12).
An observation made at scale 20 µm in this detection mode highlights the porosities of PyC layers and the deposit stratifications for the ZrC cladding layer (refer to Figure 13).

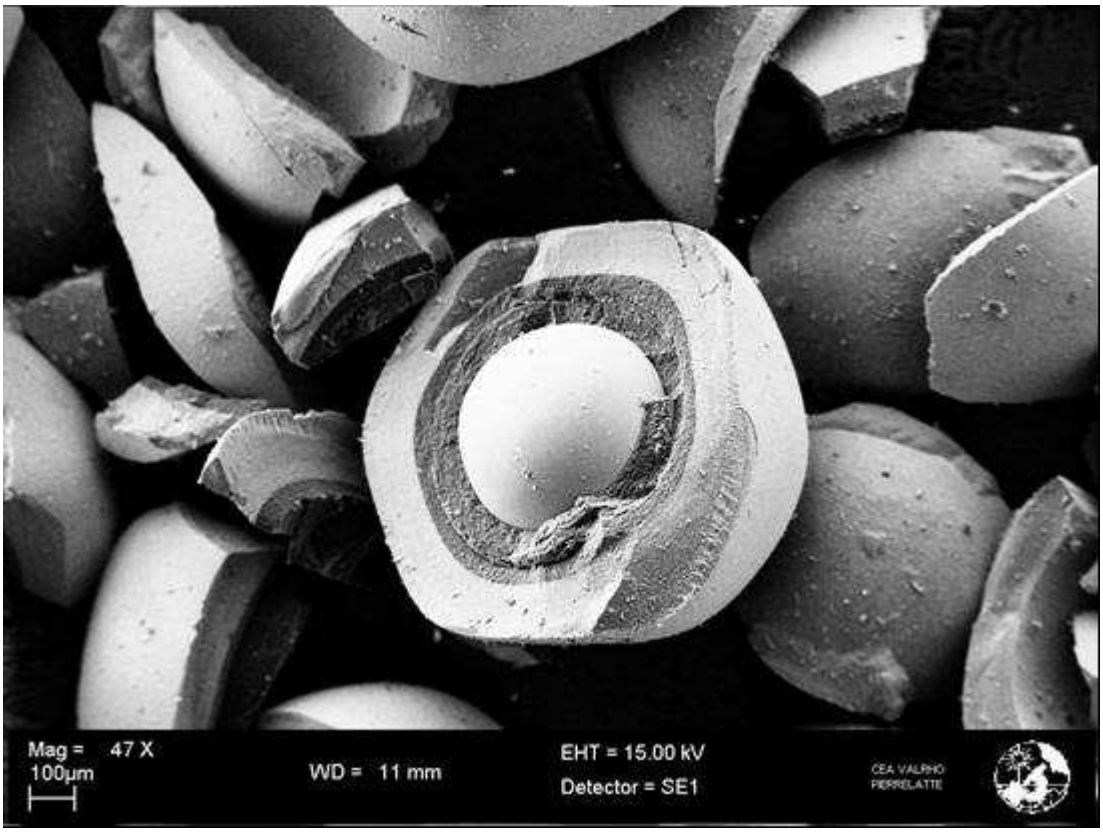


Figure 11. Observation with SEM in secondary electron detection mode. (scale: 100 µm)

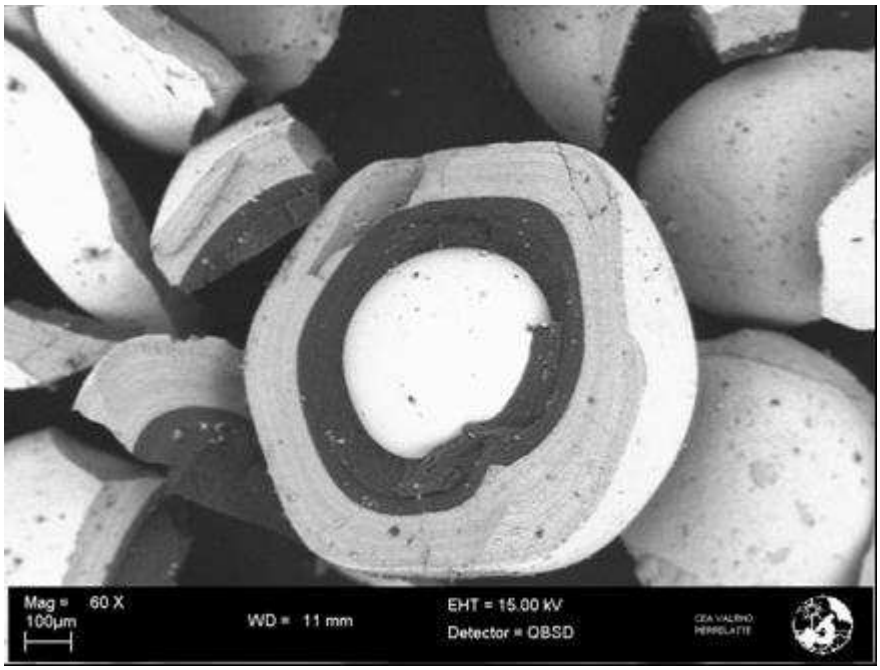


Figure 12. Observation with SEM in backscattered electron detection mode. (scale: 100 µm)

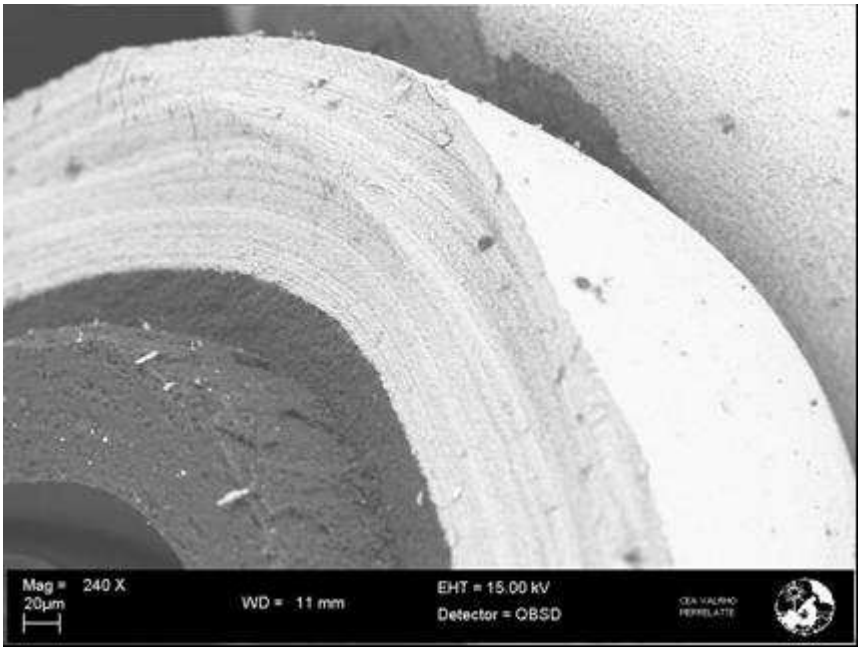


Figure 13. Observation with SEM in backscattered electron detection mode. (scale: 20 µm)

6.3. Analysis by means of X-ray diffraction

Analysis by means of X-ray diffraction was performed in two steps: a first analysis on complete particles then a second analysis on crushed particles.
Thanks to the analysis on complete particles (refer to figure 14), it was possible to note the presence of cubic ZrC and cubic YOC with a clear identification phase shift due to the geometrical shape of the sample.
The analysis performed on crushed particles (refer to figure 15) helped detect the presence of the particles' constituting components.
Analyses of the layer by means of electronic microprobe are planned so as to identify the stratum composition. Although the stoichiometric ZrC was identified by means of X-ray diffraction (DRX), these strata might be indicative of a non-homogeneous deposit with successive stacking of ZrC and free C.

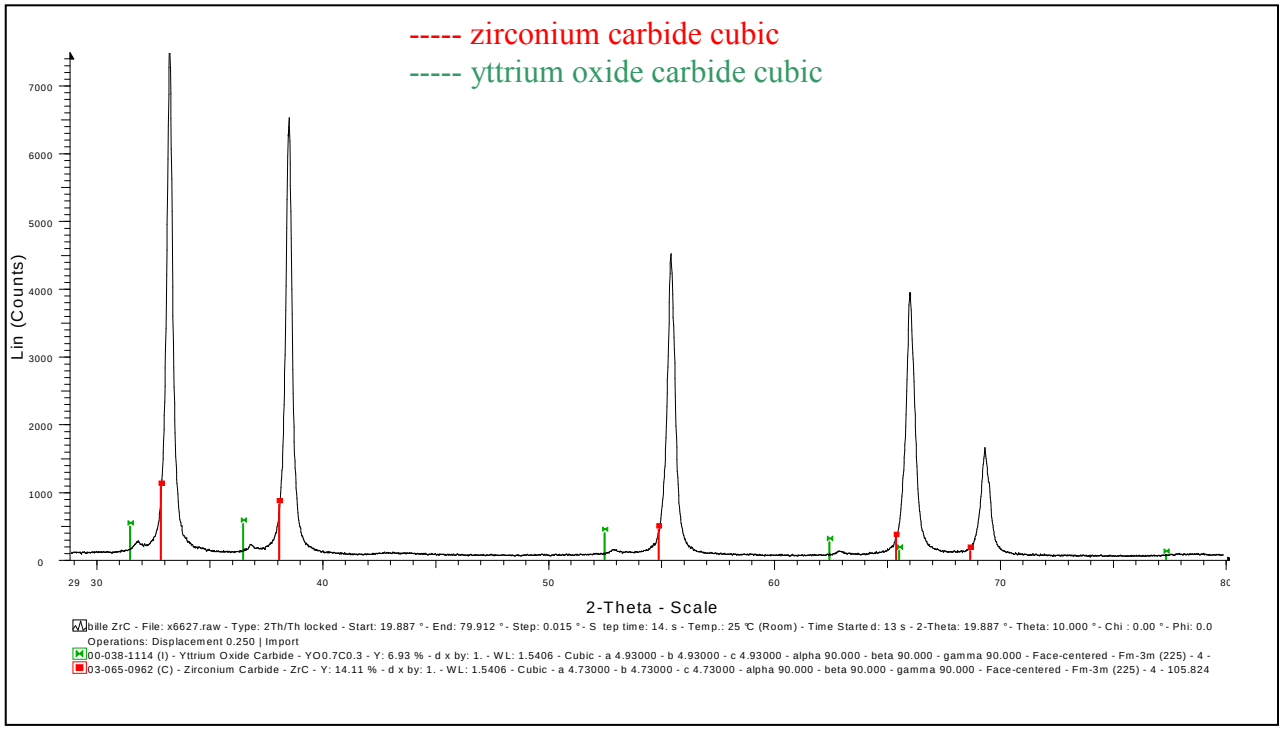


Figure 14. Spectrum performed at particle surface.

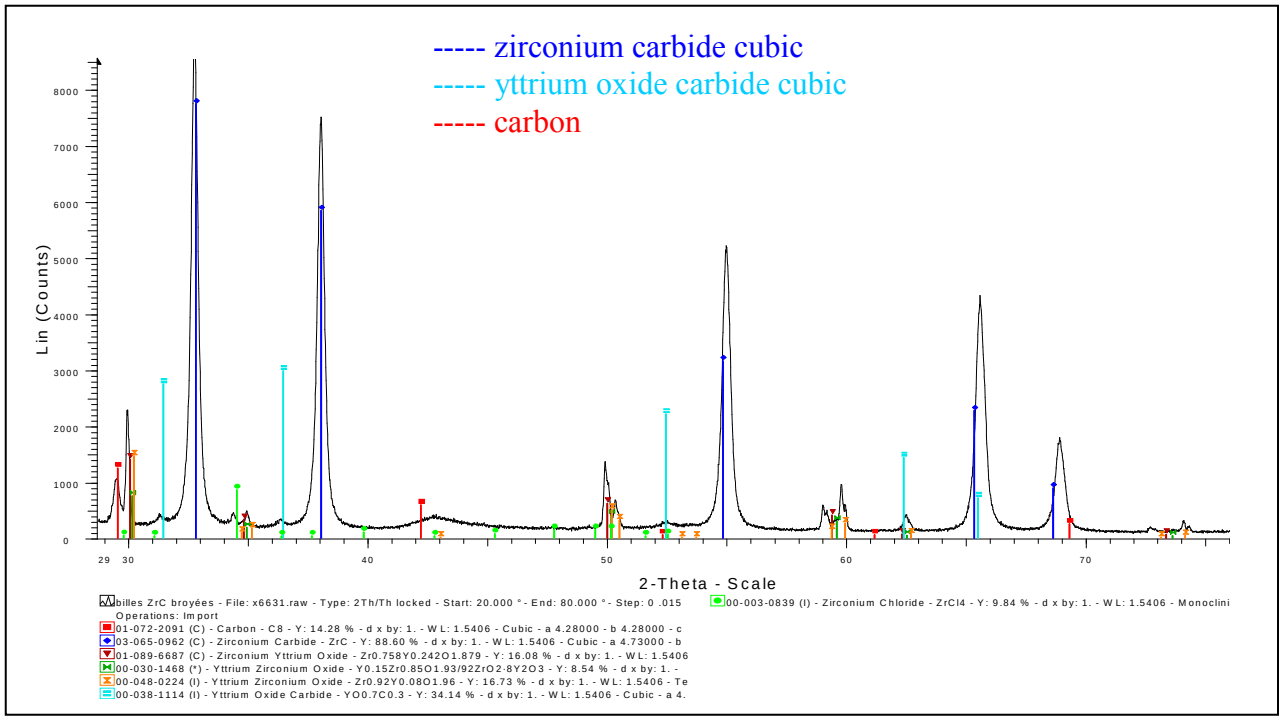


Figure 15. Spectrum performed on shells making up the various layers.

Conclusion

A new chlorinator was developed. The tests highlighted the significance of chlorination temperature and its control so as to avoid chloride recondensation. The setting-up of the reactor at the coating furnace inlet significantly reduces the risks of plugging. Thanks to thermalisation tests of the chlorinator, modifications could be embodied; they allowed correct performance of the injection of precursors during a long-lasting deposit. A thickness of the order of 130 µm was obtained, knowing that the specification is 35 µm. Crystallographic analysis of the material shows a majority cubic phase (β) as well as the presence of an yttrium oxycarbide. The main layer is made of quasi stoichiometric ZrC. The presence of zones with more or less high C or Zr content must be confirmed by other analyses.

The next step will consist of aiming at deposit conditions for which the stoichiometric ZrC range is more interesting, that is to say higher partial pressure and deposit temperature

Bibliography

[1] M. Perez, Transfert de zirconium (Technical procedure, LITEN/DTH/LTH/172.06/MP)
[2] M. Perez, C. Desrats, O. Dugne, A. Merlau, L. Obringer: ZrC in High-Temperature Reactor Fuel Technology (HTR-F1-05/11-D-4.3.1)