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$(U,Pu)O_{2-x}$ MOX pellet for Astrid reactor project

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Abstract

Since 2015, AREVA and CEA teams decided to launch yearly industrial tests of MOX pellets with an adapted GEN III design in the MELOX plant, to prepare the future manufacturing of MOX fuels bundle for Astrid reactor.

First campaign (2015) of tests was dedicated to demonstrate the feasibility of this manufacturing at half industrial scale; Main modifications involved the pelletizing station of LCT workshop (small scale line for MOX manufacturing) and one of the industrial furnaces, in order to define the range of main parameters (powder preparation, pelletizing and sintering steps and MOX pellet analyses procedures). Specified analyses results were performed in MELOX plant laboratory, completed with EPMA analyses on MOX pellet sent to CADARACHE CEA laboratory : First results show that required properties of these MOX pellet, meet the specified criteria defined by CEA teams, the most important one's are related to pellet design (dimensions and density), Pu distribution and oxygen stoichiometry.

Second campaign (2016) of tests, included a powder preparation step at industrial scale on one of the blender of the MELOX plant, in order to prepare the industrial manufacturing of MOX pellet for one fuel bundle, designed for a prototypical irradiation. Main results show again that the specified criteria are respected increasing the confidence in the process route.

Keywords: MOX, annular pellet, Astrid, EPMA.

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I. INTRODUCTION

The global program was defined in strength collaboration with CEA for each campaign of tests in order to adopt a step by step approach, because of Astrid MOX pellet manufacturing is a more complex manufacturing than those for BWR or PWR MOX pellet, for which MELOX plant have an important knowledge and feedback[1]. This approach was managed as follow:

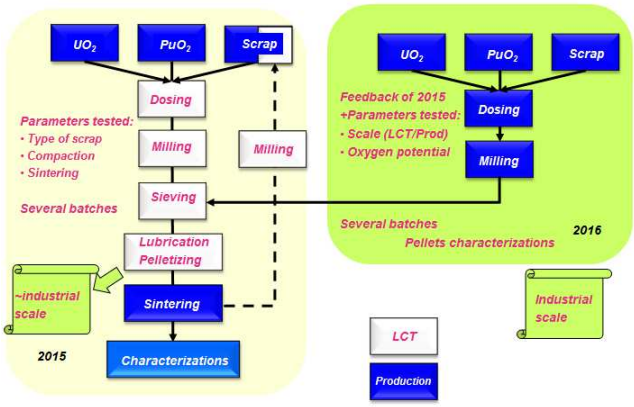
During 2015 campaign[2,3]:

- First, for sieving conditions, a Design Of Experiments (DOE) was performed to optimize the characteristics of the MOX powders blend to be compatible for pelletizing step (in term of flow-ability), using a granulator installed in LCT (laboratory scale),
- Acquiring the adapted conditions for an optimized MOX powder blend, several hundred of MOX pellets with an annular design were pelletized in the LCT workshop and sintered in the industrial furnace (sintering conditions were adapted to reach the specified oxygen hypostochiometric criteria)
- All analyses performed on these pellets in the MELOX laboratory, verified criterion of CEA specification,
- Several pellets were sent to CEA Cadarache laboratory (LEFCA) in order to perform an EPMA analyses program.

During 2016 campaign[4]:

- The goal was to increase the scale, up to industrial one for powder preparation (milling step in one of the plant blenders), so that 2 types of MOX powder blends were prepared, at LCT scale and one at production scale,
- As during previous campaign, several hundred of MOX pellets using the 2 types of blends were pelletized and sintered in the same industrial furnace,
- Again, all analyses performed on these pellets in the MELOX laboratory, verified criterion of CEA's specification.

The manufacturing scheme of this global program is presented in scheme n°1, with main manufacturing conditions of each campaigns summarized in table 1.



Scheme 1: manufacturing process for the 2 campaigns

Year	Number max. pellets	%Pu (±20% rel)	Powder preparation	Pelletizing	Sintering
2015	≤ 300	24%	LCT	LCT	Prod.
2016	≤ 300	24%	LCT + Prod.	LCT	Prod.
2017	To de defined	24%	LCT + Prod.	LCT	Prod.

Table 1 (LCT: small scale manufacturing line)

II.MOX PELLET MANUFACTURING TESTS

II.1 Raw materials

UO_2, PuO_2 and scrap powders used for all tests were sampled at the usual sampling station of MELOX plant. For 2015 campaign, a 2nd scrap lot, containing Astrid pellets was prepared in LCT miller. For 2016 campaign, a final blend, within the explored Pu content range was prepared in one of the production miller stations. Table 2 summarized the main characteristics of powders.

Year	%scrap	Scrap origin	PuO_2 origin	UO_2 origin	Prepared Blends
2015	~10%	LCT +Prod.	La Hague	Areva plants	2 (LCT)
2016	~10%	Prod.	La Hague	Areva plants	2 (LCT,prod)

Table 2: composition of blends for the 2 campaigns

II.2 Powders characteristics

Sieved granulometry device equipped with 40 to 1000µm sieves, bulk and tapped densities device and BET device for specific surface area can be carry out at each step for better powder properties characterizations[3].

II.3 Equipment and experimental conditions

II.3.1 Preliminary blending step

An optional preliminary blend step of the 3 types of powders can be carry out before the ball milling step at the 2 scales.
At LCT scale, a Turbula blender is used with pre-defined parameters, in terms of powder rate in the container inserted in the device and rotation speed (~30min^{-1}).

II.3.2 Powder blending step (Ball milling)

For dosing steps (LCT and production scale), each weigh device is calibrated and a surveillance is performed before each dosing step, using adapted weigh range standards.

In order to very well blend the 3 types of powders (in terms of powder reactivity for sintering), 2 blenders, called “ball milling station” were used in LCT and production, at 2 scales (see table 3).

Station	Ball	Powder load	Parameter U	Milling time
LCT	Same design of U-ball	1-2kg	U ~ 1	Same time (~2h)
Production		up to 60kg	U ~ 1	

Table 3: blending step parameters

Knowing the final powder properties are driven by few important parameters, the 2 scales stations were settled up in term of milling conditions (see Table 3).

II.3.3 Final blend granulation step

Each type of final blend is granulated with a granulator (Frewitt device), equipped with a ~200µm mesh grid and a four knives alternative rotor, in LCT workshop.

Previously to 2015 campaign, a DOE[2,3] was carried out for each blend to optimize the flow-ability to be compatible for powder feed rate at pelletizing step (powder feeding rate and rotor speed).

The powder feed rate and rotating speed were optimized to reach the highest powder flow-ability. These parameters were then settled up for all the next tests.

II.3.4 Lubrication step

After granulation step, the lubrication was performed with zinc stearate in the same Turbula blender, but just before the pelletizing step to prevent any thermal effect on lubricant due to Pu powder. This effect will be study later.

II.3.5 Pelletizing step

The pelletizing station of LCT is used: it's a double effect hydraulic press station, adapted to the Astrid pellet design, and equipped with 3 specific tools designed to elaborate MOX pellet with a central hole. Each green pellets batch was then placed in a Mo-boat for next process step.

Compared to PWR MOX pellet design, the pelletizing cycle was also updated and adapted to these MOX pellets designs with central hole.

II.3.6 Sintering step

Each MOX pellet batch was sintered just after pelletizing step (again, to prevent any effect on green pellet due to Pu powder thermal heating; this effect will be evaluated later), in a Mo-boat.

One of the production furnaces (scheme 2) was dedicated to each tests campaign during several weeks to respect particular Quality and Safety requirements, the sintering procedure was adapted, including the surveillance of pellet height in the Mo-boat, required for these high Pu content pellets sintered in a PWR production furnace.

The atomic oxygen-to-metal ratio (O/M) has to be hypostochiometric (i.e. O/M < 2.000) and close to 1.97 at room temperature. Previous studies have shown that the sintering of MOX fuel with around 25-30 wt% of Pu under dry Ar/4%H_2 leads to a very low O/M (~1.94) [5]. Moreover, a demixing phenomenon can occur during the cooling down phase. This demixing is consistent with the existence of a miscibility gap in the fcc phase in the U-Pu-O system [6]. As shown in Figure 1, the smaller the O/M or the greater the plutonium content, the more pronounced the demixing phenomenon.

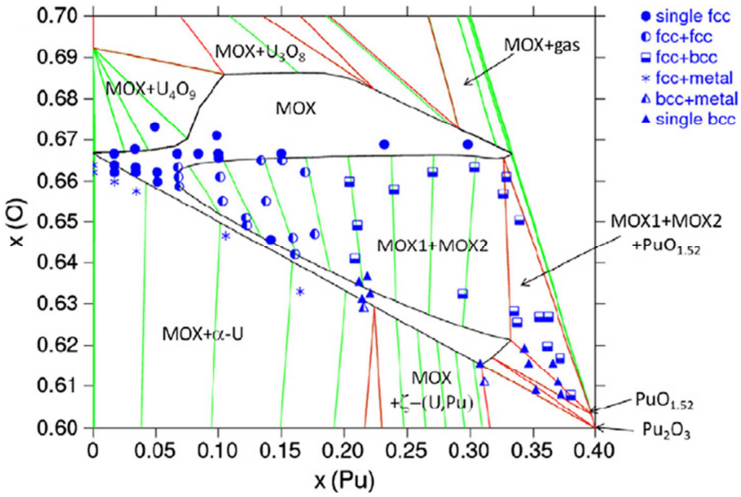
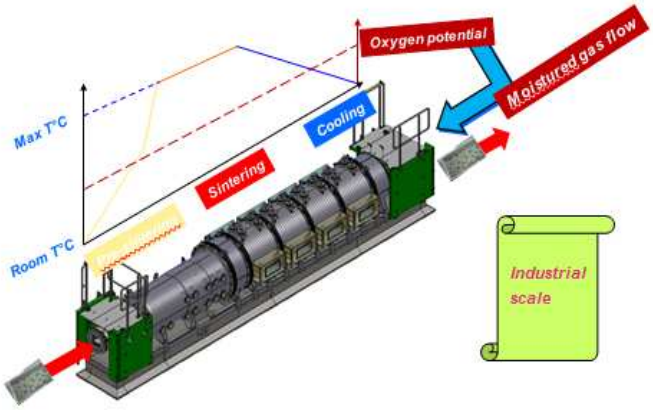


Figure 1 : Calculated phase diagram of the U–Pu–O system at 473K [6]

The oxygen partial pressure (pO_2) of the sintering gas must be increased in order to reach the targeted O/M and to limit the consequence of demixing. To that aim, several conditions (S1 to S8) consist in adjusting the moisture rate of the sintering gas Ar/4%H_2.

Knowing the CEA specified characteristics of Astrid MOX pellets, sintering conditions were precisely defined:

- Standard conditions remain unchanged (temperature cycle, boat feed speed inside the furnace, main gaz),
- Oxygen potential was adapted to warrant the specified target of under-stoichiometry.



Scheme 2: Production furnace

II.3.7 Pellet characterizations

Laser devices were used to characterize the dimensions of each pellet, using standards before each measurement.

Quality controls were also performed in laboratory and dimensions quality control stations for each sintered pellets batch manufactured during the 2016 campaign; it concerns all the specified properties (dimensions, stoichiometry, porosity, microstructure, impurities).

III.1 MOX PELLETS BATCHES AND EXPERIMENTAL CONDITIONS

III.1.1 Principle of tests during the first campaign (2015)

Knowing Areva-CEA previous background for Astrid-type pellet design, the 2015 tests campaign was managed in order to determine the influence of 3 main process parameters in the MELOX process:

- The composition of the final blend: 2 types of scrap powder lots were elaborated:
  - The batches 1 to 4 were dosed with the same production PWR scrap powder lot (noted Low in table 4),
  - The batches 5 to 8 were dosed with Astrid-type pellet design scrap powder lot from batches 1 to 4 (noted High in table 4),
  - Others components (UO_2 powder and PuO_2 powder lots) were the same for all batches
- The pelletizing conditions: 2 series of tests were conducted, by setting 2 compaction pressure targets, noted Low and High in table 4 (The ratio between the compaction pressure targets is 1,5),
- The sintering conditions: 2 series of tests were conducted with 2 sintering stage times at maximum temperature of 1700°C, noted short and Lang in table 4 (The ratio between max temperature sintering stage times is 1,4).

The table 4 summarizes the fabrication conditions used for each batch (around 35 pellets per batch).

Batches	Pu content level of scrap lot	Compaction Pressure level	Sintering stage time
1	Low	Low	Short
2	Low	High	
3	Low	Low	Lang
4	Low	High	
5	High	Low	Short
6	High	High	
7	High	Low	Lang
8	High	High	

Table 4: manufacturing conditions of 8 batches (2015)

III.1.2 Main results of batches for first campaign (2015)

The different figures, 1 to 4, present the main dimensions results of pellet batches manufactured according to conditions described in table 4.
As for PWR MOX pellet manufacturing, the results of figures 2a and 2b confirm that the major factors which influence the pellet external diameter are as following (decreasing effect):

- Compaction pressure : highest value of pressure applied during pelletizing step, leads to largest external diameter after sintering,
- The composition of the initial blend (namely the origin of the scrap lot) : batches 6 to 8 containing scrap powder prepared with pellets batches 1 to 4, show systematically lower external sintered diameter compared to results of batches 1 to 4,
- Sintering stage (ie. sintering time at max. temperature), the effect of this last factor is considered as minor.

Note: for each presented boxplot, circle is mean value, square represents range from 25% to 75% of population, minimum and maximum values of population are extremities of vertical line - Blue dashed line : specified target value - Red continuous line : minimum specified value

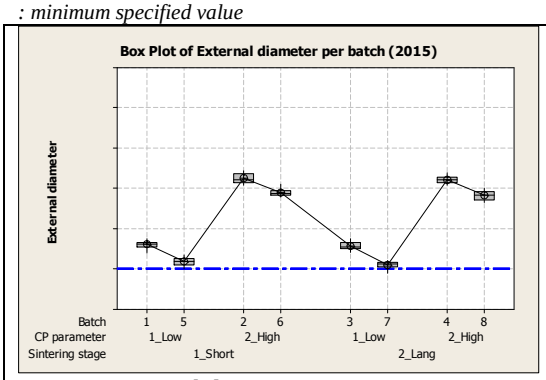


Fig. 2a: external diameter vs Compression pressure (CP parameter) and sintering parameter (Sintering stage)

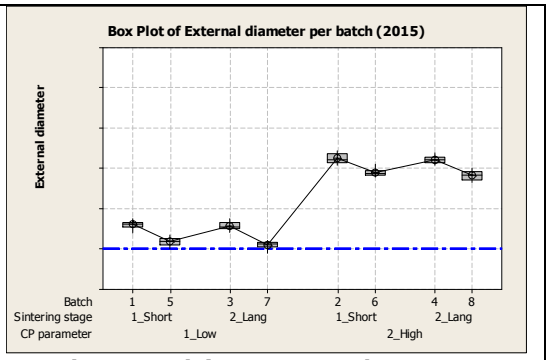


Fig. 2b: External diameters population vs sintering parameter (Sintering stage) and compression pressure (CP parameter)

For the external diameter range (noted EDR and corresponding to the difference of maximum diameter minus minimum diameter measured for each pellet) results per batch show constant mean values for each CP level; Values population are lower than one fourth of the specified tolerance.

Concerning the calculated sintered density, the mean value per batch is higher than the specified target; no particular influence is detected regarding the influence of the 3 previous factors (manufacturing conditions).

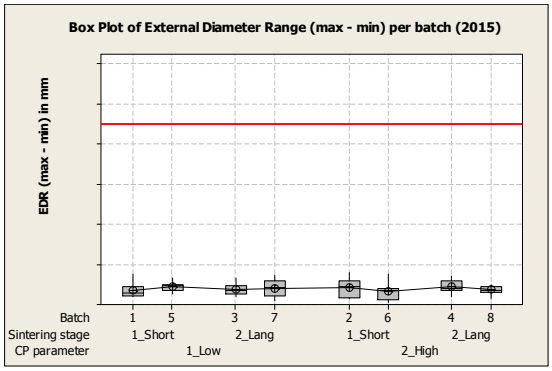


Fig. 3: EDR population vs sintering parameter and compression pressure

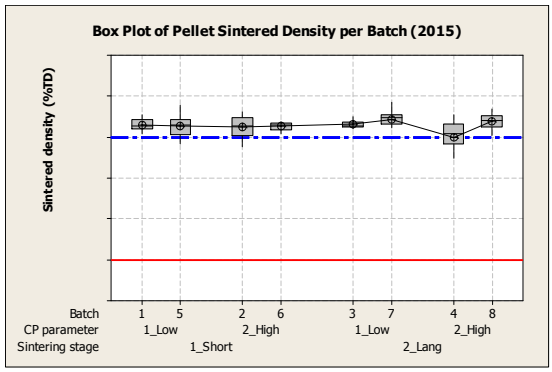


Fig. 4: Calculated sintered densities population vs sintering parameter and compression pressure

Note: for each sampled pellet, internal diameter was measured using a multiple diameters pass/fail gauge with a gap between each of less than 50µm (influence on calculated density is less than $0.01 g/cm^3$).

A linear regression model was built with all individual data to evaluate precisely the effect of each factor; ratios between the 3 regression coefficients of the model are done in table 5. The choice of these factors is in very good agreement for this model, because 98.8% of the observed variations is explained with these 3 factors.

Factors	Compaction pressure	Composition	Sintering stage
Regression coefficient	+A	-A/14	-A/28

Table 5: regression coefficients of the model (2015)

III.2.1 Principle of tests during the second campaign (2016)

Taken into account the results of first campaign, Areva-CEA decided to set the following parameters:
The scale of the powders blend:

- 2 blends were prepared to compare scales of laboratory and industrial blenders,
- The same scrap powder lot was dosed for both blends,
- Others components (UO_2 powder and PuO_2 powder lots) were the same for all batches,

The pelletizing step : same medium compaction pressure (§III.1.1) was settled-up for all the batches,
The sintering step : 8 sintering tests were conducted with the short sintering stage time at maximum temperature stage of ~1700°C (noted short in table 6), defined during campaign of tests in 2015; Only oxygen potential were modified during these 8 tests.

A total of 12 MOX pellets batches were manufactured during this second campaign. The table 6 summarizes the manufacturing conditions used for each batch (around 35 pellets per batch).

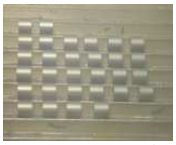
Batch	Pu content level of scrap lot	Blend origin	Compaction Pressure level	Sintering stage time	Sintering condition
1	Low	LCT+PROD	Medium	Short	S1
2	Low	LCT+PROD	Medium		S2
3	Low	LCT+PROD	Medium	Short	S3
4	Low	LCT+PROD	Medium		S4
5	Low	LCT+PROD	Medium	Short	S5
6	Low	LCT+PROD	Medium		S6
7	Low	PROD	Medium	Short	S7
8	Low	PROD	Medium		S8

Table 6: manufacturing conditions of the 8 batches (2016)

III.2.2 Main results of batches for the second campaign (2016)

The different figures, 5 to 8, present the main dimensions results of pellet batches manufactured according to conditions described in table 4.

For the external mean diameter (fig. 5), mean values (per batch) of both types of blends are very close, but located at the upper diameter limit of the specification, meaning that for next campaign the diameter tools have to be reduced from half of the specified diameters range or compaction pressure to be decreased



Sintered pellets on tray for visual inspection

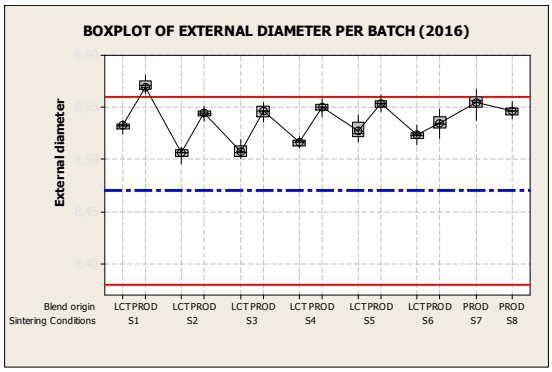


Fig. 5: External sintered diameters population per batch

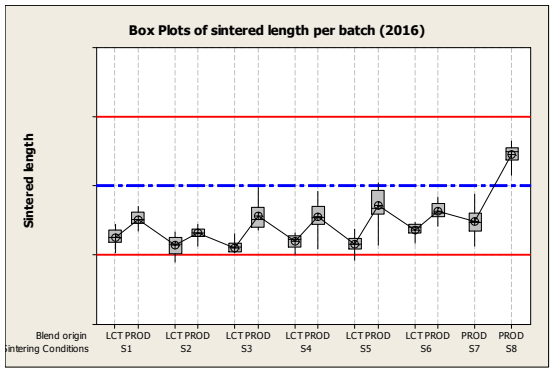


Fig. 6: Sintered lengths population per batch

For the external diameter range (EDR on fig. 7), corresponding to the difference of maximum diameter minus minimum diameter measured for each pellet, results par batch show constant mean values, which are lower than one fourth of the specified tolerance.

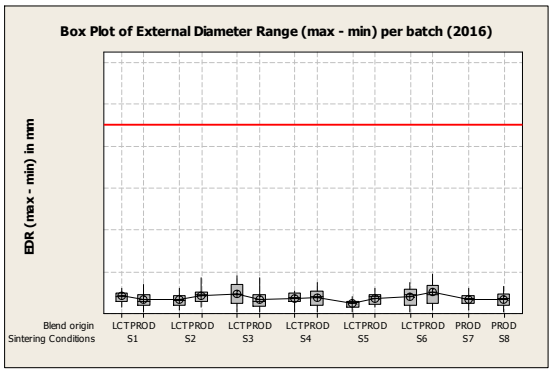


Fig. 7: External Diameter Range (EDR) population per batch

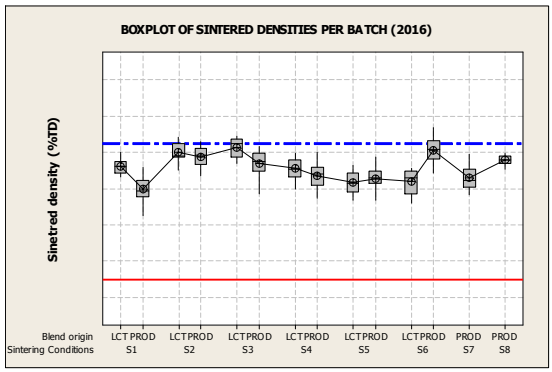


Fig. 8: Calculated sintered densities population per batch

Concerning the calculated sintered density (Fig. 8), the mean value per batch is much higher than the specified target; no particular influence is detected regarding the influence of the 3 previous factors (manufacturing conditions).

IV CHEMICAL PROPERTIES OF MOX PELLETS

IV.1 Stoichiometry of MOX pellets

For each batch, a sample of 4 pellets was analyzed in the laboratory of MELOX plant, to determine the O/M ratio, using an oxidizing-reduction method during a thermal treatment of each sample.
For both campaign, the measured value per batch was located in a range of 1.974 to 1.985, conforming to specified criteria.

IV.1 Hydrogen content

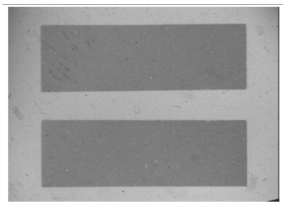
For each batch, a sample of 5 pellets was analyzed in the laboratory of MELOX plant, to determine the hydrogen content. For both campaign, the measured value per batch was located in a range of 0.4 to 1 ppm/ox, conforming to specified criteria.

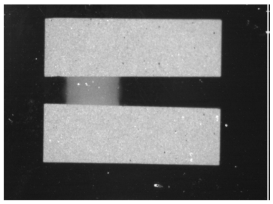
V PLUTONIUM DISTRIBUTION

V.1 Analyses with α autoradiography method

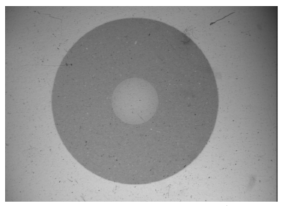
For each batch, a sample of 2 pellets was analyzed using the α-radiography method performed in MELOX plant (either with an intensified cooling down camera or with the standard film method).

The 2 pellets were cut through the length or the diameter; each was then embedded for polishing step, before to realize photographs of the whole polished surface, and then the α-radiography photographs (a film is laying few seconds

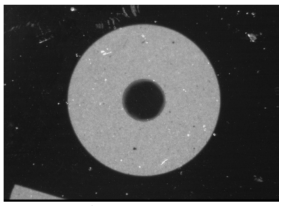




on each sample for α-radiography impression and revealed by chemical etching or using a scintillator with an intensified cooling camera to realize an α-cartography that shows the Pu distribution).
These analyses show a very good Pu homogeneity (white spots on right images are artefacts).



Standard method with film



Intensified cooling camera

Fig.9 : α-radiography photographs

V.2 EPMA ANALYSES

Several samples of each campaign were sent to CEA Cadarache laboratory[7], in order to perform EPMA analysis.

An EPMA CAMECA SX100 equipped with W filament is used to perform measurements at 20 kV on rays U Mα, Pu Mβ, and O Kα. Samples are metallized with a carbon deposit. Analyzed surfaces and volumes are around 1µm^2 and 1µm^3.

Cartographies are done with horizontal and vertical resolutions of 1µm and a 20ms acquisition time per point.

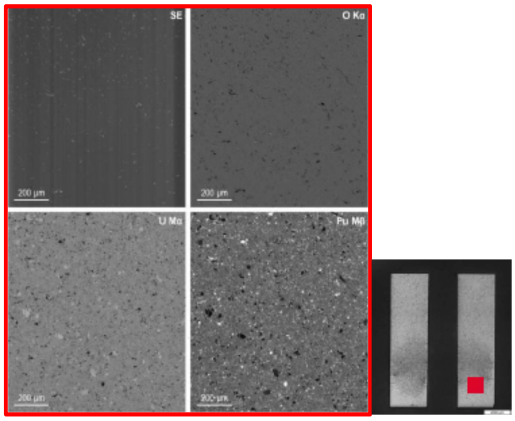


Fig.10 : Cartographies of 1 sample of 2015 (Secondary electron, O, U, Pu)

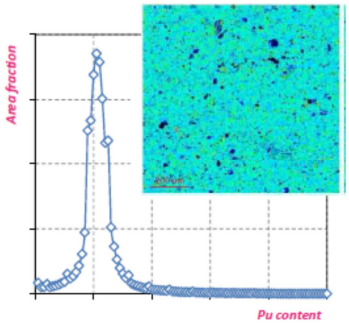


Fig. 11 : Area fraction versus Pu content of 1 sample of 2015 campaign

On the cartographies above, U-rich and Pu-rich areas are much lower than 100µm; these analyses revealed the very good Pu homogeneity of the LCT scale manufacturing. Regarding samples of 2016 campaign, analyses are still in progress.

VII Conclusion

Main manufacturing parameters were defined and tested during the two campaigns performed, at LCT (laboratory area) scale and industrial scale. These parameters concern the powder preparation (using ball milling, sieving and lubrication steps), pelletizing (compaction pressure) and sintering (industrial temperature ramp, stoichiometry managed by setting the oxygen potential) steps.

From first campaign a model was built to define the main parameters involved in pellet shrinkage in order to respect specified criterion for pellet dimensions.

During the second campaign, these parameters were applied to the manufacturing of 2 types of pellets, dosed with blends prepared at LCT and industrial scale.

For each campaign, all results measured on manufactured Astrid design pellets (several hundreds) are in compliance with the CEA specification requirements, namely, the dimensions of the pellets (mean external diameter), the microstructure (Pu homogeneity demonstrated for pellets of first campaign) and chemical properties (stoichiometry).

Further tests are scheduled this year, in order to follow the step by step approach.

Safety

Each campaign is performed under particular procedures and submitted to a prior authorization of the French Safety Authority (ASN) in order to respect safety requirements of the plant.

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