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Extended fuel cycle : results of the first two cycles of « DUO experimentation »

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Introduction

French nuclear plants primary coolant conditioning is essentially based on the boron-lithium coordinated chemistry. Today, the pH target value is 7.2 at 300°C for all the 58 French units, and the maximum authorised lithium concentration is 2.2 mg/kg [1]. To decrease dose rates, primary coolant pH in EDF nuclear plants was changed from 7.0 to 7.2 [2].

Since EDF 1300 MWe units began operating 18 month-extended fuel cycles, increasing fuel uranium oxide enrichment from 3.2 to 4 % had been necessary. This evolution led to :

- a significant increase in the boron concentration at the beginning of fuel cycles (progressively for the first two conversion cycles) ;
- a decrease of the pH at the beginning of the cycles, since today the maximum lithium concentration in normal operation is 2.2 mg/kg.

This issue does not concern the twenty 1300 MWe units operating extended cycle only. All the other French nuclear reactors can be impacted if higher boron concentrations than those used until now are imposed by new core design (Mixed OXide, ...).

As shown by experience feedback, operating at pH₃₀₀ around 6.8 may make it difficult to keep corrosion products as low as possible. Hence it may lead to :

- deposits in RCS, and particularly on the fuel cladding, which may in turn lead to axial offset anomalies [3]-[4] ;
- increase in dose rates.

One solution is to adjust the pH by increasing the lithium concentration at the beginning of the cycles, and hence to operate a modified chemistry regime. This solution is easy to implement, as soon as decided and without any modification on the units. A new maximum lithium concentration, consistent with materials behaviour and especially with fuel cladding, has to be fixed.

This is what EDF has decided to test through the « DUO experimentation ». An important feature of this experimentation is the testing of the corrosion behaviour of several fuel cladding materials.

This paper deals with the results of the controls and expertise performed during the first two conversion cycles of the DUO Experimentation.

DUO experimentation features

This experimentation deals with the specific surveillance, from the first to the third conversion cycle, of two 1300 MWe units starting implementing extended cycle operation. The reference unit and the pilot unit for this experimentation were chosen to be Golfech 1 and Cattenom 2 respectively. They had to have similar design (steam generator tubes bundle in 600 TT alloy, fuel grids assemblies, no hot spots, no flux anomalies, ...).

Golfech 1 implements a classic boron-lithium coordination pH₃₀₀ 7.2 (figure 1). Cattenom 2 operates EDF modified chemistry at the beginning of the cycles, with maximum authorised lithium concentration of 3.5 mg/kg (figure 2).

The major goal of the experimentation is to assess the impact of elevated lithium concentrations at the beginning of cycles on fuel cladding oxide behaviour, mass transport and dose rates.

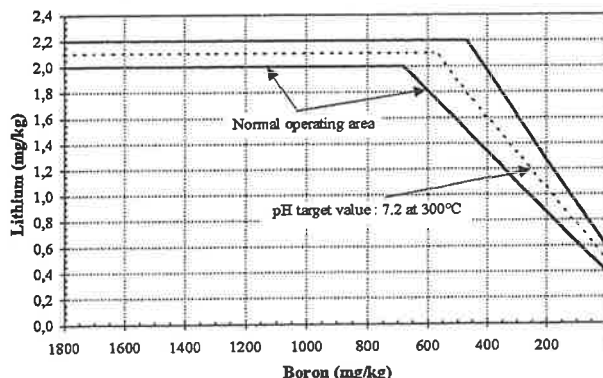


Fig. 1 : Classic B-Li coordinated chemistry pH₃₀₀ 7.2

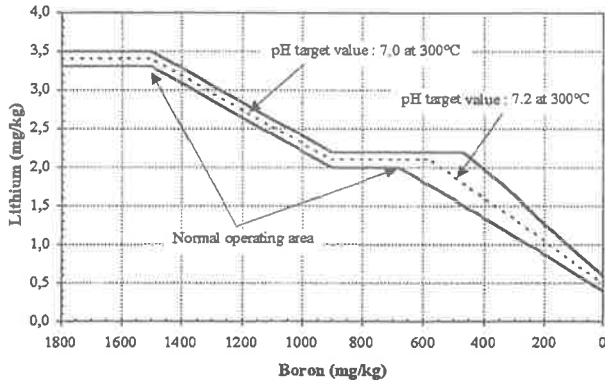


Fig. 2 : EDF B-Li modified chemistry

Surveillance program of the DUO experimentation

During operation

During each conversion cycle, the primary coolant surveillance deals with its chemical and radiochemical features (table 1).

During shutdown transients and outages

For the three conversion cycles, the surveillance concerns primary coolant activity during shutdown, surface activity and fuel oxide thickness measurements. Scrapping of crud deposits (if any) on the fuel cladding are planned at the end of the third conversion cycle (table 1).

These controls aim at assessing the performance of an extended cycles modified chemistry when elevated initial boron concentrations are used compared to a classic chemistry, which may lead to operate, at the beginning of cycles, at risky pH for fuel crud deposits and dose rates.

Table 1 : Surveyed parameters

	Field	Surveillance
During operation	Chemistry	B, Li, H ₂ Ca, Mg, Al, SiO ₂ Cr, Ni, Co CVCS filters O ₂ in boron and water makeup tanks Volumes of boron and water makeups
	Radiochemistry	Gammaspectrometry
During shutdown transient	Radiochemistry	Primary coolant activity
During outage	Contamination	⁵⁸ Co, ⁶⁰ Co, on crossover legs, SG tubes bundle, hot legs
	Fuel	Televisual inspection, oxide thickness Fuel assemblies scrapping (end of DUO experiment)
	SG tubing	Regular non destructive examinations

Duo experimentation partial results

Chemistry

During the first two conversion cycles on Golfech 1 and Cattenom 2, despite load following, the boron-lithium coordinated chemistry regime matched the specifications (Fig. 3 and 4). Data out of the normal operating area are essentially due to shutdowns, physical

testing, rapid load variations and makeups for tritium dilution in RCS. No specific pollution was observed during these conversion cycles in Golfech 1 and in Cattenom 2.

The initial boron concentrations at hot zero power and full power are reported in table 2.

In the Cattenom 2 pilot unit, operation with a lithium concentration between 3.5 and 2.2 mg/kg increased from about one week to two weeks from the first to the second conversion cycle ; operation with a lithium content between 2.5 and 2.2 mg/kg increased from about two to seven weeks.

In the Golfech 1 reference unit, pH was around 6.8 at 300°C at the beginning of the second conversion cycle (similar to first conversion cycle) and 2 to 3 days were needed to reach 6.9. It took overall about 24 weeks to reach a pH of 7.2 at 300°C. In Cattenom 2, pH at the beginning of the cycles was always above 6.9 at 300°C, and 25 weeks were needed during the second conversion cycle to reach a pH of 7.2 at 300°C. However, just before criticality, pH is better controlled in Cattenom than in Golfech.

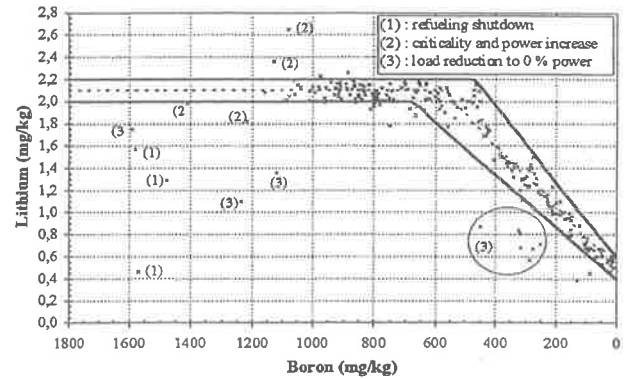


Fig. 3 : Golfech 1, 2nd conversion cycle : B-Li diagram

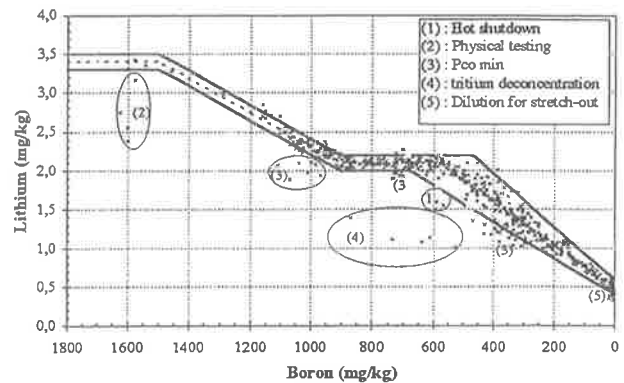


Fig. 4 : Cattenom 2, 2nd conversion cycle : B-Li diagram

Table 2 : Boron at hot zero power and full power

	GOLFECH 1 (mg/kg)		CATTENOM 2 (mg/kg)	
	B at hot zero power	B at full power	B at hot zero power	B at full power
Last cycle before conversion		970		1020
1st conversion cycle	~ 1450	1020	~ 1480	1020
2nd conversion cycle	~ 1450	1010	~ 1580	1100

Water and boron makeups may generate oxygen ingress in RCS which may impact the coolant-materials interactions. Table 3 summarises the makeups volumes in RCS during the first two conversion cycles in Golfech 1 and Cattenom 2. The greater makeup volumes in Golfech 1 compared to Cattenom 2 can be explained by more load following in Golfech. Similarly, the smaller volumes used during the second conversion cycle on both units compared to the first conversion cycle is explained by less load variations.

Table 3 : Golfech 1 and Cattenom 2 makeups to RCS

Conversion cycle	Makeup water		Boron makeup water	
	Volume (m ³)	Mean dissolved O ₂ (µg/kg)	Volume (m ³)	Mean dissolved O ₂ (µg/kg)
Golfech 1				
1	12304	37	827	1700
2	9242	49	714	1777
Cattenom 2				
1	9600	45	467	2200
2	8528	51	444	1523

In table 4 are reported the results of corrosion products measurements performed in Golfech 1 and Cattenom 2 during power increase at the beginning of the conversion cycles or during power decrease before refueling shutdown. These results agree with the values typically observed in French plants. For both units, a significant increase of soluble nickel is observed between the beginning of the first and second conversion cycle. In Golfech 1, higher chromium values can also be noted. These data should be discussed further after the third conversion cycle is completed in both units.

Table 4 : Soluble corrosion products in Golfech 1 and Cattenom 2

Unit	Conversion cycle	% Power	Ni (ng/kg)	Co (ng/kg)	Cr (ng/kg)
Power increase at beginning of conversion cycles					
GOL 1	1	100	350	6	1600
GOL 1	2	100	3170	10	1190
CAT 2	1	8	11000	<DL	60
		50	140	<DL	50
		100	260	<DL	230
CAT 2	2	8	1355	22	117
		50	453	<DL	764
		100	1012	<DL	NA
Power decrease at end of conversion cycles					
GOL 1	2	70	215	<DL	190
		0 (290°C)	20000	NA	800
		0 (175°C)	862000	NA	900
CAT 2	2	75	890	<DL	690
		0 (286°C)	610	NA	1150
		0 (175°C)	>200000	NA	3210

DL = Detection Limit = 4 ng/kg Co ; NA = Not Available

Radiochemistry

Spectrogammaometry was used to measure cobalt 58, cobalt 60 and chromium 51 in RCS during the first two conversion cycles in Golfech 1 and Cattenom 2. Activities

are overall below :

- 30 MBq/t for ⁵⁸Co in Golfech and 40 MBq/t in Cattenom ;
- 5 MBq/t for ⁶⁰Co in both units ;
- 30 MBq/t for ⁵¹Cr in Golfech and 20 MBq/t in Cattenom.

Some higher activities could sometimes be observed, most of them related to significant makeups or load reductions to 0 % power.

The activities measured during shutdowns are presented in table 5.

Table 5 : Shutdown activities

	Golfech 1		Cattenom 2	
	⁵⁸ Co peak activity (GBq/t)	Total released activity (GBq)	⁵⁸ Co peak activity (GBq/t)	Total released activity (GBq)
Last cycle before conversion	160	100000	165	100000
1st conversion cycle	170	60000	207	134000
2nd conversion cycle	105	70000	197	135000

NA = Not available

In Golfech 1, the cobalt 58 peak activity was lower for the second conversion cycle than for the previous two cycles, whereas the total released activity slightly increased from the first to the second conversion cycle. In Cattenom 2, activities remained overall stable between the first and the second conversion cycle. So today, no significant effect of the conversion cycles is observed.

Deposits

Cobalt 58 and cobalt 60 surface activity were measured on steam generators (SG) tube bundle, hot legs (HL) and crossover legs (CL) : results are reported in tables 6 and 7 for Golfech 1 and Cattenom 2 respectively. Moreover, dose rates were measured around steam generators and legs (table 8). Compared with the previous two cycles, the results from the second conversion cycles show that :

- ⁵⁸Co activity seems stable, or slightly decreasing in both units, except on Cattenom 2 steam generators where an increase has been observed for the last cycle (figure 5). However, these variations are typical for ⁵⁸Co ; they are usually observed on plants and also in Cattenom 2 before the first conversion cycle ;
- ⁶⁰Co activity has increased in Golfech 1 since the beginning of conversion. The origin of this increase is probably an abnormal input of cobalt (i.e. stellites), because this nuclide is the only concerned. An analysis of the behaviour of other 1300 MWe units will probably confirm this hypothesis ;
- ⁶⁰Co activity seems stabilised, or slightly decreases in Cattenom 2, after an increase at the end of the first conversion cycle ;
- dose rates seem stable in both units. Some values presented in table 8 can be explained by fuel rod

clad failures prior to conversion and dose rates impacted by fission products.

Except on Cattenom 2 steam generators, cobalt 58 surface activities tend to decrease.

Overall, at the end of the second conversion cycle, deposited activities in Golfech 1 and Cattenom 2 do not show any peculiar trend compared to usual French results. These trends should be confirmed after the third conversion cycle is completed in both units.

Table 6 : Surface activity in Golfech 1

	SG (GBq/m ²)		HL (GBq/m ²)		CL (GBq/m ²)	
	⁵⁸ Co	⁶⁰ Co	⁵⁸ Co	⁶⁰ Co	⁵⁸ Co	⁶⁰ Co
Last cycle before conversion	2.4	0.3	1.8	0.7	4.3	0.6
1st conversion cycle	2.3	0.5	1.5	0.9	3.7	0.8
2nd conversion cycle	2.4	0.6	1.2	2.0	3.5	1.0

Table 7 : Surface activity in Cattenom 2

	SG (GBq/m ²)		HL (GBq/m ²)		CL (GBq/m ²)	
	⁵⁸ Co	⁶⁰ Co	⁵⁸ Co	⁶⁰ Co	⁵⁸ Co	⁶⁰ Co
Last cycle before conversion	2.1	0.5	2.3	1.5	1.7	0.7
1st conversion cycle	2.2	0.6	1.5	1.8	1.5	0.7
2nd conversion cycle	3.2	0.6	1.4	1.0	1.7	0.6

Table 8 : Dose rates

	Golfech 1 (mSv/h)		Cattenom 2 (mSv/h)	
	SG	Legs	SG	Legs
Last cycle before conversion	0.11	0.28	0.15	0.27
1st conversion cycle	0.14	0.40	0.12	0.22
2nd conversion cycle	0.13	0.26	0.15	0.29

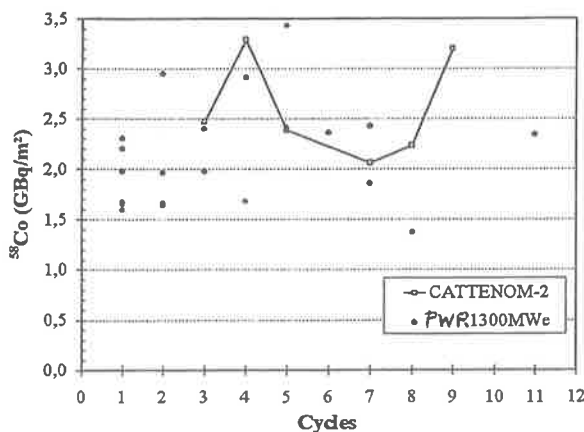


Fig. 5 : Cobalt 58 activity on SG tubes bundle in Cattenom 2 and other French 1300 MWe PWRs

Fuel assemblies :

In order to assess the impact of the reactor coolant chemistry on the fuel cladding corrosion, oxide thickness measurements and crud analyses were planned on characterised fuel assemblies loaded in the Golfech 1 and

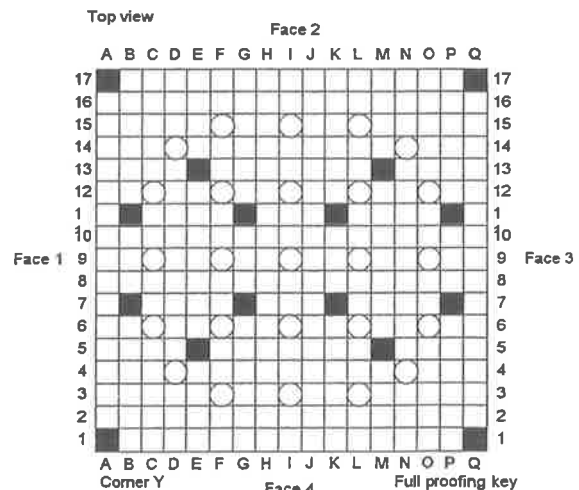
Cattenom 2 reactors.

Four characterised fuel assemblies were loaded in both the Golfech 1 and the Cattenom 2 reactors. The fuel rods claddings are made of Zircaloy-4, alloy M4 or alloy M5TM. Each alloy comes from the same tube batch. The chemical composition of the alloys is reported in table 9.

The fuel rods were loaded into eight assemblies so as to distribute uniformly all the rods cladding batches into each assembly. Their distribution in the assemblies is shown in figure 6. Concerning the advanced alloys, the location of the corresponding rods were chosen in order to be able to measure zirconia layer thickness along four axes 90° apart. However, some of them were also loaded in peripheral location in order to run in-depth visual examinations.

Table 9 : Chemical composition of fuel rods cladding alloys

Alloy	Sn (%)	Nb (%)	Fe (%)	Cr (%)	V (%)	O (%)
Zircaloy-4	1.2-1.5		0.2	0.1		0.12
M4	0.5		0.5		0.5	0.12
M5 TM		1				0.12



Legend : black squares : rods with cladding other than Zircaloy 4
empty circles : guide tubes

Fig. 6 : Characterised assemblies location map

The zirconia layer thickness measurements were performed using the blade device developed by FRAMATOME, based on the principle of measurements by the Eddy Current technique [5].

During each cycle outage, the device is installed on a criss-cross measurement table, allowing blade insertion into each row of rods at a chosen measurement altitude.

All analysed rod, particularly those with claddings made of advanced alloys, are therefore measured during blade insertion and extraction from all four assembly faces leading to more than 2000 measurements collected per campaign. Statistical process using the « Lagos » and « Zircone » software programs is used for this analysis. The measurement uncertainty is estimated to be ± 5 µm.

During the first two conversion cycles, neither in core

axial offset anomalies nor abnormal cruds on assemblies had to be reported. Hence, only oxide thickness measurements were carried out on fuel rods.

Concerning Zircaloy-4, the maximum oxide thicknesses measured at Golfech 1 and Cattenom 2 at the end of each cycle are plotted on figure 7. For both reactors and given the burnups reached, the results are within the scattering generally observed on this alloy in French (900 and 1300 MWe) and foreign reactors implementing a 2.2 mg/kg maximum lithium chemistry.

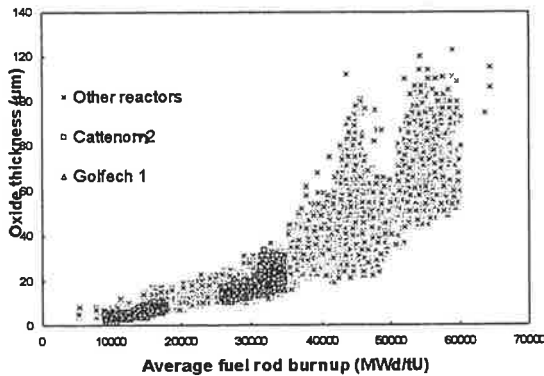


Fig. 7 : Zircaloy 4 external corrosion experience

Similarly, the results obtained on the advanced alloys on both reactors, are within the scattering observed on these alloys in French (900 and 1300 MWe) and foreign reactors implementing elevated lithium chemistry (figures 8 and 9, alloy M4 and M5TM respectively).

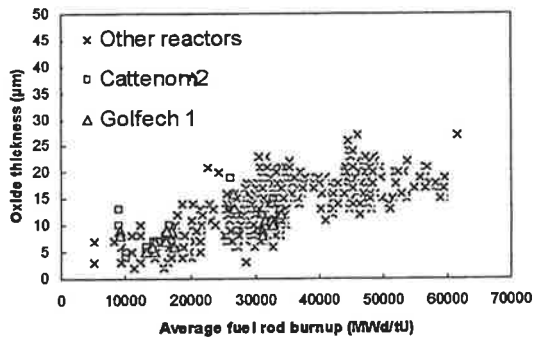


Fig. 8 : Alloy M5TM external corrosion experience

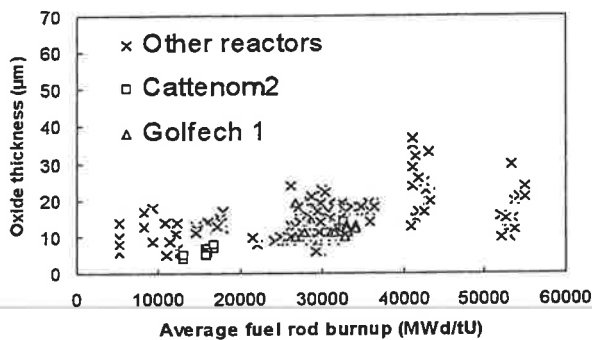


Fig. 9 : Alloy M4 external corrosion experience

The high lithium chemistry does not seem to have an obvious impact on the corrosion behaviour of fuel cladding during the first two cycles.

Discussion

The results of the DUO experimentation surveillance program show a good behaviour of the fuel cladding in the Cattenom 2, the pilot unit implementing EDF modified chemistry with maximum authorised lithium concentrations of 3.5 mg/kg at the beginning of the cycles.

There is no significant difference in both units behaviour (contamination and mass transport), other than the differences that were existing prior to the beginning of the DUO experimentation.

The results from the third conversion cycles will be important to confirm the observed trends.

No axial offset anomaly has been noticed in Golfech 1 and Cattenom 2, nor in all the twenty EDF 1300 MWe units on-going conversion cycles ; most of these 20 units already began their third conversion cycles, being thus confronted to the worst conditions at the beginning of the cycles.

This reinforces the position on which all the specialists agree, stating that core features are also an important factor which is not taken into account into the DUO experimentation [6].

From these results, it appears possible to improve pH at beginning of cycles, beneficial to a better behaviour of RCS. It can be noticed that the impact of boron concentrations up to 1800 mg/kg at beginning of cycles can be managed with EDF modified chemistry, ensuring $\text{pH}_{300} \geq 6.9$.

Studying operating with a constant lithium concentration of 3.5 mg/kg could also be of interest in order to reach optimum $\text{pH}_{300} = 7.2$ as soon as possible.

Non destructive steam generator tubing examinations proved that no abnormal corrosion due to elevated lithium concentrations occurred on 600 TT alloy, since the beginning of extended cycle operation in Cattenom 2. These results will have to be confirmed after the completion of the third conversion cycle.

Conclusion

Given today's core design of French plants and the available results from the DUO experimentation, extended cycle operation with a low pH at the beginning of the cycle does not seem to generate any significant crud deposits on fuel rod cladding. Hence, no axial offset anomaly nor increase of dose rates due to the presence of crud deposits has been observed. However, a few more cycles with elevated initial boron concentrations are needed to assess the influence of increased cycle length on dose rates.

Oxide thickness measurements results show that operating with EDF modified chemistry, hence lithium concentrations up to 3.5 mg/kg at the beginning of the cycles, is encouraging. No influence of elevated lithium concentrations was observed on oxide thickness and advanced fuel cladding alloys show a good behaviour.

While any beneficial impact of a constant pH of 7.2 at 300°C during throughout the cycle on dose rates is not proved, the easy implementation of increased lithium concentration at the beginning of the cycles seems to be enough to face issues due to French 18-months extended cycles management. However, the examination of the French 1300 MWe behaviour after complete conversion to extended cycles is essential to conclude on the DUO experimentation.

Achieving very high burnups (60 GWd/tU) or issues with waste management could lead EDF to change its strategy and examine again the possible use of enriched boron 10. According to recent studies carried out in the Robust Fuel Program, the impact of boron on flux anomalies will also have to be taken into account when defining EDF strategy on using enriched boron 10.

Today, given the pH improvement obtained by operating EDF modified chemistry with increased lithium concentrations up to 3.5 mg/kg at the beginning of fuel cycles, generalising this chemistry regime to all the French plants will be considered.

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