AUTOMATIC CONTROL OF THE LITHIUM CONCENTRATION OF THE REACTOR COOLANT IN PWR PLANTS.

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Introduction

Under normal operating conditions, the long-term control of reactivity in pressurised water reactors (PWR) is achieved by varying the boric acid concentration in the reactor coolant. The aim of adjusting the lithium hydroxide content (^{7}LiOH) is to maintain the reactor coolant at an alkaline value, so as to compensate for the effects of boric acid on the materials in contact with the reactor coolant. The *pH* has been set at 7.2 (at 300°C) for PWR in operation in France, thanks to the lithium – boron graph known as the "co-ordinated chemistry diagram" (figure N°1).

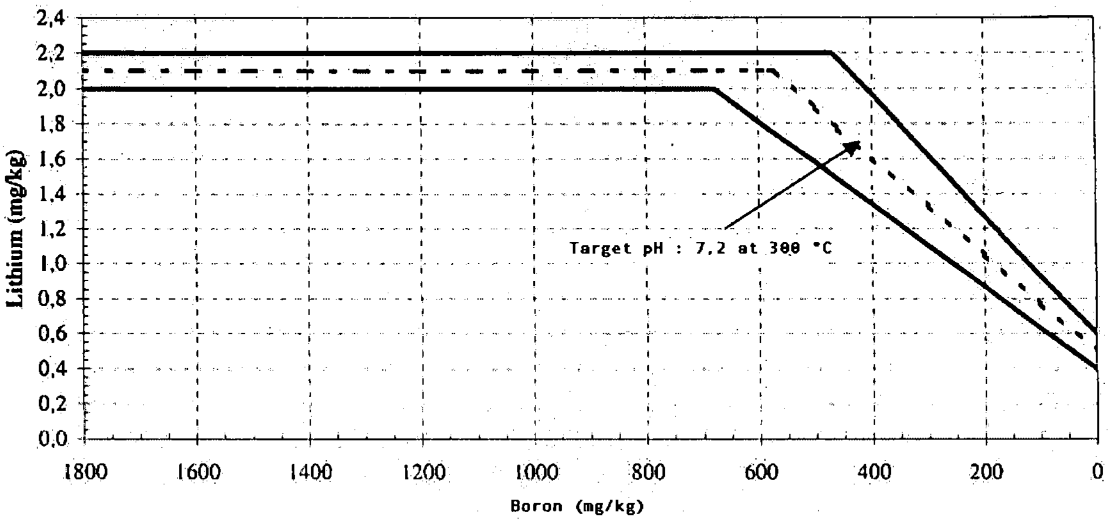


Figure 1: Co-ordinated chemistry at *pH* = 7.2 (300°C).

Observance of the *pH* is a fundamental factor in the control of reactor coolant chemistry. It contributes mainly to the optimisation of the production and transport of corrosion products. The consequences of failure to observe the *pH* of the reactor coolant, particularly by exceeding the low *pH* limits through a lack of lithium (^{7}Li) relative to the expected value, are therefore the dissemination of corrosion products, giving rise to well-known problems of contamination. The dose rates incurred while performing maintenance operations during unit outage are increased as a consequence [1]. Other problems that may arise are those of anomalies in neutron flux of the "axial offset anomaly" (AOA) type, which especially affect cores with a high rate of burn-up [2], or even in certain cases an observed drop in the expected rate in the primary loops [3, 4]. Conversely, when the high *pH* limits are exceeded due to an excess of ^{7}Li relative to the expected value (mainly by natural nuclear reaction: $^{10}B(n,\alpha)^7Li$), this can result in corrosion phenomena on the fuel cladding [1, 3].

In contrast to the majority of the other plant operators throughout the world who operate their PWR plants at base load, French PWR units are operated in load follow mode. This practice makes it possible to adjust the generation of electricity to consumption (approximately 80% of French power production is of nuclear origin). Operation in load follow mode is maintained throughout almost the entire fuel cycle, apart from the stretch-out phase. Typically, this operating mode gives rise to several drops and rises in load over the course of a single day on the units in question, with amplitudes possibly going from full power to the technical minimum.

However, for the purposes of neutron control, the successive variations in power are accompanied by boration and dilution operations, which in turn constitute water movements that disturb the ^{7}Li concentration, causing the lower threshold of the lithium-boron diagram to be exceeded and jeopardising observance of the "target" *pH* value of the reactor coolant (figure N°2).

Figure 2a : power evolution

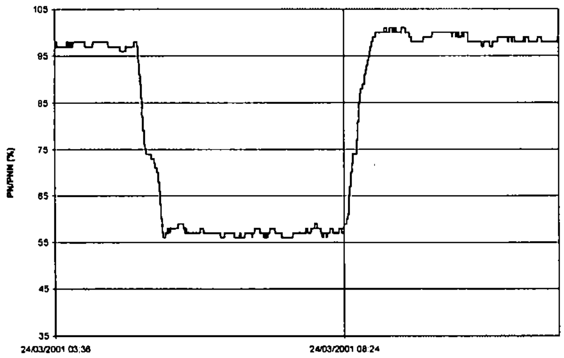


Figure 2b : boron evolution

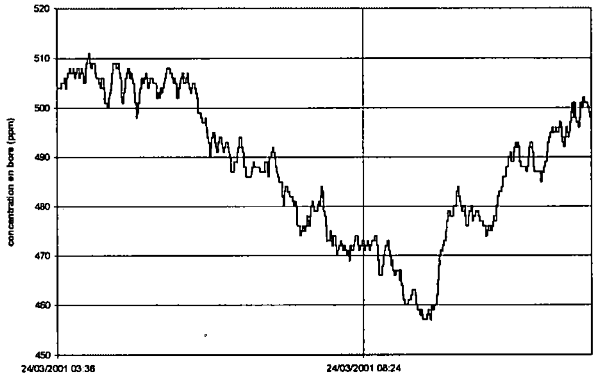
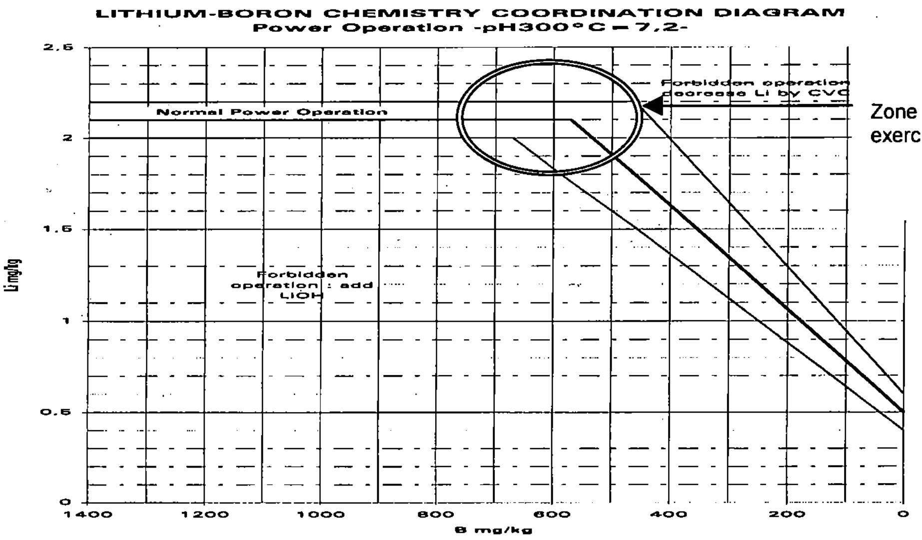
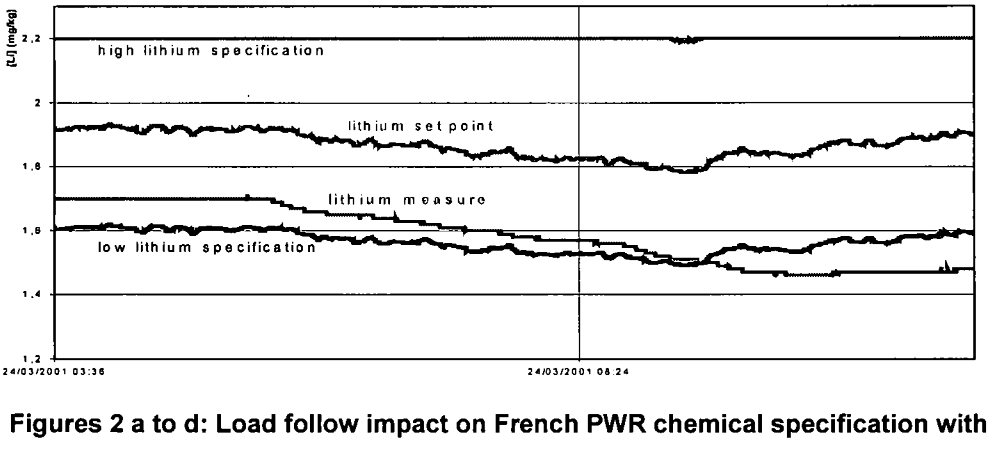


Figure 2 c: Co-ordinated chemistry at *pH* = 7.2 (300°C).



Zone of the exercise

Figure 2d : Load follow without lithium content correction



Figures 2 a to d: Load follow impact on French PWR chemical specification without ^{7}Li

The chemists employed at the plants are responsible for ensuring that the lithium-boron diagram is observed, which is a chemical specification linked to nuclear safety. When a unit is operated in load follow mode, it is necessary to readjust the ^{7}Li concentration several times when a stable full power state is reached (sampling of reactor coolant; laboratory analysis of the ^{7}Li concentration; comparison of the result with the expected value; if ^{7}Li is lacking, preparation and manual injection on the charging side of the CVCS of a suitable dose of ^{7}LiOH). This operation involves several chemistry technicians and can take from one hour to several hours depending on the circumstances: work performed during normal working hours or on call-out (as the power variations occur most frequently at weekends). This implies that the time required to return to the correct *pH* can prove to be very long. Furthermore, on account of the initial design, it is not possible to compensate in real time each time the upper and lower limits of the lithium-boron diagram are exceeded.

Countermeasures, consisting in conditioning water and boric acid makeup tanks with ^{7}LiOH, have been used. However, these countermeasures are difficult to implement, particularly for power plants built as pairs of units, which have a common makeup circuit and in which the overall boron concentration of the reactor coolant is generally different for each reactor. Furthermore, they require the handling of large quantities of ^{7}LiOH, often under unsuitable conditions (risks linked to personnel safety). They can also constitute a risk of serious operating error (e.g. over conditioning that can lead to accidental overshoot at high *pH*).

Given the specific operating mode of French units, observance of the lithium-boron diagram and consequently observance of reactor coolant *pH* is considered to be a priority relative to management of ^{7}Li (^{7}Li recycling practices or prototypes [5]). For this reason EDF and FRAMATOME-ANP have developed an automatic lithium hydroxide injection device, which serves to compensate in real time whenever the upper or lower limits of the lithium-boron diagram are exceeded and to prevent excursion at low *pH*. A prototype of this device is installed on unit N°2 of Tricastin NPP. The purpose of this document is to describe its principles and the main characteristics, to provide experience feedback on its operation and to present its potential.

Description of the automatic lithium hydroxide injection device

The automatic lithium hydroxide injection system consists of:

- a conductivity measurement equipment used to determine the lithium concentration,
- a central unit that serves to generate the command to the automatic injection device on the basis of the acquisition and the processing of certain process parameters,
- a compact electro-mechanical assembly (the SKID) that ensures the injection of lithium hydroxide by a connection to the process via the CVCS.

The SKID

At first, a lithium hydroxide solution with a lithium content of 5000 mg/kg is made up by the operator in a preparation tank equipped with a heater and a stirrer and then transferred to the main feed tank by means of a transfer pump. The solution is then ready for injection. Injection is actuated by opening of an air-operated valve and start-up of a dosing pump. The latter allows the rate of injection into the reactor coolant system to be adjusted from 0 to 10 l/h. In order to avoid the risk of air being injected into the reactor coolant system by the dosing pump, two redundant level sensors serve to stop the pump when the low-low threshold is reached in the main feed tank. The start-up or shutdown of the SKID, as well as the adjustment of the rate of injection, are controlled by a central I&C unit (INFI 90). The SKID delivers to the reactor coolant system through a connection on a stuboff located on the return line of the pump seal system and the miniflow lines of the CVCS charging pumps.

The central I&C unit

The central I&C unit is structured around the "INFI-90" programmable logic controller, which receives all the process measurements, determines the lithium concentration of the reactor coolant in real time and controls lithium hydroxide injection. This PLC controls the SKID equipment by means of a relay and power cabinet. A switch located on the cabinet allows the operator to take over control of the SKID in manual mode. The PLC is connected to a PC that serves to enter the data and to view the results.

The measurement of lithium concentration

The PLC determines the concentration of lithium in real time on the basis of a measurement of the electrical conductivity provided by a probe. The probe is supplied with reactor coolant taken from the nuclear sampling system. The measurement line is equipped with a hand-operated valve to isolate it and a flow gauge to ensure that the measurement is representative. The conductivity measurement probe is connected to the central I&C unit by means of a transmitter.

Figure 3 :

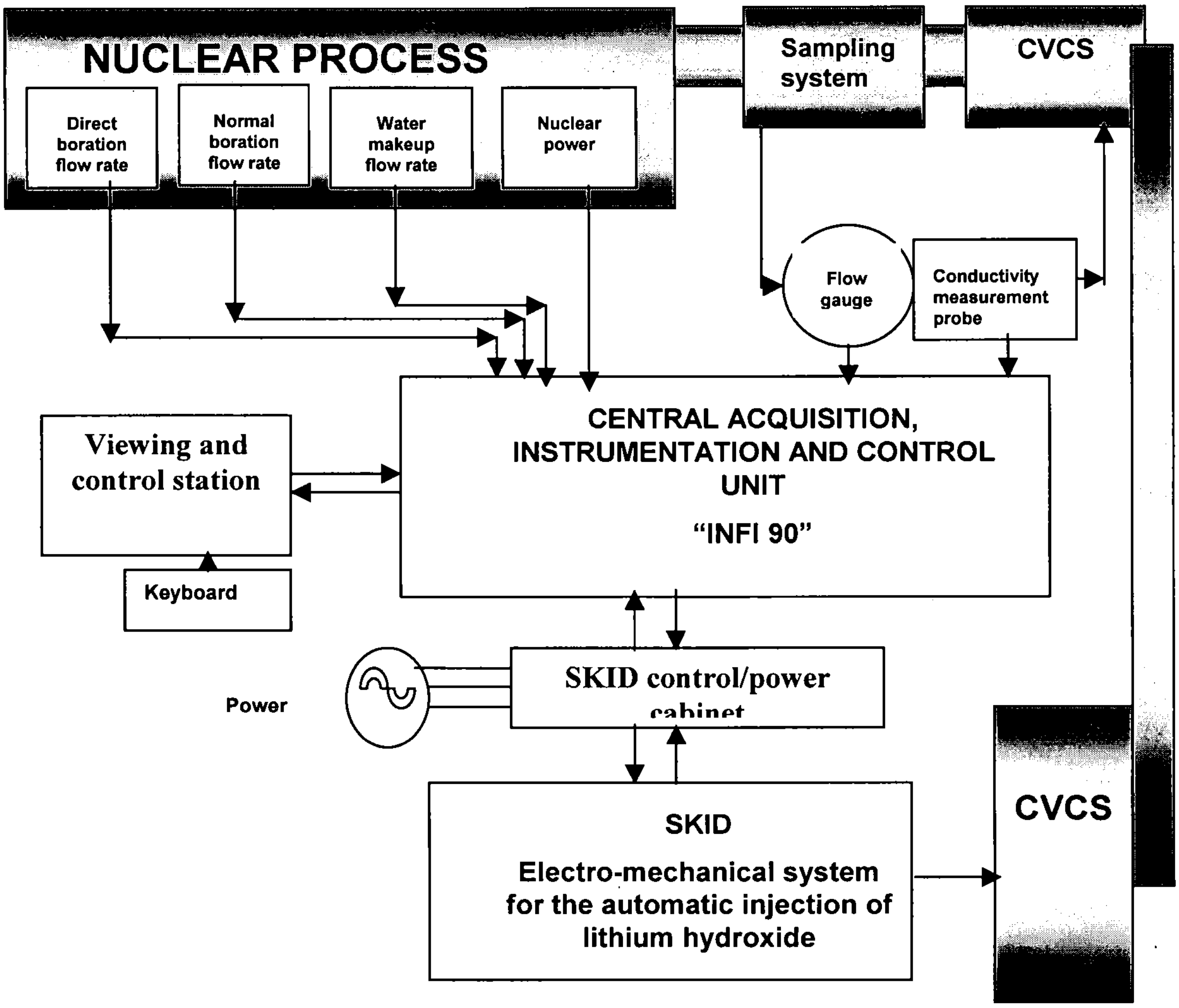
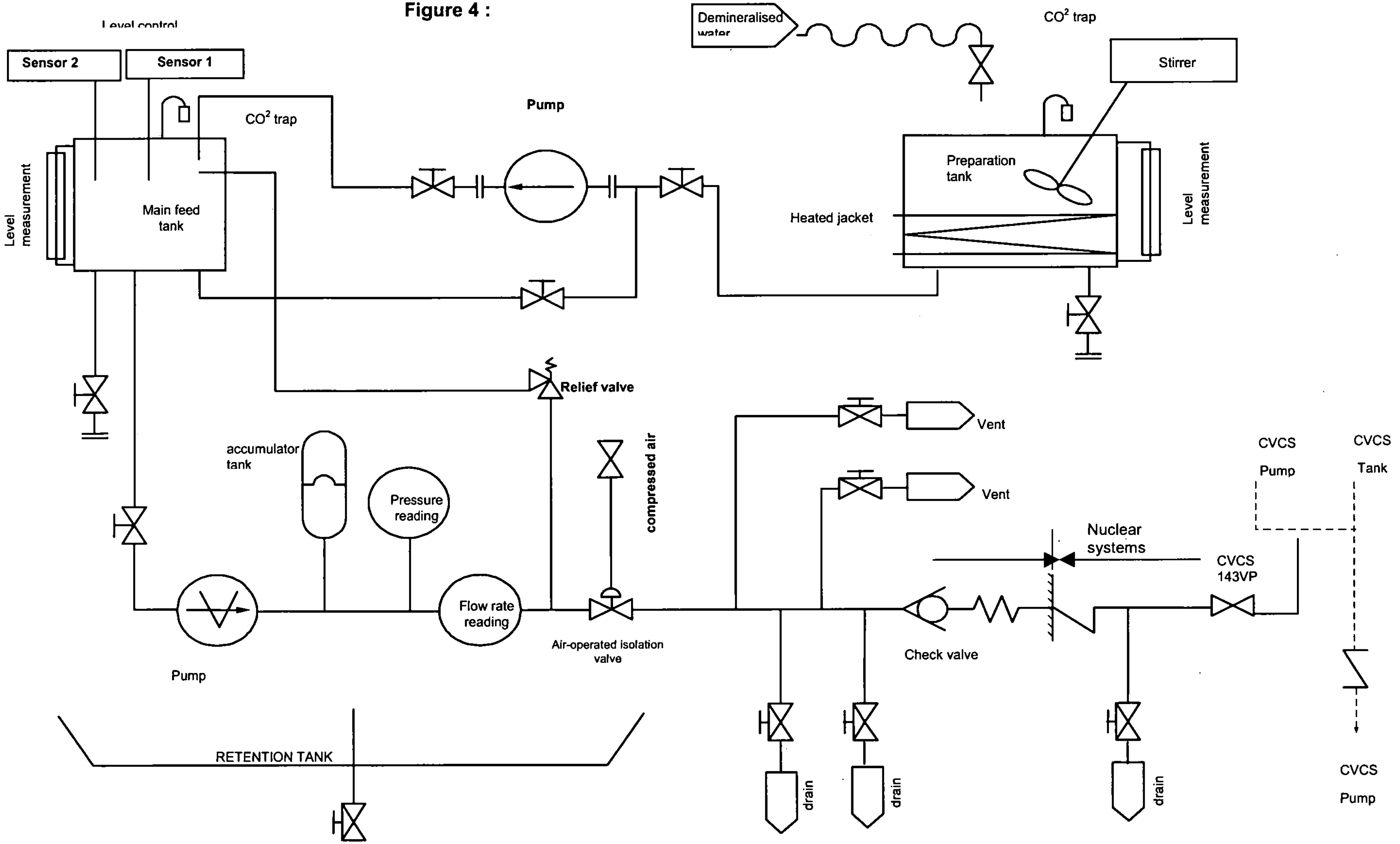


Figure 4 :


Level control
Sensor 2
Sensor 1
Level measurement
Main feed tank
CO² trap
Pump
Demineralised water
CO² trap
Stirrer
Preparation tank
Heated jacket
Level measurement
Relief valve
Vent
Vent
accumulator tank
Pressure reading
compressed air
CVCS Pump
CVCS Tank
Nuclear systems
CVCS 143VP
Flow rate reading
Air-operated isolation valve
Check valve
Pump
RETENTION TANK
drain
drain
drain
CVCS Pump

Online lithium measurement

The lithium concentration is determined on the basis of electrical conductivity, the value of which is converted to lithium concentration by calculation.

Measurement principle

The lithium concentration is calculated on the basis of the conductivity and the dissociation constants of the various chemical balances involved in boric acid/lithium hydroxide/water media.

Analytical formulae have been established and two coefficients ($□_1$ and $□_2$) were introduced in order to allow for the influence of impurities on the measurement.

The calculation of lithium concentration is carried out in two phases:

a) Calculation of the [H^+] concentration and therefore of the pH of the solution:

$$pH = pHFunction\{(\lambda_{\mu S/cm} - \beta_1), [CB]\}$$

b) Calculation of lithium concentration:

$$(CLi)_{mg/kg} = conductivityFunction\{(\lambda_{\mu S/cm} - \beta_2), [CB], pH\}$$

where: *[CB]* = overall boron concentration in the fluid in mg/kg,

CLi) = lithium concentration in the fluid in mg/kg,

pH = calculated pH of the medium

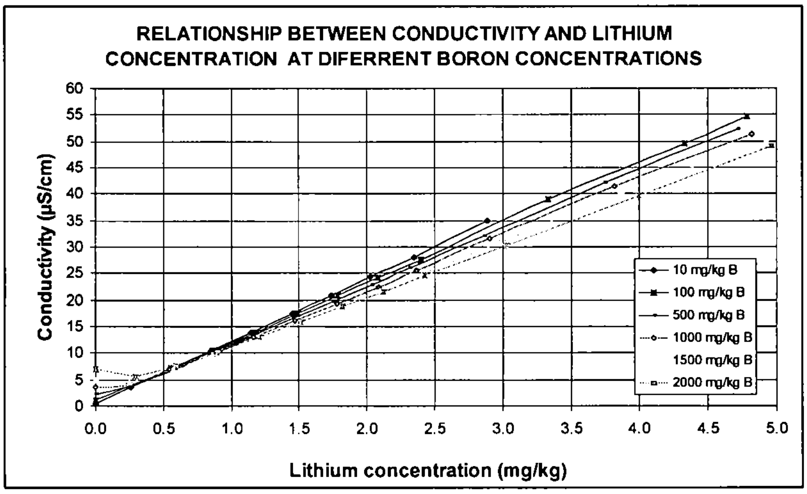
$□_1$ and $□_2$ = corrective terms to compensate for impurities.

Validation of the measurement method

Tests were carried out in the analytical chemistry laboratory of the Université de Pau (France) to validate the method of determining the lithium concentration on the basis of a measurement of conductivity.

The validation test showed that the relationship between the conductivity measurement and the lithium concentration depended on the boric acid concentration, as can be seen on the graphs below.

Figure 5: Relationship between conductivity and lithium concentration at different boron concentrations



The validation tests also showed that the lithium measurement, calculated on the basis of a measurement of conductivity, gave values that agreed, for a wide range of overall boron concentrations, with the measurements obtained in parallel using atomic absorption spectrophotometry (AAS).

Figure 6a: Comparison of lithium measurements obtained by conductivity and AAS – boron concentration of 500 mg/kg

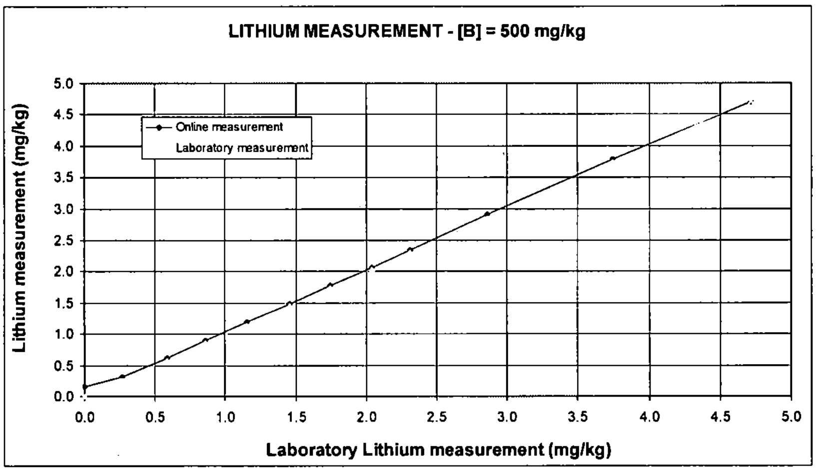
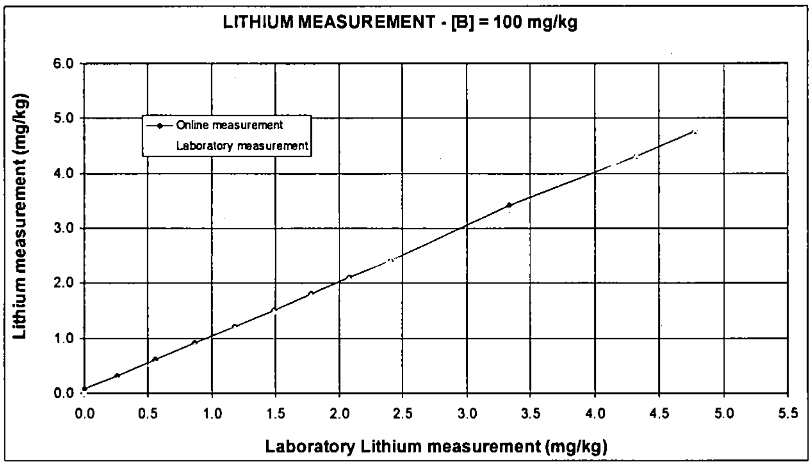


Figure 6b: Comparison of lithium measurements obtained by conductivity and AAS – boron concentration of 100 mg/kg

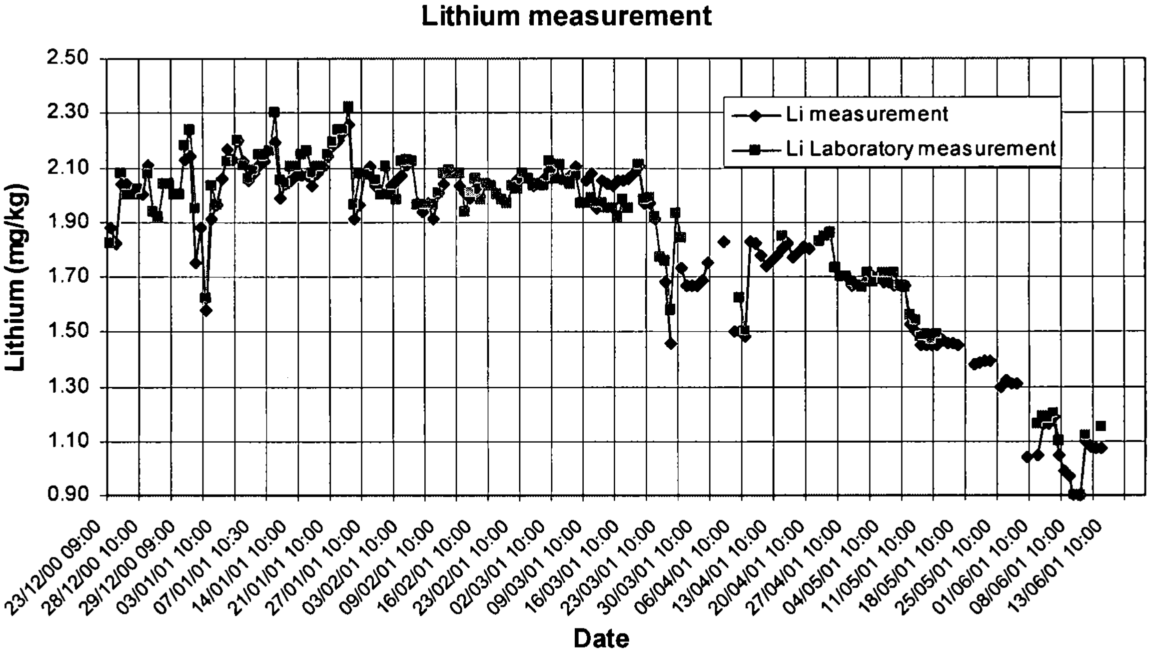


Outcome of measurements on site

During the validation campaign on the prototype installed at Tricastin, the plant's laboratory carried out regular analyses of the lithium concentration in the reactor coolant using AAS, in parallel with the concentrations calculated by the PLC.

The results obtained are represented on the graph below.

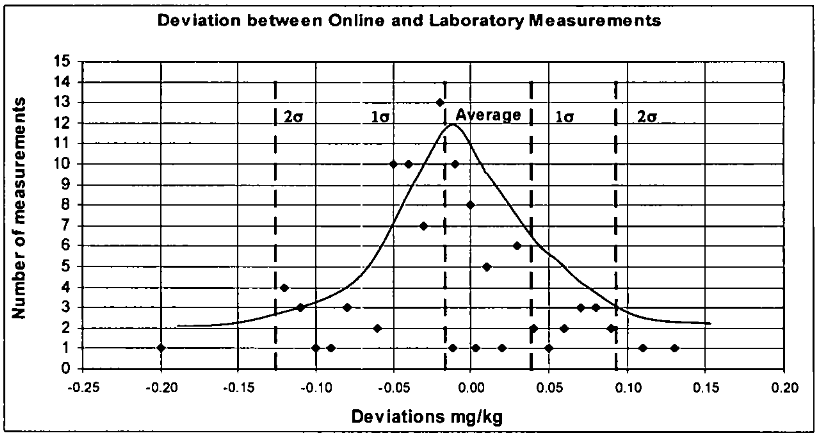
Figure 7: Comparison of lithium measurements obtained by conductivity and by AAS – outcome of on-site measurements



Analysis of the results showed that the measurements obtained by the PLC are correct.

However, for certain points of measurement, more significant deviations between the automatic measurements obtained by conductivity and the manual measurements obtained using AAS (> 0.1 mg/kg of Li) were observed. The deviations are generally due to a lack of anticipation in the correction of the effect of ionic impurities on the measurement (coefficients $\square_1$ and $\square_2$).

Figure 8: Deviation between online and laboratory measurements



The table below shows the confidence interval of the measurement for various probabilities.

Table 1: Deviation between online and laboratory measurements

Deviation between automatic and manual measurements □Li (mg/kg)	
97 % of measurements (2 □□	± 0.11
72 % of measurements	± 0.05

It can be seen from the above table that: ~ 97 % of the measurements are given to ± 0.11 mg/kg,

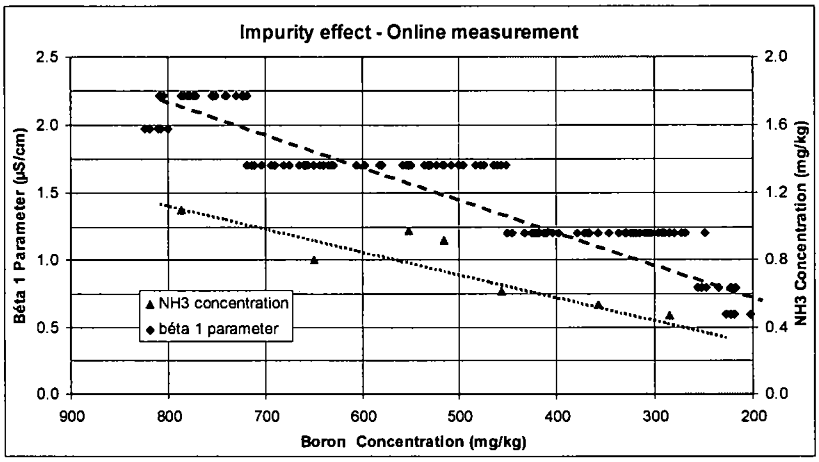
and that ~ 72 % of the measurements are given to ± 0.05 mg/kg.

To conclude, it can be considered that the lithium measurement response is correct.

Influence of impurities on the measurement

Monitoring of impurities in the reactor coolant showed that the most important pollutant was NH_3 (a product of the reaction of N_2 with the products of radiolysis of water), as the other pollutants measured (Cl, F, NO_3, SO_4) were less than or equal to the analysis detection limit (< 5 µg/kg) during the test campaign.

Figure 9: Impurity effect - Online measurement



From the above graph it can be seen that the coefficient $□_1$ is effectively a function of the NH_3 content in the reactor coolant and the coefficient increases as an absolute value with the concentration in NH_3.

- $□_1$ varies from 2.2 at the beginning of the cycle, for 1.1 mg/kg of NH_3, to 1.2 at the end of the cycle, for 0.4 mg/kg of NH_3.

Experience feedback

In order to validate the automatic lithium hydroxide injection (PLC), variations in reactor power were scheduled. These variations are accompanied by modifications in the boron concentration that lead to excursions in lithium concentration into the low pH zone of the boron-lithium diagram.

For each dilution and boration of the reactor coolant, the PLC evaluates the need for lithium, in real time, and injects the appropriate quantity of lithium hydroxide.

The prototype described in the previous paragraph was therefore tested on unit 2 of the Tricastin NPP (900MWe) during the first half of 2001.

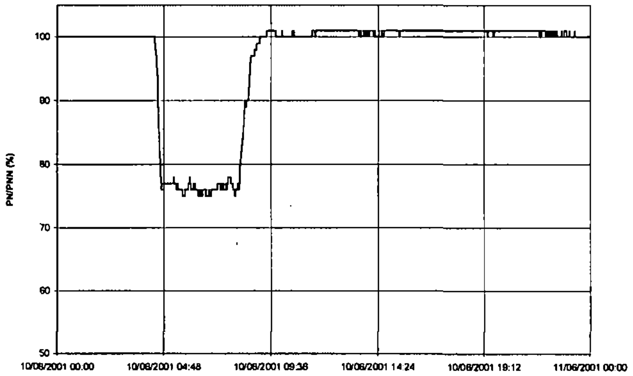
Observance of the chemical specifications

25 load reduction transients were carried out, which made it possible to confirm the results obtained during the initial computer simulations: the FRAMATOME-ANP control fulfilled the expectations in terms of observance of the boron/lithium correlation.

The lithium concentration was maintained constantly within the limits of the boron/lithium diagram (deviation less than 0.05mg/kg relative to the reference lithium value).

An example of a load reduction transient is given in figures 10a to 10e and shows PLC performance.

Figure 10a : Nuclear power curve during a load follow



Figures 10b : Boron content curve during a load follow

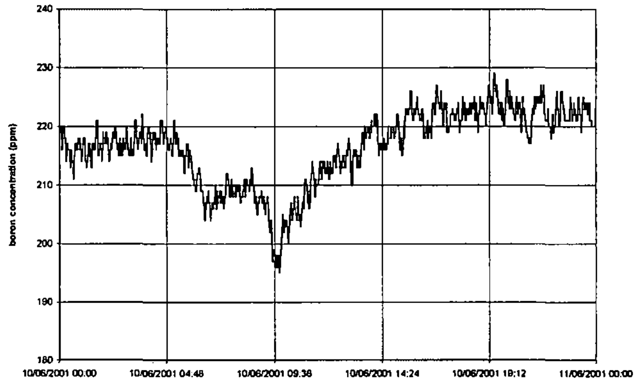


Figure 10c : Water handling curve made by operators (borication) during this load follow

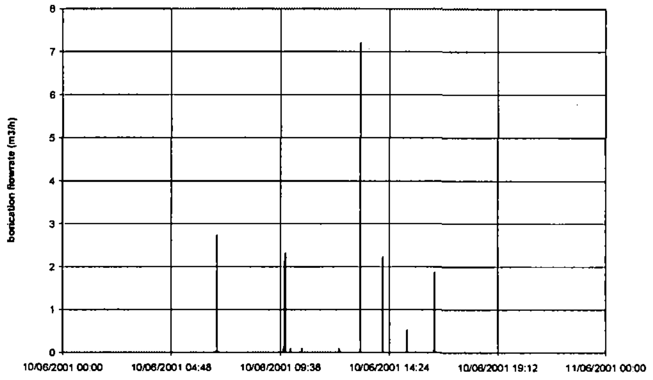


Figure 10d : Water handling curve made by operators (dilution) during this load follow

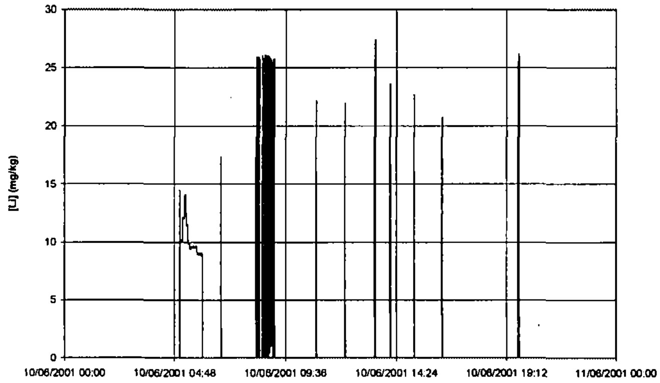
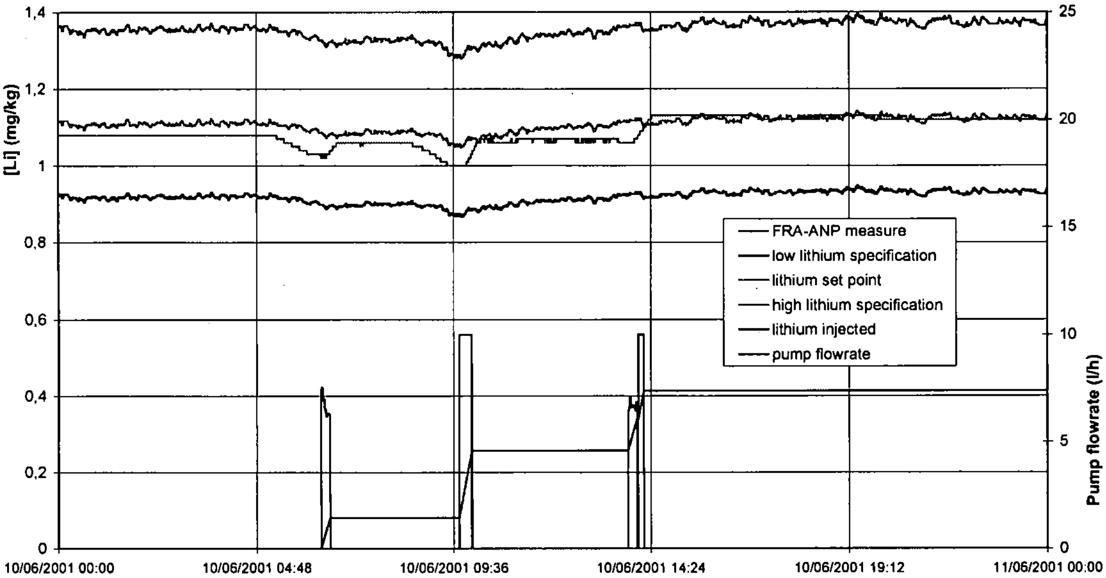


Figure 10e : 7Li content monitoring by automatic injection during a load follow transient



On this transient, the automatic lithium hydroxide injection system was actuated 4 times for a total period of 53 minutes. The system starts up:

- either when the deviation between the measurement and the reference is too great (>0,05mg/kg), under the effect of the closed regulation loop,
- or when major water movements (dilutions for example) give rise to a significant drop in lithium hydroxide concentration in the reactor coolant, under the effect of the open regulation loop.

In this case, the quantity of lithium hydroxide solution injected was 7.4 litres.

Thus minor actuation of the injection equipment allowed the reference lithium hydroxide specification to be followed very closely.

Perspectives

After a period of familiarisation with the prototype, the site chemists soon appreciated the system for the ease with which it allows the chemical specifications to be guaranteed efficiently.

The grounds for their judgement are as follows:

- the reduction in operating constraints associated with the preparation of the lithium hydroxide solution and its injection,
- good ergonomics achieved thanks to the viewing and control station, allowing the monitoring, recording and analysis of all the important physical parameters.

In the light of this favourable feedback, EdF envisages the generalisation of this prototype to all the plants in operation in France.

References

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[3] - P. Cohen - Water coolant technology of power reactors (American Nuclear Society, 1980).

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