

## CONTROL OF FEEDWATER COMPOSITION OF BWR POWER PLANT

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### Abstract

Corrosion behaviour of fuel element cladding, cycle structural materials and dose rate increase are relevant to physico-chemical characteristics of process coolants and to adopted operational conditions.

A careful control of cycle chemistry, during loading and shutdown periods, is necessary to verify material choices, the polishing system and chemistry specifications.

For this purpose ENEL carried out some preliminary experimental tests employing continuous control system and samples for specific analytical determinations.

The cycle points checked during about two months were :

- main condensate
- condensate after polishing system
- outlet of low pressure heaters
- final feedwater
- inlet and outlet of clean-up system
- drains to condenser.

The physico-chemical analysis were related to corrosion product levels (Cu, Fe, Ni, Co) and water chemistry (pH, conductivity, dissolved oxygen ecc.).

The preliminary results allow to express some considerations about sampling procedures, detection limits and reliability of analytical employed methods.

The acquisition <sup>data</sup> time and some morphological oxide pictures are also showed.

### INTRODUCTION

The evolution of a BWR design definition, which was particularly fast about the 70's (1), accounts for the search of more and more reliable, safe and economical exercise and design choices.

From this viewpoint it is to be seen the evolution of BWR which involved before reaching the present-day structures, on the one hand, a series of changes regarding systems and components (elimination of secondary steam generators, installation of jet pumps inside the reactor, elimination of copper alloy preheaters, pump forward high pressure drains, choice of condensate treatment components etc.) ; on the other, the definition of optimal physico-chemical specifications of process fluids which are connected with the constructive characteristics of the above mentioned components.

Exercise statistical data obtained over the last few years point to the prior need of a good behaviour of structural material, limitation of cycle activity and efficacious heat transfer from surfaces in thermal exchange.

In relation to this we must mention the IGSCC phenomena occurred in thermally altered areas of AISI 304 pipelines from 4" to 28" and the efforts made to limit their effects (2+6), the impact of condenser tightness on cycle, namely cooling water inleakages and copper releases, eventual leakages from condensate treatment system, and resin escapes, the importance of the evolution of <sup>60</sup>Co concentration on cycle activity (7) linked with activation of elements

conveyed by the oxides which detach themselves from pipeline surfaces and/or structural components, valves, internals, etc.) (8+10), the influence of extent and nature of films and/or oxides on tightness of fuel sheaths (11).

All this emphasises the importance of extensive and reliable control of process fluids physical-chemical characteristics of plant in service, as happens more and more frequently all over the world (12+18).

For this purpose ENEL is making several experimental inquiries in order to define throughly the main fluids of Caorso power station cycle by means of specific analyses both in full power conditions and in transient conditions.

## 2. INSPECTIONS PERFORMED

The physical-chemical characterisation of cycle fluids has been performed for Caorso power station. The plant, a BWR-4 with a 840 Mwe continuous nominal power, was built by G.E. and Ansaldo Impianti and started in May 1978.

The main process characteristics and the building choices adopted are given in the sketch of figure 1 and on table 1.

The sampling of fluids concerned with condensate-feedwater cycle (Fig. 1) was performed locally (at polishing inlet-IP, polishing outlet-UP) and by means of lines for the conveyance to rack placed in turbine building (low preheaters outlet-URBP, high preheaters outlet-URAP and drainages conveyed to condenser-RD).

The sampling system used is not homogeneous for all points under control. In particular it is carried out either by means of "fast" loops from which samples are taken, or directly from process pipelines (table 2).

The chemical controls so far performed refer to the determination

of metals present in the cycle (Cu, Fe, Co and Ni) both in soluble and in suspended form, by using a millipore 0,45  $\mu$ m filter and three ion-exchange membranes (Acropar Sa-6406).

The determinations have been reached by means of atomic absorption analysis with graphite furnace, after acid digestion of samples.

During sampling operations we tried to keep: Re  $\geq$  8.000, flow-rate  $\approx$  0,5 l/min and filtered volume  $\geq$  litres (11).

Finally, on some more significant filters, morphological inspections of oxides present were performed by means of electronic scanning microscope with microprobe.

## 3. RESULTS AND DISCUSSION

The examination carried out, which extended over a period of a year and were intensified in the last two months, regard two service conditions of the plant: re-start after scheduled stop and constant load.

Together with the analysis carried out on samples taken from plant, the blanks, the membranes, the millipore filters and reagents were determined in order to quantity, for the elements under examination, their contribution, also in relation to procedures chosen for samples dissolution. The data were therefore processed with statistical criteria in order to determine their dispersion and variation coefficient. It was thus found out that iron and copper concentrations are extremely variable whilst nickel and cobalt ones are generally very low with some anomalous high value which cannot be clearly interpreted.

Also the detention limits of the measurements referring to the whole analytical procedure were determined (table 3).

Successively the significant values of the single chemical species

were found in order to limit the influence of the blank to less than 10 % of the absolute value of determination (absolute analytical value  $\geq 10.35$ , with  $S_b$  blank standard deviation).

Figure 2 shows the concentration data obtained during start-up (from 0 to 77 % of nominal power). Table 4 shows the concentration data, obtained during constant load service, as well as the sampling conditions adopted, which have been already mentioned.

As far as Fig. 2 data (re-start) are concerned, the following considerations are drawn :

- suspended iron and copper are removed from condensate treatment system;
- iron and copper in solution are only partially removed by polishing system.

From an analysis of results, relatively to period of routine service, the following considerations can be drawn :

- iron and copper concentration values, apart from building choices adopted for sampling system, are in compliance with bibliography data (15, 20, 21);
- nickel and cobalt concentration values in cycle are significant in analytical conditions adopted, only at low-and-high pressure heaters outlet, where mean values equal respectively to 200 and 250 ppt for nickel and 80 and 100 ppt for cobalt were found. The latter prove considerably higher than those found in the mentioned bibliography. On the other hand, it has not been possible so far to determine the eventual contribution of sampling line.

Inspections by means of electronic scanning microscopy allowed to identify some recurring morphologies of cycle oxides. In particular Figures 3 and 4 show magnetite and lepidocrocite oxides sampled respectively from polishing inlet and high pressure pre-heaters outlet.

#### 4. CONCLUSIONS

The inspections so far carried out, which regard only a part of this study, allow to point out the importance of the sampling conditions which are to be adopted for the required determinations. In particular, with the analytical methodologies used, sampling volume plays an important role on measurement reliability, considering the significant concentration variations of various chemical species inspected.

Analysis methodologies must be chosen very carefully, also in compliance with chemical characteristics of sampling system used (millipore filters and ion exchange membranes).

The measurement values, for total iron, copper and nickel in constant load service conditions, are similar to those verified in BWR plants of the same generation. Cobalt concentrations are sensibly higher.

Studies are in progress in order to improve the sampling system and to define the most reliable sampling conditions and type of analysis to be adopted for a more satisfactory characterization of cycle fluids.

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<u>SYSTEM-COMPONENT</u>	<u>DESCRIPTION/LOCATION</u>	<u>MATERIAL</u>
1) Condenser	Once-through, river water	Aluminum-brass
2) Condensate treatment	5 precoat filters, 1360 t/h per each filter, velocity 10 m/h	Polipropilene support
3) Low-pressure pre-heaters	Three lines with five pre-heater for each line	A-213, 304 L stainless steel pipes
4) High-pressure pre-heaters	Two lines with one heater	A-213, 304 L stainless steel pipes
5) Vessel, piping etc.	Forged steel with internal cladding	Steel : A-533 cladding : AWS 309SM fuel : Zircalloy
6) Clean-up	Two lines with a precoat filter and on 25 t/h per line mixed bed	Stainless steel filter supports, system lines A-312 TP-304
7) Moisture separators reheaters	Four lines	Carbon SA-423 Gr.1 steel pipes
8) Systems connection piping	Condensate, feedwater, steam drainages	Carbon A-106 Gr. B; A-515 Gr. 65 steel

TABLE 1 - MATERIALS OF SYSTEM AND COMPONENTS EMPLOYED IN CAORSO POWER STATION

Checked points	Sampling device	Sampling line characteristics		
		diametre	length	material
1) Polishing inlet	Sampling from process piping without probe	1/4"	~ 15 m	AISI 304
2) Polishing outlet	Sampling from process piping without probe	1/4"	~ 15 m	AISI 304
3) Low-pressure heaters outlet	ASTM isokinetic probe and fast line to rack	1"	~ 60 m	AISI 316
	Sampling inside the rack without probe	1/4"	2 m	AISI 304
4) High-pressure heaters outlet	ASTM isokinetic probe and fast line to rack	1"	~ 100 m	AISI 316
	Sampling inside the rack without probe	1/4"	~ 3 m	AISI 304
5) Inleakages	Sampling from manometre device and fast line to rack	3/4"	~ 80 m	AISI 304
	Sampling inside the rack without probe	1/4"	~ 5 m	AISI 304

TABLE 2 - SAMPLING SYSTEM EMPLOYED

Sample	Element	Number of analysis or determination	Mean value µg	Standard deviation µg	Variation coefficient %
Millipore	Iron	18	3,876	3,587	93
	Copper	18	0,782	0,492	63
	Nickel	9	0,185	0,282	152
	Cobalt	9	0,000	0,000	0
Membranes	Iron	17	4,557	3,377	74
	Copper	17	0,696	0,348	50
	Nickel	12	1,469	2,705	184
	Cobalt	9	0,031	0,063	203
Detection limit	Iron	9	2,808	1,327	47
	Copper	8	0,650	0,528	82
	Nickel	11	2,003	0,965	48
	Cobalt	13	1,545	0,698	45

Table 3 - Analysis of blanks. Quantity of Fe, Cu, Ni and Co (µg) measured in system. Detection limits of analyses.

Sampling point	Element	N Number of samples	X Mean value	S <sub>x</sub> Standard deviation	Median
I.P.	Fe-sol (ppb)	6	1.25	0.70	1.20
I.P.	Fe-susp (ppb)	7	12.70	3.35	12.90
I.P.	Cu-sol (ppb)	7	1.21	0.68	1.23
I.P.	Cu-susp (ppb)	7	0.59	0.23	0.45
U.P.	Fe-sol (ppb)	6	0.45	0.23	0.35
U.P.	Fe-susp (ppb)	10	1.04	0.52	1.00
U.P.	Cu-sol (ppb)	10	0.29	0.20	0.28
U.P.	Cu-susp (ppb)	7	0.08	0.08	0.05
U.R.B.P.	Fe-sol (ppb)	5	0.6	0.70	0.10
U.R.B.P.	Fe-susp (ppb)	10	1.34	0.13	1.00
U.R.B.P.	Cu-sol (ppb)	10	0.20	0.05	0.02
U.R.B.P.	Cu-susp (ppb)	9	0.05	0.03	0.05
U.R.B.P.	Co-sol (ppt)	9	62	29	49
U.R.B.P.	Co-susp (ppt)	3	21	21	20
U.R.B.P.	Ni-sol (ppt)	3	195	72	161
U.R.A.P.	Fe-sol (ppb)	6	0.27	0.27	0.20
U.R.A.P.	Fe-susp (ppb)	9	1.29	0.88	0.90
U.R.A.P.	Cu-sol (ppb)	8	0.17	0.06	0.19
U.R.A.P.	Cu-susp (ppb)	8	0.04	0.02	0.03
U.R.A.P.	Co-sol (ppt)	8	84	98	55
U.R.A.P.	Co-susp (ppt)				
U.R.A.P.	Ni-sol (ppt)	7	244	42	259
R.D.	Fe-sol (ppb)	5	0.62	0.35	0.60
R.D.	Fe-susp (ppb)	4	31.15	40.70	13.70

Tab. 4 - Metallic species analysis of Caerco condensate-feedwater cycle at constant load

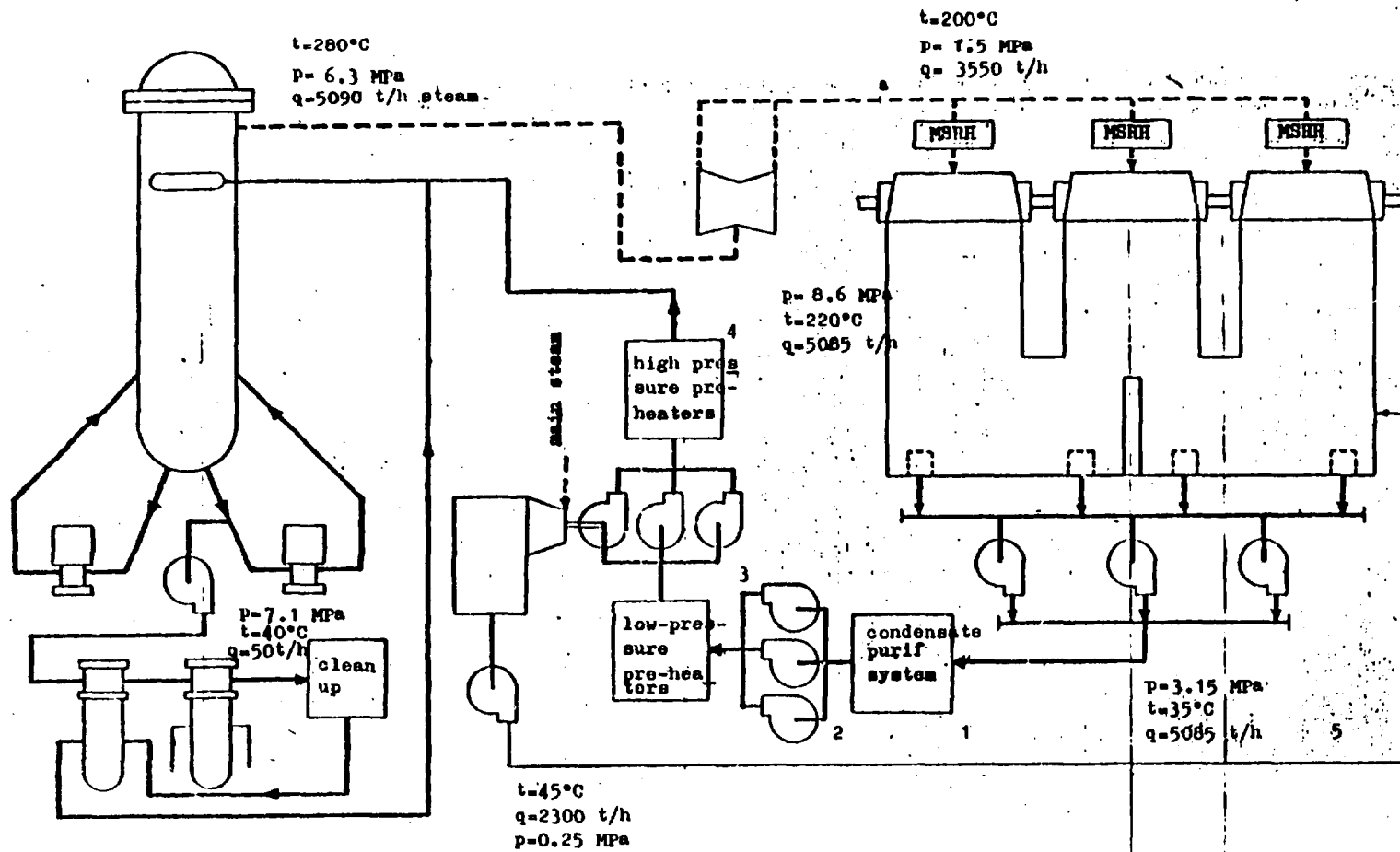


Fig. 1 - Sketch of cycle and sampling points

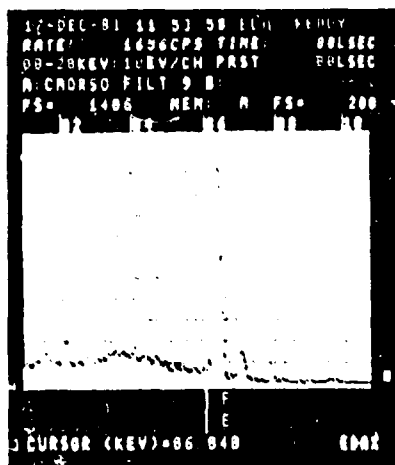




106 ISE M 5000 S GS

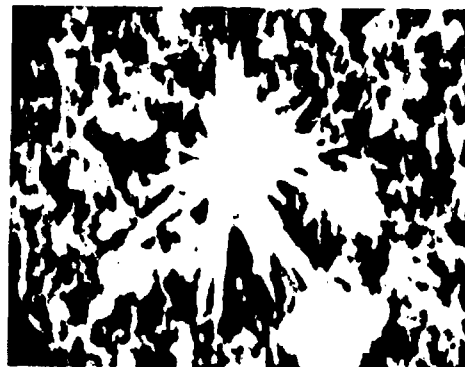


Filter n. 9 of 3-XII-82-IFC :  
Typical lepidocrocite crystal



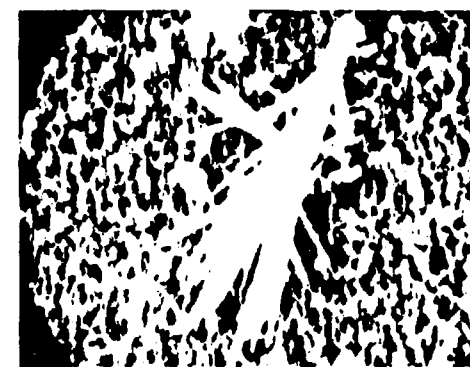
Microanalysis of lepidocrocite  
crystal

ISE M 5000 S GS



Filter n. 21 of 4-XII-82-URAP :  
y FeOOH crystal

ISE M 2500 S GS

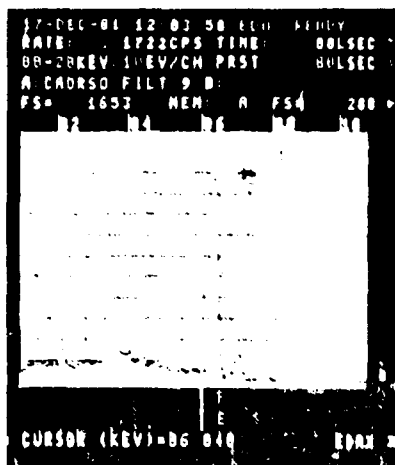


Filter n. 21 of 4-XII-82-URAP :  
y FeOOH crystal

ISE M 5000 S GS



Filter n. 9 of 3-XII-82-IFC  
Magnetite octahedric crystal



Microanalysis of magnetite cry-  
stal

ISE M 10000 S GS



Filter n. 21 of 4-XII-82-URAP  
Fe<sub>3</sub>O<sub>4</sub> association of magnetite

ISE M 20000 S GS



Filter n. 21 of 4-XII-82-URAP  
Fe<sub>3</sub>O<sub>4</sub> association of magnetite

Fig. 3 - Characteristic oxides of polishing inlet

Fig. 4 - Characteristic oxides of final feed water