CRITICAL PH IN COOLING WATERS

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1. Introduction

In order to reduce the thermic waste from industrial cooling and process water systems, more and more industrial plants are obliged to recycle cooling water.
This recirculation concentrates considerably the levels of salts present, and some may reach the solubility limit : calcium carbonate, calcium sulfate, calcium phosphate, etc.
The soft waters, in general found in Belgium, calcium carbonate is frequently the mineral form of precipitate.
It is of course very important to have an easy and reliable method to detect in fore-hand the first signs of possible precipitation of calcium carbonate into cooling loops.

Since 1981, Laborelec (consulting agency for power stations) has developed the "critical pH-method " based on the analytical principal introduced by FEITLER in 1972.

During more than ten years this measurement has been executed in the lab by auto-matic lab titrators. Development of industrial titrators has made it possible to adapt the method for on-line measurement and monitor the cooling loops more frequently.

In the following pages we explain the principle of the method, the experimental procedure, the description and programming of the on-line analyser and the comparative results of the lab and on-line systems.

2. Measurement principle

If small quantities of concentrated base slowly are dosed to concentrated cooling water, the pH of the solution will go up first, then passes through a maximum and finally declines drastic (figure 1).

The following equations explain the phenomenon :

$OH + H \longleftrightarrow HOH$

$H_2CO_3 \longleftrightarrow H + HCO_3$

$HCO_3 \longleftrightarrow H + CO_3$

$Ca + CO_3 \longleftrightarrow \underline{CaCO_3}$

When base is dosed in water, the OH neutralises the H + of the first reaction, what leads to a shift of the second and third reaction to the right side. The last reaction generates carbonates and frees protons. The carbonates combine with calcium to form calcium carbonate that precipitate in the fourth reaction.
The excess of protons reduce the pH of the solution.
In this phase, addition of base results in a reduction of the pH.
That maximum point is called : "the critical pH".

(see figure 1)

3. Selected material

3. 1. Measuring electrode

The determination of the critical pH can be done in two ways.

The first by measuring the turbidity of the solution, namely the latter one increases when the calcium carbonate precipitates, or secondly by measuring the evolution of the pH by potentiometric method.

The compared evolution of the pH and turbidity results in the conclusion that only micro-electrodes (ex. METROHM 6.0204.100.JE) are suitable.
The traditional pH electrodes (ex. METROHM 6.0202.100.JB) introduce measuring errors due to the thickness of the glass body of the electrode (figure 2).

(see figure 2 and 3)

3. 2. The titrator and the titration speed

All lab and industrial titration systems are actually equipped with microprocessors which control the analysis and calculate the inflection points. Most of the titrators are equipped to detect final end point or S shape curves.
The critical pH does not belong to this family.
The evolution of the pH curve is of (inverse V type).
The selected titrator depends therefore from the different titrator curves it can offer.

Whatever the choice of the instrument is, it should minimum have the following characteristics :

- monotone continuous titration
- injection of small quantities of reactive
- long time interval between two injections
- possibility to detect titration curve
- thermostatisation of the titration vessel

3. 3. Temperature set point of the sample

Significant results are only correct if the sample is kept at a temperature of two degrees above the maximum temperature of the circulation water.

T° analysis = T° max + 2°C

In order to obtain this temperature, the titration vessel is executed with a heating jacket. The jacket is fed by heated water from a thermostat bath. The precision of the regulation must be at least 0.2°C.

4. Procedure

Check up the highest temperature of the heat exchanger exit in the installation.

Adjust the temperature loop and regulate the maximum temperature of the titration vessel at 2°C above the maximal temperature of the cooling water sample.

Prepare a solution of 0.1 N base and fill the burette in order to have a correct addition.

Wait until the temperature of the sample is correct.

Start the analysis.

5. Interpretation of the results

Figure 4 represents two types of pH evolutions obtained during the measurement of the critical pH.
(see figure 4)

Generally the more the tested water sample is away from the precipitation situation, the higher is the critical pH and also the more the added volume of base will be.
On the other hand, a precipitating water type does not show any maximum.

6. On-line analyser type adi 2015

As mentioned before, the on-line analyser for detection of the critical pH should be executed with following possibilities :

- automatic sampling system (50 ml)
- dosing system (burette) for addition of precise fixed volumes of NaOH 0.1 N

- pH and temperature amplifiers
- thermo controlled analysis vessel
- possibility to program a continuous monotone titration with a fixed time between two injections of NaOH.

6. 1. Build up of the analyser Fig. 1A

The analyser is built up of 2 parts who are completely separated from each other.

6. 1. 1. Wet part of the system

Consist of :
- possibility of max. 2 burettes
- possibility of 2 sample selection valves
- possibility of 4 extra addition valves
- different type of titration vessels
- different sample systems (from 0.1-100 ml)
- max. 2 amplifier cards

6. 1. 2. Control part

Consist of :
- keyboard for programming
- power converter board => transforming current
- measurement processor board => measurement transmitters
- interfaces => control of the modules
- RS232 => data communication
- analog output => 4-20 mA

6. 2. Hardware for the critical pH application Fig. 1 B

- 1 burette of 20 ml 0.IN NaOH
- 1 macro sampling device with pipette of 50 ml
- pH amplifier + combined pH micro-electrode
- temperature amplifier + Pt 100 sensor
- jacket titration vessel 40-100 ml
- extra valve for addition of HNO3 1N (during cleaning)
- automatic stirrer (flexible shaft type)

7. Programming of the analyser

7. 1. Sequence of the basic actions Fig. 2

The complete programme for the analysis sequence is time based.
Inside the analyser is a time block that controls all activity second by second (open valve, close valve etc.).
In Fig. 2 you will find the different basic actions in one time block : RUN :

- sample selection
- sampling
- preconditioning of sample
- analysis
- calculation
- output control
- print
- rinse

7. 2. Overview of the analysis cycle for the detection of the critical pH Fig. 3

As for a complete analysis of the critical pH some steps of the former basic programme follow several times to another. Therefore we adjusted and programmed the total programme over different "RUNS".

The complete analysis cycle is build up in 4 big steps or runs.

More in detail we can summarize the programme (see Fig. 4).

RUN 1 : Sampling

RUN 1 consists of :

- sample selection
- rinsing of the macro pipette with fresh sample
- filling of the burette with NaOH 0.IN
- empty + 3 x rinse of the analysis vessel
- ml fresh sample inject in the analysis vessel

RUN 2 : Preconditioning of the water sample

The preconditioning of the water sample : in this case consist of heating up the sample with 2°C higher than the max. temp. of the circulation water :
T° analysis = T° max. + 2°C

RUN 2 consists of :

- measuring of the temperature of the sample (Pt 100)
- "if statement" : if the temperature of the sample is equal to the requested
- temperature, then we go th RUN 3.
- "if statement" : if the temperature of the sample is not correct, then RUN 2 is start up again.
- measuring the initial pH of the sample

RUN 3 : Analysis

In this run the final analysis of the critical pH is done (monotone titration).
A fixed volume of 0.1 ml NaOH 0.IN is added to the sample and after a waiting time of one minute the pH is measured.
This result is memorized in the analyser and again 0.1 ml NaOH is added to the sample. After one minute the pH is measured again.
By taking the difference in pH of 2 successive measurements the "delta pH" (pH) is calculated.
As long as this pH > O the system goes on with dosing NaOH (always in steps of 0.1 ml).
If the pH reaches < 0 then this means that the critical pH is achieved and we can go to run 4.

RUN 3 consists of :

- dosing of 0.1 ml NaOH 0.1N (by burette)
- minute waiting time
- measuring the pH
- calculate the pH
- "if statement" : if the pH > 0 go to RUN 3
- "if statement" : if the pH > 0 go to RUN 4

RUN 4 : Result processing

This run consists of the processing of the different results and the print out of the requested information.

RUN 4 consists of :

- addition of 10 ml NH03 1N to the sample (by valve) to avoid problems with the precipitated carbonate in the next analysis.
- printing out of the results : initial pH, critical pH and dosed NaOH to attempt the critical pH.

Remark :

In Fig. 4 is a schematic print out of the different actions within the 4 runs and this action by action. In the final programming of the analyser it is of course possible to programme several actions at the same time.

The software of the analyser is build up in programme lines. That means that for each valve (max. 3 + max. 4 extern valves) and for each burette (max.2) one line is available, further there is a programme line available for the drain, sample loop, the analysis, the calculations, the print out and the analog outputs.

The total software package of the ADI 2015 is realised in 19 programmable lines. The programme is composed over 2 different programme sheets (see Fig. 5) : one with the different time blocks (time programming sheet 1) and one with further details for the different actions programmed within this specific time blocs (time programming sheet 2).

For a valve this means that we only on "sheet 1" find a line and nothing on "sheet 2" for a valve it is only possible to open or to close.

For a burette we can find lines back on both sheets. On the first sheet we have to fill in which tune block we want to use a burette and on the second sheet we are programming the action we want (filling, dosing or cycling ...).

For the analysis itself that means that on sheet 2 the different titration parameters have to be indicated.
Once a complete programming of the ADI 2015 is done, we can test the application.

8. Results of testing slide 2a, 2b

8. 1. Test of reproducibility using

- 0.05 N NaOH
- 0.1 N NaOH

8. 2. Parallel test of lab titrator and on-line titrator with conc. NaOH 0.05 N

Volumes for both instruments are not very reproducible.
pH values are acceptable. The choice is 0.1 NaOH

8. 3. Results water sample SERAING

- Slide 3A at 40°C
- Slide B 50°C

8. 4. Results water sample "Pont Brulée" without metagon at 45°C

8. 5. Results "Pont Brulée" without metagon

Conclusion : Both systems work correct.
The on-line system works sometimes better reason :
On the ADI 2015 is an automatic system.

Figure 1 : Evolution of the pH during the determination of the critical pH

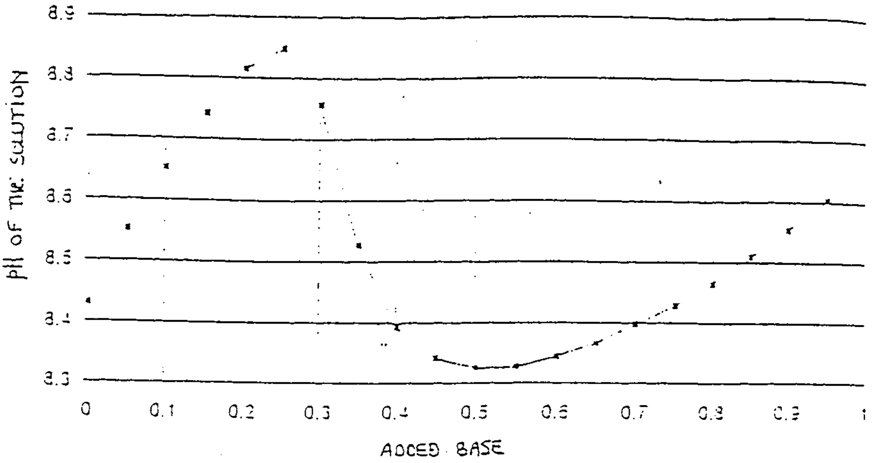

Figure 2 : Evolution of the measured pH in function of the used type of electrode

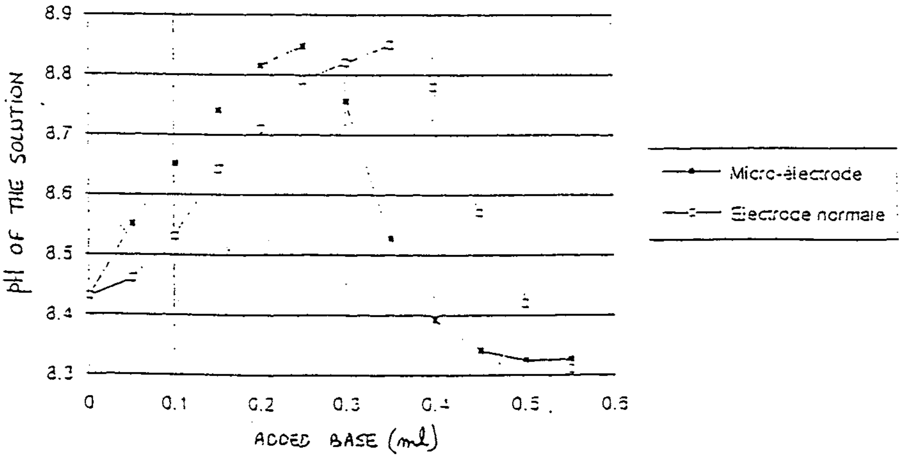

Figure 3 : Evolution of the turbidity during the determination of the critical pH

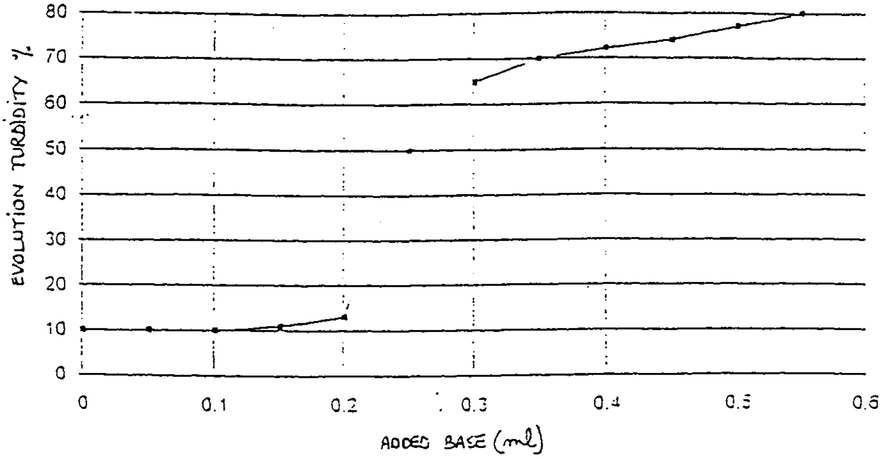

Figure 4 : Evolution of the pH in different situations of the water