

CALCIUM CARBONATE-CARBONIC ACID EQUILIBRIUM

INTRODUCTION

Physico-chemical characteristics study of natural waters, like that behaviour on environmental background, is very often deal with specific cases, for the complexity sake of relations between present ions.

This equilibrium is unstable behaviour due to variation of temperature and dissolved gas amount (dissolved or expelled), that bring new reactions and results in contact water place. Privately, problems of treatment, calcifying or corrosion nature are generated by physico-chemical equilibrium variations and bring to technical problems for water catchment and water supply. Study of these problems always brings to «calcium-carbonic equilibrium».

1. OPTIMAL CONDITIONS TO BALANCE

1.1. Wanted characteristics

Water characteristics (Alkalinity, Hardness and pH) are fixed according to next considerations:

Water Equilibrium

Ideal conditions:

- to be in balance of calcic saturation, essential condition to minimum deposit of calcium carbonate and this created accretion should be not destroyed,
- to have adequate concentration in calcium ions so that accretion be stuffy but no excessive,
- not including very strong proportion of SO_4^- or Cl^- ions could to make porous deposit, consequently inexpedient,
- to be with pH as high as possible in order that metal corrosivity be minimal,
- contain 4 to 5 mg/l oxygen content, prerequisite to speed precipitation of accretion on metals.

To gratify these conditions, representing point of water on the Hallopeau's graphical method must be to the corresponding saturation line, lightly above. In this range, rough estimate for alkalinity about 60 to 100 mg/l as CaCO_3 .

Also, so no scaling possible to bring representing point on the good range (above saturation line, to have saturation index between 0 and 0, 1).

Approval of the consumer.

Hardness will not have to be too excessive.

Remember trouble so excessive:

- Carbonated hardness > scaling and bad foaming,
- Permanent hardness (noncarbonated hardness) > bad foaming

Public health.

The clinical aspect which has received the greatest attention in recent years is the value of an infusion of Mg given early to patients with acute myocardial infarction. The evidence on this is inconsistent and a further trial is being set up in an attempt to resolve some of the uncertainties.

It means influence to be independent of hardness amount. Also, it is not needful to decrease strongly.

The table hereafter, indicates the recommended values by various French texts.

Durété des eaux : valeurs recommandées par différents textes					
Désignation des caractéristiques	Unités	France Décrets 89.3 - 90.330 et 91.257	Documents techniques n° 50-1 de mars 1970 du Centre Scientifique et Technique du Bâtiment		Livre de M. NEUVEU sur la corrosion des conduites
			Valeurs des éléments entraînant l'obligation d'un traitement	Valeurs souhaitées	
pH.....	-	> 6.5 < 9	< 7.2	> 7.2	au moins = à pHs
TAC.....	°F	-	< 6 ou > 25	de 10 à 20	-
Titre hydrométrique total (TH).....	°F	- (optimum 12 à 15)	< 6 ou > 30	de 8 à 15	-
Titre hydrométrique temporaire (TT)	°F	-	-	-	10 °F
CO ₂ total					
CO ₂ libre	mg/l	-	> 30	< 10	-
CO ₂ agressif.....	mg/l	-	-	-	néant
CO ₂ équilibrant	mg/l	-	-	-	< 30 mg/l
Oxygène dissous.....	mg/l	-	> 9	de 6 à 9	de 3 à 6 mg/l suivant vitesse dans conduites
Minéralisation totale (résidu sec) ..	g/l	< 1.5	-	-	-
Magnésium en Mg ⁺⁺	mg/l	< 50	> 4 °F	< TH/5	< 100
Chlorures en Cl ⁻	mg/l	< 200	> 7 °F	< 3 °F	-
Sulfates en SO ₄ ⁼	mg/l	< 250	> 9 °F	< 5 °F	-
Nitrates en NO ₃ ⁻	mg/l	< 50	> 1 °F	< 0.5 °F	-
Résistivité.....	Ohm	-	< 2000	2500 -3000	

2. BASIC CONCEPTS REGARDING TO WATER BALANCE

2.1. CONCEPT OF EQUILIBRIUM

2.1.1. GENERAL CONSIDERATIONS

Most of natural waters include dissolved gas, in more or less great quantity, and particularly, carbonic gas or carbon dioxide (CO₂)

From which does the dissolved carbon dioxide in water come?

The first origin of fresh water (spring, well, river, lake) often is the rainfall. During rainfall, there is a weak dissolution of the air carbon dioxide.

Then, by infiltration of rainwater in the ground, a much more important dissolution of carbon dioxide; itself released in the surface layers, by biological (in the topsoil). At last, in-depth, the water can dissolve carbon dioxide of geological origin.

Also this water contains dissolved salts, dissociated pretty much, that is:

- salts of strong acids and bases,
- salts of weak acids and bases,

Put water in equilibrium state, is give it, by required treatment, steady specific, in time which passes, between its storage after treatment, and its use by consumer.

Water balance depends of two factors:

- suitable specific,
- nature of materials likely to be contact with it.

To obtain the equilibrium state, it must be carried out the following stages:

- practical choice of materials, which will have to be most inert with action of water, so that balance of one is not compromised.
- give to water, stable intrinsic characteristics, and taking into account these materials.

The consecutive disadvantages with an unbalance of water are due as follows:

- aggressivity in relation to limestone, concrete and cement,
- corrosion of the metal components,
- the calcifying behaviour.

In first both cases, works and equipment concerned are damaged and even destroyed, and water acquires turbidity and coloring.

In last case, drains are narrowed, even sometimes blocked, and envisaged flows do not forward any more.

...

2.1.2 ESSENTIAL DATA OF EQUILIBRIUM

2.1.2.1. COMPOSITION OF WATERS

The essential components of water are:

Carbonic gas - CO₂ present carbonic gas in the air, also is it in almost all supply water, in which it dissolves, while combining partially with water, to form the carbonic acid (H₂CO₃), which is essential agent of water aggressivity, and which is partially dissociated in ions.

With a given temperature, the quantity of carbon dioxide, likely to dissolve in the water in contact with free air, is defined by temperature, and constant tension of carbon dioxide in the atmosphere.

It is by:

- 0.70 mg/l at 10°C
- 0.53 mg/l at 20°C.

Actually, quantities of carbon dioxide dissolved in water, are frequently much higher, because of following factors:

- pressure and content carbon dioxide of gases in contact with the underground tablecloths, often higher than those of free air,
- slowness of gas extraction to free air (surface water in great quantity).

Oxygen - Nitrogen

These gases dissolve in water, without dissociating.

Hydrogen sulphide (H₂S)

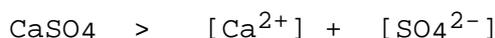
Slight dissociation.

Salts from strong acids and bases

These salts are in its entirety dissociated in ions.

Most important are sulfates and chlorides.

Water which was in contact with gypseous grounds (calcium sulphate) will charge of anions and cations, according to the reaction:



Salts from strong bases and weak acids

Almost these salts are completely dissociated in ions.

Most important are calcium salts (salts of the carbonic acid):

- calcium bicarbonate Ca(HCO₃), which only exists in aqueous solution,
- calcium carbonate CaCO₃, not very soluble (approximately 15 mg/l for T=25 °C and 25 mg/l for T= 100 °C).

Other elements, especially sodium and magnesium, give place to similar salts.

However, let's note that their carbonates are much more soluble than calcium carbonate.

To also note, case of humic acids (weak organics acid).

As carbonates, salts of humic acids are dissociated and their anions join, with also, with H⁺ ions attend in water.

In comparison with various elements contained in natural water, salts of humic acids usually are in very weak concentration. Generally, salts of carbonic acid only are salts of weak acids and strong bases to consider. Thus, taking into preceding remarks, one will neglect salts of humic acids, as well as hydrogen sulphide attendance.

2.1.2.2. COMPONENT OF WATERS

One distinguishes :

Fundamental elements:

These are elements found in all natural water:

- H_2CO_3 , H_2O , Molecules,
- HCO_3^- , CO_3^{2-} , H^+ , OH^- , Ca^{++} ions.

Feature elements:

These are others ions. They can be, or not, in water, on which they give its particular character.

These are, for example:

- SO_4^{2-} , Cl^- anions ... expressed by N,
- Mg^{++} , Na^+ , K^+ cations ... expressed by P.

Whereas the fundamental elements are always present in natural water, the characteristic elements are not it always.

Their presence gives a character on water: chlorinated water, sulphated water, magnesia, etc.

2.1.3. ESSENTIAL DEFINITIONS:

pH

pH is an acidity scale:

it is the negative logarithm of the hydrogen ion activity

$$\text{pH} = -\log [\text{H}^+]$$

Alcalinity

A good notion for water mineralization: bases and salts of weak acids (carbonate and bicarbonate, silicate).

Expressed, in French, by two titles expressed carbonated hardness of water:

- "Titre Alcalimétrique simple" (TA), i.e. phenolphthalein Alkalinity
- "Titre Alcalimétrique Complet" (TAC), i.e. Total Alkalinity.

The acquaintance of "TAC" and "TA" allows determining fraction of bases, carbonates or bicarbonates.

These titles can be expressed in various units:

- *equivalent* (by volume unit); to be exact equivalent-gram, which is quotient of atomic mass (or molar) by ion charge (polarity);
- *milliequivalent* (by volume unit); milliequivalent is the thousandth part of equivalent
- *mg/l as CaCO₃*; milligram per liter of calcium carbonate

• french *degree* (°F); which is fifth part of milliequivalent per liter (1 equivalent = 5000°F)

Nota: 1 °F = 10 mg/l as CaCO₃

Salts of strong acids

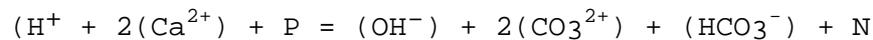
Corresponding as *non carbonated* hardness (or steady) give by chlorides and sulfates.

2.1.4 IONIC BALANCE OF WATERS

Fundamental relations of ionic balance.

The concentrations in ions (or moles) are dependent between them by following fundamental relations:

Relation who expresses electric neutrality of cations and anions present in water:

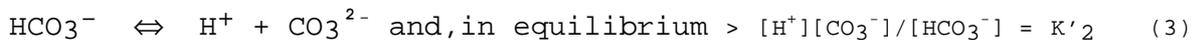
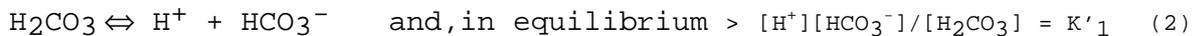
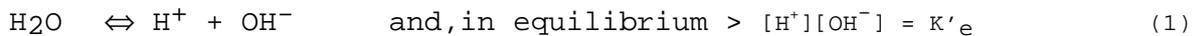


unit: mole or millimole/liter, where:

$$N = 2[SO_4]^{2+} + [Cl^-] + \dots$$

$$P = 2[Mg^{2+}] + [Na^+] + [K^+] + \dots$$

Relations who express dissociation balances of water and the carbonic acid:



K'e, K'1 and K'2 are dissociation constants for a given temperature and ionic strength (the ionic strength is function of concentrations and charge of species attend in solution).

If the solution is saturated with calcium carbonate, the application of thermodynamic equilibrium equation, CaCO₃ <> Ca²⁺ + CO₃²⁻ lead to relation:

$$[Ca^{2+}] [CO_3^{2-}] = K'_s \quad (4)$$

where,

K's = constant, with given temperature and ionic strength,

[] = stoichiometric molar concentration (mol/l).

In practice, relations above are simplified because one realizes that by holding account of the constants values, some concentrations have, according to studied cases, a negligible value.

It's the case of values of (H⁺) or (OH⁻), of which one or other (or simultaneously both) is negligible.

This last possibility occurs in particular with chemical balance for which:

$$(\text{H}^+) = (\text{OH}^-) \approx 10^{-7}$$

Let's note that water is chemically neutral with pH 7, and at temperature close to 23 °C.

With different temperature, chemical pH of neutrality deviates from the value above.

At all events, this chemical neutrality is not sign of water in equilibrium.

It is also case of values for (H_2CO_3), (HCO_3^-) or (CO_3^{2-}) species, of which one at least (or two of them) is negligible.

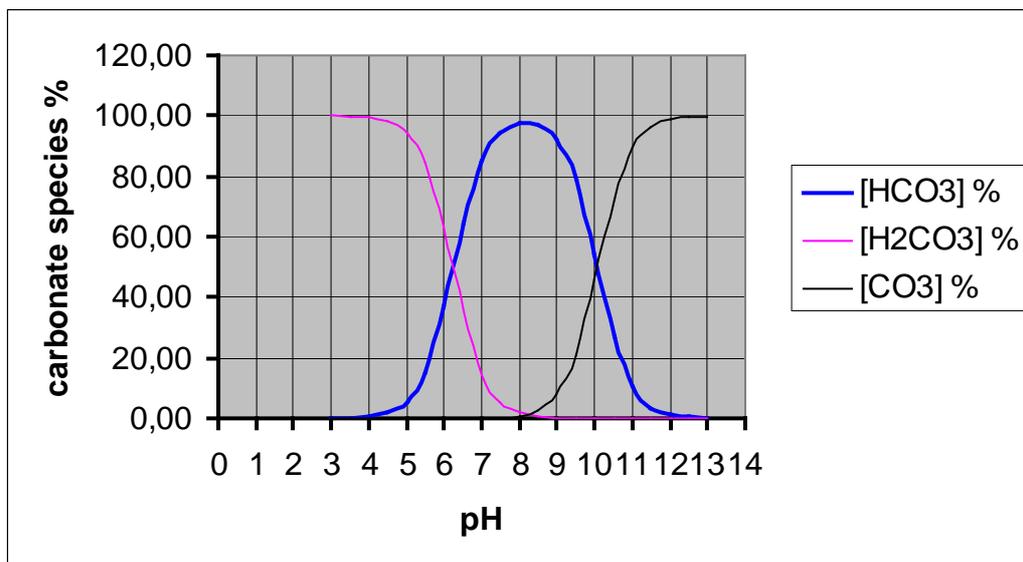
Let us recall that these three concentrations are terms of total CO_2 .

There are methods which comprise, at the same time, calculations and charts, and which make it possible to study, in a relatively simple and rigorous way, balances of natural water.

Foot-note:

The four relations between the six concentrations of the fundamental elements make it possible to consider a graph reported to two axes of co-ordinates, relative each one to a fundamental element or a function of these elements.

Each point of the graph then represents perfectly given water (example attached, of water with almost null salinity).



...

3. METHODS OF CALCULATION

3.1. General

Numerical values of the equilibrium constants.

- Temperature and ionic strength influence.

K'_e , K'_1 and K'_2 apparent equilibrium constants referring to (1), (2) and (3) relations usual express by power of 10, and to simplify, by negative logarithms noted pK' .

• Temperature influence

For infinitely diluted solutions (i.e. with null ionic force), values of pK' , are, according to temperature, following ones (according to Larson and Buswell):

T °C	pK _e	pK ₁	pK ₂
0	14.940	6.583	10.627
10	14.526	6.476	10.490
18	14.239	6.410	10.400
20	14.167	6.393	10.377
25	14.000	6.366	10.329
30	13.836	6.345	10.290
40	13.537	6.314	10.220
50	13.263	6.297	10.172
60	13.016	6.294	10.143
70	12.700	6.301	10.124
80		6.315	10.122

The values indicated to the table imply adoption of mole/liter, like unit of concentration, in the relations (1), (2) and (3) of preceding ones.

• Ionic strength influence

Natural water cannot be regarded as infinitely diluted solutions: their ionic force is not null.

For each studied water, the applicable K' constants, will result from those of preceding table by means of following relations (according to Larson and Buswell):

$$pK'_e = pK_e - \varepsilon \quad \text{that is} \quad K'_e = K_e \cdot 10^\varepsilon$$

$$pK'_1 = pK_1 - \varepsilon \quad \text{that is} \quad K'_1 = K_1 \cdot 10^\varepsilon$$

$$pK'_2 = pK_2 - \varepsilon \quad \text{that is} \quad K'_2 = K_2 \cdot 10^{2\varepsilon}$$

ε term is expressed with ionic strength (μ), by equation:

$$\varepsilon = \sqrt{\mu} / (1 + 1.4\sqrt{\mu})$$

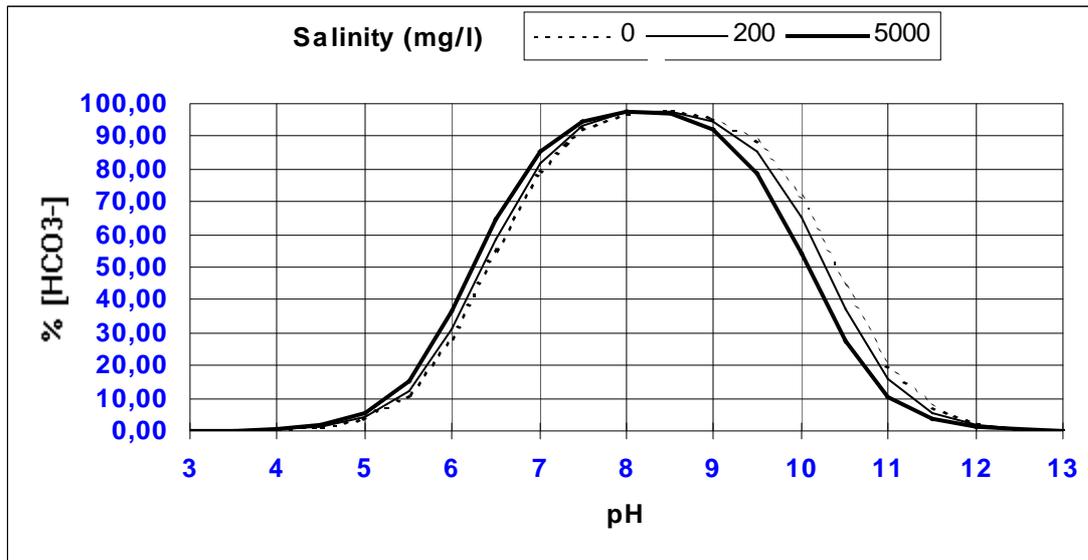
Ionic strength given by :

$$\mu = \sum c_n v_n^2 \quad (\text{Lewis et Randall, 1921})$$

where, c_n is concentration of the n^{th} ion of v_n charge, this concentration in moles/l.

It is useful to note that values of ionic strength are about $0.1 \cdot 10^{-3}$ for water, far from mineral-bearing, and they can reach and exceed $60 \cdot 10^{-3}$ for very mineral-bearing water, the corresponding values of ε term respectively being 0.01 and 0.18

Herewith, to see variations of $[\text{HCO}_3^-]$ according to salinity and pH (temperature = 25°C):



• Variations of 3 carbonic forms according to temperature and ionic strength.

Examination of attached table shows variations with a very weak salinity for water (almost null ionic strength), average and very strong (temperature 25 °C).

To note that pH which give $[\text{HCO}_3^-]$ maximum are inversely proportional value to salinity:

Salinity (mg/l)	0	200	30000
$[\text{HCO}_3^-]\%$	97.96	97.80	96.83
$[\text{H}_2\text{CO}_3]\%$	1.02	1.11	1.63
$[\text{CO}_3^{2-}]\%$	1.02	1.09	1.54
pH	8.35	8.25	7.75

Finally, calculation of concentrations of fundamental elements, is possible, as soon as one knows characteristic values of couples, such as pH and TAC (or pH and total CO_2 , or $[\text{Ca}^{2+}]$ and total CO_2), this making it possible to determine calcium-carbonic balance.

...

3.2. CALCULATION METHODS

Many equations express calcium-carbonic equilibrium, and take into consideration a wide range of these specifics, but by simplification, in neglecting plenty of equations. That way, many authors fortify one's self to study *pure* solutions of CaCO₃.

We instance:

STROHECKER FORMULA

pH in equilibrium = 11.39 - 2 log [compound CO₂]

↓

or saturation pH (pH_s)

at any rates where CaO < CO₂, equation comes about:

pH_s = 11.49 - log [compound CO₂] - log CaO

LANGELIER FORMULA

pH_s = pK'₂ - pK'_s + p[Ca²⁺] + p[Alcalinity]

This expression, takes into a part of total mineralization, agreed calcium amount like important element, and is very profitable. There are many studies and diagrams.

In particular:

- Legrand-Poirier diagram, which, one the one hand, take into the practical ionic strength calculate with complete chemical analysis and on the other, use [Ca²⁺]-total CO₂ pair,
- Hallopeau-Dubin diagram, which take into an approximate estimate of ionic strength, and use pH-alkalinity pair, and also use simplified equations. See farther.

LEGRAND and POIRIER METHOD

To my knowledge, it's the only rigorous method not neglecting any of the factors influencing balances. However, in spite of abacuses carried out by the authors to simplify calculations, the establishment of balance curve, which it's necessary to trace by points, is extremely hard. The advent of microcomputers allowed the development of this method. The talk, even brief, of LEGRAND and POIRIER method, here, would not offer a great interest.

This one is well described in the work written by authors themselves, helped of P. Leroy (see Bibliography to end of text).

HALLOPEAU-DUBIN METHOD

The graphic method, primarily use two axis to plot a "typical point" of water, according to:

- pH, plot in the diagram, on linear scale y-axis,
- alkalinity, plot in the diagram, on logarithmic scale x-axis.

Free CO₂ is plotted on right logarithmic scale y-axis.

A template act for *reference curve* to neutralization of carbonic acid enables to plot (to each type of waters) pH range, alkalinity and CO₂ range, but also, to test recarbonation (remineralization).

Note that diagram had been set to *mineralization = 200 mg/l*, and cannot take into variations of them according to treatments, so it's only succinct an approach to calcium-carbonic equilibrium, and utilization of Hallopeau' equations make it possible the reality of these balances.

The computerized Hallopeau's method (with dichotomy procedure) (EQUIL software, DOS support), expand by author; use Hallopeau-Dubin'equations (see Biblio) and any constants or well-known chemical formulas.

For instances:

- variation of thermodynamic ionic product constants, according to temperature, varies as follows:

$$\begin{aligned} pK_1 &= 6.583 - 12.3 TP + 163.5 TP^2 - 646 TP^3 \\ pK_2 &= 10.627 - 15.04 TP + 135.3 TP^2 - 328 TP^3 \\ pK_s &= 8.022 + 14 TP - 61 TP^2 + 444 TP^3 \end{aligned}$$

(Where TP = temperature of water in °C/1000).

- Calculation of ionic strength (μ): dry residue (mg/l) x 25.10^{-6}

NB: dry residue \neq mineralization (total inorganic dissolved solids)

- coefficients of ionic activity (to pK) :

$$\text{for } pK_1 > \varepsilon_1 \quad = \quad \sqrt{\mu} / (1+1,4\sqrt{\mu})$$

$$\text{for } pK_2 > \varepsilon_2 \quad = \quad 2\varepsilon_1$$

$$\text{for } pK_s > \varepsilon_s \quad = \quad 4\sqrt{\mu} / (1+3,9\sqrt{\mu})$$

- apparent pK (pK')

$$> \quad pK'_1 = pK_1 - \varepsilon_1$$

$$> \quad pK'_2 = pK_2 - \varepsilon_2$$

$$> \quad pK'_s = pK_s - \varepsilon_s$$

_Free CO2 :

$$\text{Log}_{10} [\text{CO}_2] = \text{Log}_{10} [\text{TAC}_{\text{CaO}}] + pK'_1 - \text{pH} + 0.2 - \text{Log}_{10} p$$

-pH_s (theoretical pH for calcium carbonate saturation):

$$\text{pH}_s = C - \{ \text{Log}_{10} [\text{TAC}_{\text{CaO}}] + \text{Log}_{10} [\text{THCa}_{\text{CaO}}] \} + \text{Log}_{10} p$$

Where,

TAC_{CaO} : Alkalinity expressed in CaO (Calcium Oxide),

THCa_{CaO} : calcic hardness expressed in CaO,

$$C = pK'_2 - pK'_s + 9.195$$

-Saturation index (Langelier) : SI = pH - pH_s

-Stability index (Ryznar index) : RI = 2 pH_s-pH

Note: aggressive CO₂ calculation is made by dichotomy procedure (CO₂ neutralization by CaCO₃):



For each iteration, new values for pK', pH, pHs, dry residue, Alkalinity, Calcium, Free CO₂ are calculated according to fraction of neutralized CO₂.

All basification, acidification, recarbonation or softening proceed that way with using appropriate chemical equations.

Advantage of Equilwin computerized method with respect to graphical Hallopeau's method.

The deviation of calculation for Hallopeau's diagram occurs:

1 - it doesn't take into variations of mineralization next treatment: no variations of ionic strength and activity, and consequently of used pK' in Hallopeau-Dubin equations.

2 - bad tracing protocol with graph.

Examples of spacing difference.

Aggressive water in Test:

EquilWin v2.0

File Edit Parameter Option Settings Help

Characterization: Basic parameters

Value	Unit	Parameter	Min	Max	Remark
10	°C	Temperature	0	80	
6.1	-log(H+)	pH	0	14	
2.5	°F	Alcalinity(1)	0.1	1000	
30.5	HCO3 mg/L	Alcalinity(2)	1.22	12202	
25	CaCO3 mg/L	Alcalinity(3)	1	10000	
5	°F	Calcium(1)	0.1	1000	
20	Ca2+ mg/L	Calcium(2)	0.4	4000	
1	Ca2+ meq/L	Calcium(3)	0.02	200	
50	CaCO3 mg/L	Calcium(4)	1	10000	
70	mg/L	Dry residue	50.5	100000	
13537.97	Ohm.cm	Resistivity	18765.5	999999	
73.87	uS/cm	Conductivity	53.29	999999	

Processed 442 iterations.

Computerized calculation:

EquilWin v2.0

File Edit Parameter Option Settings Help

Characterization: Result

Parameter	Unit	Remark
pHs	-log(H+)	9
Free CO ₂	mg/L	48.11
Saturation index	none	-2.9
Water	none	Aggressive
Alk/CaO	CaO	0.5
Aggressive CO ₂	mg/L	44.36
CaCO ₃ (CCPP)	mg/L	-100.82
Ryznar stability index	none	11.9
Ryznar's remark	none	Very important corrosion

Processed 442 iterations.

Neutralization with filtration by calcium carbonate (80% of purity as CaCO₃):

The screenshot shows the EquilWin v2.0 software interface. The left pane displays a tree view of the simulation process, with 'Process' expanded to show 'Neutralization' and 'Per filtration' selected. The right pane displays a table of simulation results for the process 'Correction of aggressivity: Neutralization: Per filtration: Result'.

Parameter	Value	Unit	Remark
pH	7.96	-log(H ⁺)	Water in equilibrium
pHs	7.86	-log(H ⁺)	
Free CO ₂	3.91	mg/L	
Alkalinity (Alk)	12.55	*F	
Calcium	15.05	*F	
Saturation index	0.1	none	
Dry residue (DR)	232.76	mg/L	
Stability index (Ryznar)	7.76	none	
Alkalinity increase	10.05	*F	
Calcium increase	10.05	*F	
Sodium increase	0	mg/L	
Consumption of pure reagent (100 %)	100.47	g/m ³	
Calcium carbonate (CaCO ₃)	80	%	
Consumption of commercial reagent	125.58	g/m ³	

>>> Graphical plot: See next page

$$\frac{TAC}{TCa} = 0.5$$

- Neutralisation -
(Colcoire)

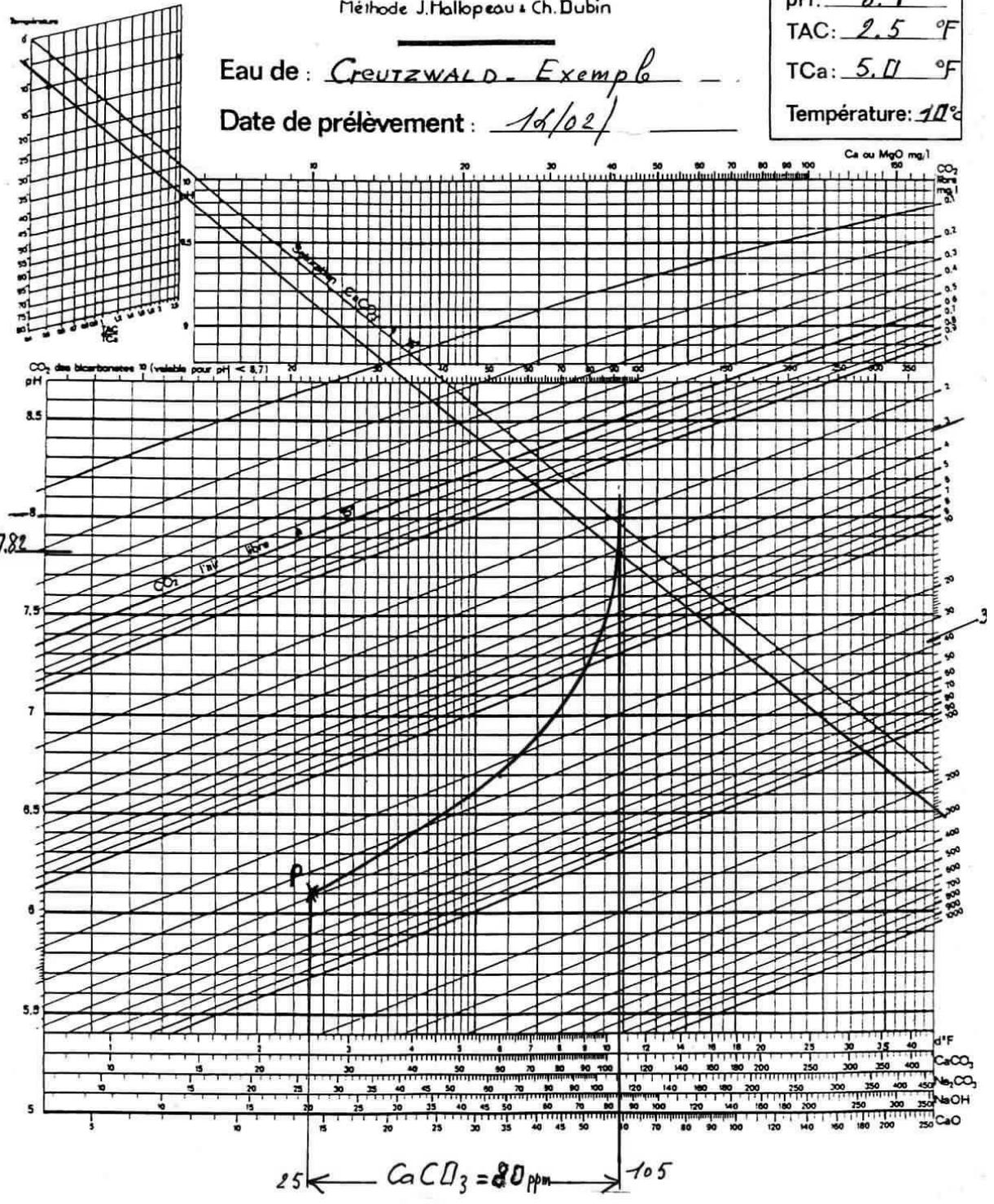
GRAPHIQUE CARBONIQUE

POUR EAUX CLASSIQUES
Méthode J. Hallopeau & Ch. Dubin

pH: 6.1
TAC: 2.5 °F
TCa: 5.0 °F
Température: 10°C

Eau de: CREITZWALD - Exemple

Date de prélèvement: 16/02/



Calculation deviation:

	Equil	Graph
pH	6.1	6.1
pHs	9.0	9.1
Free CO ₂ , mg/l	48.11	38
Aggressive CO ₂ , mg/l	44.36	35
S.I	-2.9	-
Alkalinity, as CaCO ₃	25	25
Calcium, as CaCO ₃	50	50
Alc/CaO	0.5	0.5
Dry Residue, mg/l	70	200

And next neutralization with calcium carbonate(CaCO₃, 100%):

	Equilwin	Graph
Equilibrium PH	7.96	7.80
pHs	7.86	7.82
Free CO ₂ , mg/l	3.9	3
S.I	0.1	-0.02
Alkalinity, as CaCO ₃	125.5	105
Calcium, as Ca ²⁺	150.5	-
Alc/CaO	0.83	0.5
Dry Residue, mg/l	232.76	200
Rate of CaCO ₃ ,mg/l	100.47	80

Note: about 20% of deviation for treatment rate (!)

4. Bibliography

Larson & Buswell - «Calcium, carbonate saturation index and alkalinity interpretations »
J.A.W.W.A, novembre 1942.

Langelier - « Effect of temperature on the pH of natural waters »,
J.A.W.W.A, février 1946.

J. Hallopeau - « Les équilibres carboniques dans les eaux » - Terres et Eaux, 1960/1961.

L.Legrand & G.Poirier - « Chimie des Eaux naturelles », Eyrolles, 1976.

D.Coucke, P.Ravarini et al. - « A comparison of the different methods for determining the behaviour of water to calcium carbonate », Aqua, 1997, n°42.