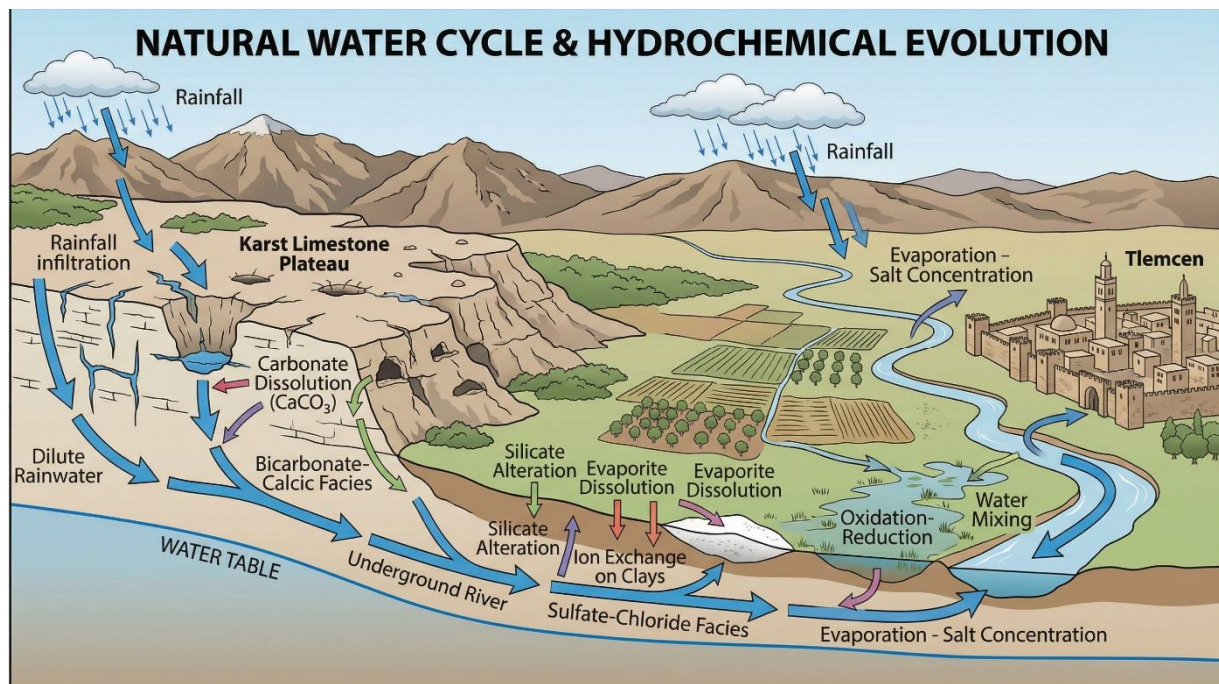




HYDROCHEMISTRY

Sabrina GUETTAIA

Course for Master 1 Hydrogeology students



HYDROCHEMISTRY

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Hydrochemistry

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Summary

This document is a handout of hydrochemistry that presents natural water chemistry as the science studying the composition, reactions and evolution of dissolved substances in groundwater and surface water, in relation to thermodynamics, acid-base and redox balances, and water resources management. It recalls the basic notions of the structure of the water molecule, its properties related to hydrogen bonds, the definition of solutions, dissolution, conductivity, as well as ion formation, ionization energies, redox couples and oxidation-reduction reactions. He then describes the different expressions of concentration (mass, molar, equivalent, activity, ionic strength) and the major processes of chemical alteration of rocks and waters (hydration, hydrolysis, oxidation, reduction) that control the formation of soils, the mobility of metals and the geochemical evolution of water. It follows the genesis of chemical composition from meteoric waters to groundwater and surface water by detailing atmospheric inputs, the dissolution of CO₂, carbonates and silicates, the effects of evaporation-precipitation and the influence of lithology, climate, biology and mixtures on hydrochemical facies (bicarbonate, sulfated, chloride, calcium, magnesium, sodium). A large part is dedicated to water analysis methods (in situ measurements, spectrophotometry, atomic absorption, ion chromatography and HPLC, electrochemical and titrimetric methods) presenting for each the principle, the fields of application, the advantages, limitations, interferences and analytical performances, completed by chapters on quality assurance, ion balance, relationships between parameters, drinking water standards and evaluation compliance. The document also deals with the dissolution and reconstitution of salts (solubility product, evaporation, crystallization, chemical precipitation, material balances) with examples and applications such as desalination, treatment of saline effluents and metal recycling. Finally, he introduces the notion of hydrochemical facies and ion signatures, their classification and the use of interpretation diagrams (Piper, Stiff, Schoeller Berkloff) to analyze the spatial and temporal evolution of waters in regulatory and environmental contexts.

Preface

This handout is designed as an advanced course support in hydrochemistry, it responds to a growing need for rigorous training in natural water chemistry, in a context where the sustainable management of water resources, quality monitoring and understanding of anthropogenic impacts are becoming major issues for contemporary societies. By bringing together in a single volume the fundamental notions of solution chemistry, the detailed description of rock weathering processes, the genesis of the chemical composition of water and the main methods of analysis and interpretation, the book offers the reader a coherent and progressive vision of water chemistry. It is primarily intended for students in earth sciences, hydrogeology, environment, civil engineering or chemistry, but it can also serve as a reference for engineers, technicians and practitioners who are required to deal with issues related to the quality of groundwater and surface water.

The spirit of this course is to continuously articulate theory and practice: each chapter begins with a structured conceptual reminder, followed by applied examples, data tables, and exercises that invite the reader to manipulate quantities, perform calculations, and interpret results. The first chapters return to the structure of the water molecule, its particular physicochemical properties and the notion of aqueous solution, in order to base the study of natural waters on a detailed understanding of the microscopic mechanisms that govern solubility, ionic dissociation, acid-base equilibrium and redox reactions. The following chapters extend this foundation by addressing the different expressions of concentration (mass, molar, equivalent, activity) and by showing how these quantitative tools are essential for describing and comparing waters of various origins, whether they are low-mineralized waters or highly concentrated systems. Through this progression, the reader is led to move from the molecular level (structure, ionization, energy) to the scale of watersheds and aquifers, where weathering and transport mechanisms control the overall composition of the water.

The book gives an important place to the processes of chemical alteration: hydration, hydrolysis, oxidation, reduction by illustrating them with examples of common minerals and by highlighting their geochemical and environmental consequences. This approach makes it possible to understand how, over time, water shapes the geosphere and is loaded with dissolved elements, giving rise to hydrochemical facies characteristic of the geological and climatic contexts crossed. The preface thus insists on the idea that the chemical composition of water is never the result of chance: it is the result of a permanent "dialogue" between water, rocks, the atmosphere, the biosphere and human activities, a dialogue that hydrochemistry seeks to decipher. With this in mind, the paper highlights the influence of lithology, climate, biological processes and water mixtures on the observed facies, and prepares the reader to use graphical tools such as Piper, Stiff or Schoeller Berkloff diagrams to synthesize and interpret these chemical signatures.

Another ambition stated in this preface is to familiarize the reader with the modern analytical methods used to characterize the waters and to draw his attention to the quality of the data produced. By detailing field measurements (pH, conductivity, dissolved oxygen), spectrophotometry, atomic absorption, ion chromatography, HPLC and various electrochemical or titrimetric methods, the course not only presents techniques: it discusses their principles, fields of application, limitations, interferences and metrological performance. The preface emphasizes that the reliability of any hydrogeochemical interpretation depends on the rigor of the analytical chain, from sampling to processing of results, including quality control, ion balances and data consistency. By also integrating normative aspects (drinking water quality, regulatory limit values, measurement uncertainties), the book is positioned as a useful tool not only for

understanding, but also for making decisions in the context of water resource management and protection.

Finally, the preface highlights the pedagogical and evolutionary vocation of this handout. It has been designed to accompany the student in his training, as a common thread that he can consult at different levels of depth: overall reading for an overview, detailed study of certain chapters for a project or a dissertation, targeted use of tables, examples and exercises to prepare tutorials or case studies.

In a context where pressures on water resources are multiplying and where water quality is at the heart of environmental concerns, this course is intended to be both a reference manual and an awareness tool, inviting the reader to consider water chemistry not as an abstract set of formulas, but as a key to understanding the functioning and vulnerability of hydrosystems.

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1. Introduction

The study of the chemistry of natural waters is an essential scientific field that is at the crossroads of several disciplines: chemistry, geology, hydrology and environmental sciences. This branch of knowledge examines the origin, constitution and transformations of elements dissolved in the different types of natural waters: groundwater, rivers, lake expanses and precipitation, by trying to decipher the physico-chemical processes that determine their properties. The teaching material presented is part of this approach by offering teaching on the chemistry of natural waters. Designed as a comprehensive didactic tool, it gradually guides the learner from the basic principles of chemistry in solution to contemporary techniques for the analysis and exploitation of hydrogeochemical information. Through its organized structure, enriched with quantified examples, summary tables and practical applications, this manual aims to provide the theoretical and methodological knowledge essential for assessing water quality, deciphering its mineral composition and identifying the parameters that influence it.

In its first section, the course revisits the fundamental principles governing the chemistry of water and aqueous media, highlighting the molecular architecture and particular characteristics of H₂O, including its polarity, Hydrogen bond interactions and their contribution to the remarkable dissolving power of this substance. These attributes explain why water can solubilize a wide range of mineral and organic substances, carry ionic species, and be the preferred medium for many chemical transformations, including acid-base equilibria and oxidation-reduction processes. The content then examines the genesis of ionic species (positively or negatively charged), the principle of electroneutrality, the energies required for ionization and redox systems, all fundamental elements for understanding the mobility of chemical constituents in aquatic environments. These conceptual reminders make it possible to reinforce the basic knowledge in general chemistry and to transpose it into an applied framework, that of hydrochemistry, where the objective is to establish links between the dissolved species observed and identifiable physico-chemical mechanisms.

The handout then addresses the various methods of quantifying the composition of natural solutions through the notions of mass, molar, equivalent concentration and activity, as well as the concept of ionic strength. This section, illustrated with examples of calculations and tabulated data, is essential for mastering the quantitative vocabulary of hydrochemistry, since any rigorous analysis of analytical results is based on a solid understanding of these parameters. Attention is paid to the difference between the actual concentration and the "effective" concentration (activity), which takes into account inter-ionic interactions in solution and becomes decisive when studying highly mineralized waters. Through exercises and real-world situations, students learn how to transform raw analytical data into quantities that are better suited to geochemical interpretation, such as milliequivalents per litre, ion balance equilibrium, or total ionic strength of the solution.

A central part of the teaching is dedicated to the mechanisms of chemical alteration that affect rock and mineral formations in contact with water, and which constitute the main origin of the dissolved elements present in natural waters. The main transformations involved: hydration, hydrolysis, oxidation and reduction are explained in detail, with illustrations of characteristic minerals (feldspars, clay minerals, carbonates, ferrous oxides) and their neoformation products. Mineral hydration, the swelling of clays, the transformation of feldspars into clays by hydrolysis, the solution of carbonates or metallic corrosion show how water gradually modifies the lithosphere while becoming charged with dissolved ions. These transformations are of importance that goes beyond the geological or geomorphological framework; They also determine practical aspects such as water hardness, metal mobilization, infrastructure sustainability and pedogenesis.

Beyond the basic mechanisms, the teaching material traces the acquisition of the chemical composition of water throughout the hydrological cycle, from meteoric water from rainfall to groundwater and surface water. It demonstrates how rainfall, already weakly mineralized by atmospheric inputs (marine particles, terrigenous dust, dissolved gases), undergoes modifications during infiltration through soils and bedrocks: dissolution of edaphic CO₂, genesis of carbonic acid, dissolution of carbonate and silicate minerals, cation exchanges with clays and interactions with organic compounds. The impact of lithological nature (silicate, carbonate, evaporitic rocks), climatic conditions (temperature, rainfall regime, evaporation), biological activity (microbial activity, plant cover) and water mixtures is clearly established, as it leads to distinct hydrochemical signatures (calcium bicarbonate facies, magnesium bicarbonate, sodium chloride or sulfate, etc.). Also, it highlights the notion of the "chemical footprint" of water, a true mirror of the geological, climatic and anthropogenic processes that shape it.

Another significant component of this course is dedicated to the techniques of chemical analysis of water and their constraints, because theoretical understanding only makes sense when it is coupled with an expertise in measurement tools. The document systematically presents field measurements (pH, temperature, conductivity, dissolved oxygen), spectrophotometric approaches, atomic absorption spectrometry, ion chromatography, high-performance liquid chromatography (HPLC), as well as various electrochemical and volumetric techniques. For each methodology, the operating principle, the field of application (major elements, nutrients, metals, organic molecules), the advantages, the restrictions, the potential interferences and the analytical performances (detection and quantification thresholds, precision) are discussed. This approach aims to make the learner aware of both the capabilities and limitations of the available techniques, so that he or she can select an analytical strategy appropriate to the research objectives and interpret the data critically.

Finally, the document integrates the dimensions of quality control, standardization and advanced interpretation of data, linking theory to practical issues of water resource management and preservation. It deals with the quality control of measurements (analytical blanks, duplicates, certified reference materials, ion balance), the relationships between parameters (electrical conductivity, TDS, hardness) and the criteria for validating the analyses. The normative framework for drinking water, regulated parameters (e.g. lead, nitrates, pesticides, microbiological indicators) and the consideration of analytical uncertainty are also addressed, which makes it possible to situate hydrochemical practice in a regulatory and decision-making context. The book concludes with a presentation of the hydrochemical facies and the main graphical tools used (Piper, Stiff, Schoeller-Berkaloff diagrams) to represent and interpret in a synthetic way the composition of the waters and their spatio-temporal evolution, thus offering a complete methodology from sampling and analysis to geochemical and environmental interpretation.

Aquatic chemistry is a disciplinary field that explores the chemical mechanisms governing the composition, distribution and transport of chemicals within natural aquatic ecosystems, whether groundwater, rivers, lakes or oceans.

Finally, hydrochemistry plays a critical role in the sustainable management of water resources, the protection of aquatic ecosystems, and the understanding of the natural and anthropogenic geochemical processes that influence water bodies.

2. Chapter 1 (Water chemistry)

Water chemistry encompasses the study of its composition, chemical and physical properties, as well as the interactions between its molecules and dissolved constituents. It is important to note that natural

water is not a pure substance; It is a complex mixture containing various minerals and organic compounds associated with its molecules.

This area of study is particularly focused on the following:

The molecular composition of water is made up of curved molecules formed by two hydrogen atoms and one oxygen atom, with the angle between the O-H bonds measuring about 104.5 degrees.

Water's unique chemical and physical characteristics, including its ability to dissolve many substances—often referred to as a universal solvent—are largely attributed to the presence of hydrogen bonds.

The chemical processes that take place in water, including acid-base and redox reactions, as well as parameters such as pH, conductivity, and dissolved ion concentration.

The review and management of natural water sources (such as springs, surface water and groundwater) to comply with designated physical-chemical criteria, including those required for the production of drinking water.

The study of water chemistry aims to understand the chemical characteristics of water and its components, as well as the chemical transformations that occur in it. This understanding is essential to water quality management and use across many disciplines.

2.1. Solutions and dissolution processes

According to the International Organization for Chemical Standardization (IEC) definition, a solution is a homogeneous mixture composed of a solvent, which is the main component, and one or more solutes. For example, in a mixture of 5 mL of ethanol and 50 mL of water, water is the solvent while ethanol is the solute. The process by which a solute dissolves in a solvent is called dissolution.

2.1.1. Experience

When distilled water, devoid of ions, is introduced into the container, the bulb remains extinguished. On the other hand, the addition of salt (NaCl) to distilled water causes the bulb to ignite, thus demonstrating that ionic solutions are electrically conductive. Conduction is impossible when the electrodes are placed in solid NaCl. Therefore, it is the dissolution of salt in water that allows conduction (Figure 1).

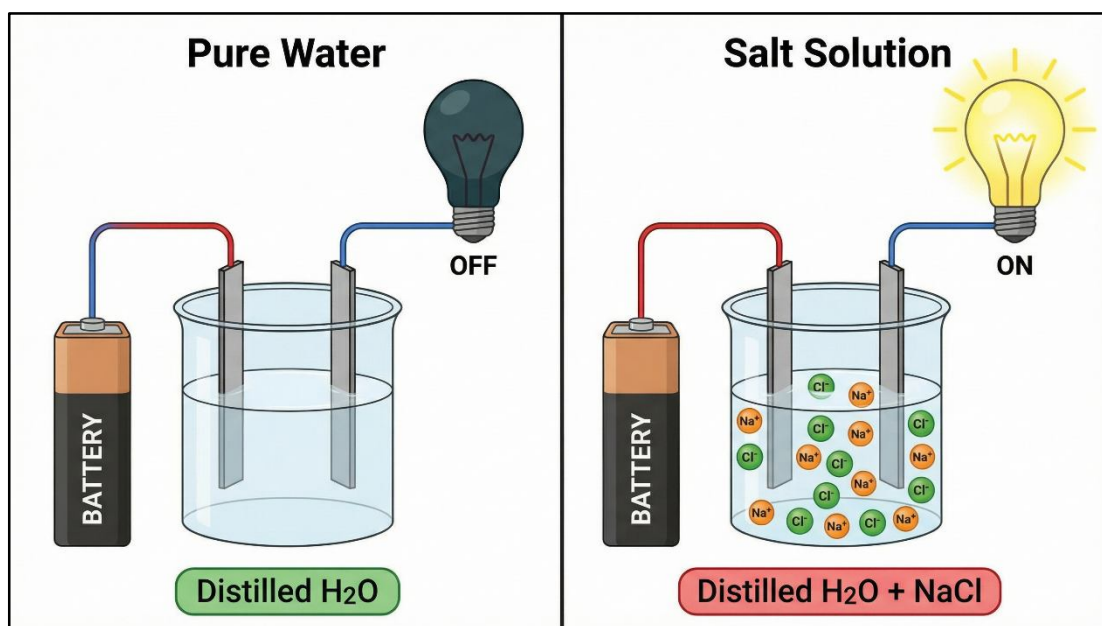


Figure 1. distilled water.

When introducing solid sodium chloride (NaCl) into water, water molecules facilitate the dissociation of Na⁺ and Cl⁻ ions, which are coated with water molecules, resulting in a solution capable of conducting electricity (Figure 2).

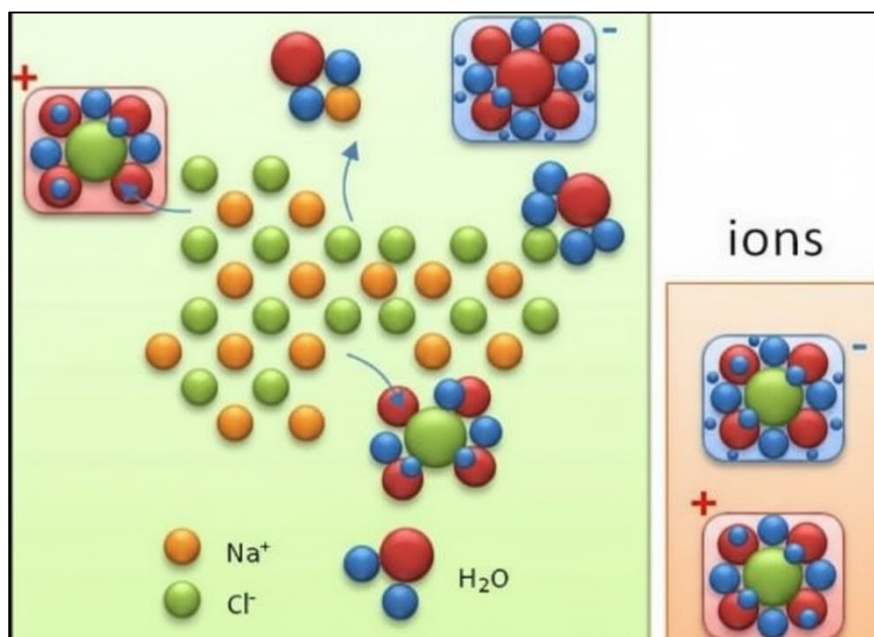


Figure 2. Ion separation.

2.2. Acquisition and evolution of the chemical load

2.2.1. Atomic structure and electrical neutrality

Every atom in the ground state is electrically neutral, composed of:

Protons: positive charge (+1 elementary charge = $+1.602 \times 10^{-19}$ C).

Electrons: negative charge (-1 elementary charge = -1.602×10^{-19} C).

Neutrons: zero charge.

Fundamental principle: In a neutral atom, the number of protons equals the number of electrons.

2.2.2. Formation of ions and electrical charge acquisition

Unlike a physical transformation, a chemical transformation involves chemical compounds that are likely to undergo changes during the process. This means that these compounds can combine or dissociate to create new molecules, or exchange electrons, resulting in a gain or loss of electrical charge.

The formation of an ion results from a gain or loss of electrons, and more specifically by:

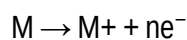
- The removal of electrons results in the creation of a cation, which carries a positive charge.
- The acquisition of electrons leads to the formation of an anion, which carries a negative charge.

2.2.3. Mechanisms of ion formation

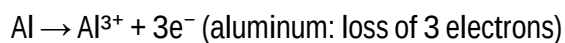
* Ionization by loss of electrons (formation of cations)

General Process:

Neutral atom $\rightarrow$ Cation + electron(s)



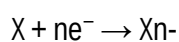
Examples:



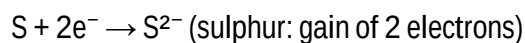
* Ionization by electron gain (formation of anions).

General Process:

Neutral atom + electron(s) $\rightarrow$ Anion



Examples:

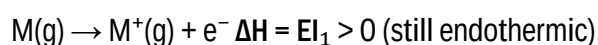


2.2.4. Ionization Energy

- Ionization energies

* First ionization energy (EI_1)

Definition: Minimum energy required to remove the first electron from a gaseous atom in the ground state:



Periodic trends:

Along a period ($\rightarrow$): EI_1 increases (increasing nuclear attraction)

Along a group ($\downarrow$): EI_1 decreases (shielding, nuclear distance)

Numerical examples:

1. Li: $\text{EI}_1 = 520 \text{ kJ/mol}$ (easy to ionize)
2. F: $\text{EI}_1 = 1681 \text{ kJ/mol}$ (difficult to ionize)
3. Cs: $\text{EI}_1 = 376 \text{ kJ/mol}$ (very easy to ionize).

* Successive ionization energies

For multiple ionizations:

$$\text{EI}_1 < \text{EI}_2 < \text{EI}_3 < \dots < \text{EI}_n$$

Example of magnesium:

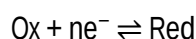
1. $A_1(\text{Mg}) = 738 \text{ kJ/mol} : \text{Mg} \rightarrow \text{Mg}^+ + \text{e}^-$
2. $A_2(\text{Mg}) = 1451 \text{ kJ/mol} : \text{Mg}^+ \rightarrow \text{Mg}^{2+} + \text{e}^-$

Observation: $\text{EI}_2 \gg \text{EI}_1$ because an electron is torn from an already positively charged cation.

2.2.5. Redox Couple Concept

* Definition and scoring

Redox couple: Association of an oxidized form (Ox) and a reduced form (Red) linked by an electron exchange:



Examples:

1. $\text{Cu}^{2+}/\text{Cu} : \text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$
2. $\text{Fe}^{3+}/\text{Fe}^{2+} : \text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$
3. $\text{H}^+/\text{H}_2 : 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$
4. $\text{Cl}_2/\text{Cl}^- : \text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$

* Half-electron equations

Building Rules:

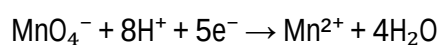
Balancing Elements Other Than H and O

Balancing oxygen with H_2O

Balancing hydrogen with H^+

Balancing charges with electrons

Example: $\text{MnO}_4^-/\text{Mn}^{2+}$ couple in an acidic medium:



2.3. Concentration of natural water solutions

The amount of solute contained in a given volume of solution is represented by the concentration of that solution, usually expressed in moles per litre (mol/L) (Figure 3). For example, a solution with a concentration of 1 mol/L contains one mole of solute per litre of solution.

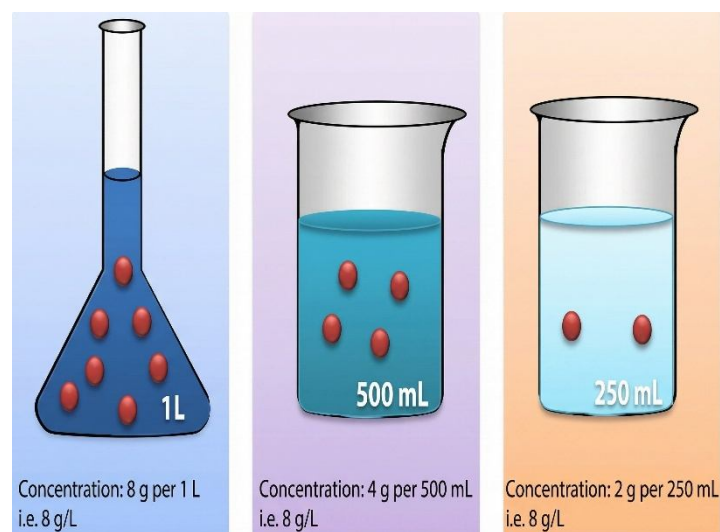


Figure 3. Concentrations of solutions.

There are several ways to express concentration:

1. **Mass concentration** : the ratio between the mass of solute and the volume of the solution, expressed in g/L or mg/L.

2. **Molal concentration (molality):** ratio between the number of moles of solute and the mass of the solvent, expressed in mol/kg.

3. **Molar concentration (molarity):** ratio between the number of moles of solute and the volume of the solution, expressed in mol/L.

2.3.1. Equivalent concentration (reaction quantity)

The term "normality" in the context of an acidic solution refers to the amount of moles of ion that can be released per litre of solution. In the case of an oxidation-reduction reaction, it refers to the amount of moles of electrons that can be exchanged per litre. The equivalent concentration is defined as the number of gram-equivalents or mole-equivalents of solute present in a litre of solution. More precisely, one milliequivalent (meq/L) corresponds to one thousandth of an equivalent per litre.

Example 1 : For a solution of Na_2SO_4 at 1 mol/L, there are 2 Na^+ , so the concentration of Na^+ is twice that of the salt, multiplied by the charge of Na^+ (1).

Example 2 : For 250 ml of a solution containing 140 mg Na_2CO_3 :

Mass concentration: $0.14 / 0.25 = 0.56 \text{ g/L}$

Molar mass of $\text{Na}_2\text{CO}_3 = 106 \text{ g/mol}$

Molarity: $(0.56 \times 1) / 106 = 0.0053 \text{ mol/L}$

Normal: $2 \times 0.0053 = 0.0106 \text{ meq/L}$

a) Chemical equivalent: The chemical equivalent of an element is the ratio between its atomic mass and its valence. Example: $\text{eq}(\text{Na}^+) = 23/1 = 23$; $\text{Eq}(\text{SO}_4^{2-}) = (32+16 \times 4)/2 = 48$

(b) Quantity in response: As stated by Stabler (1911), the amount of the reacted substance is determined by dividing the mass of the element by its chemical equivalent. This chemical equivalent is represented by the letter r preceding the symbol of the element (e.g., $r\text{Na}^+$). The formula for calculating the quantity that has reacted (meq/L) is as follows: quantity of the reactant = mass of the element / chemical equivalent.

Example

For water with the following composition:

Cations	mg/L	Anions	mg/L
Ca^{2+}	80	HCO_3^-	240
Mg^{2+}	18	SO_4^{2-}	42
K^+	2,5	Cl^-	34
Na^+	16	NO_3^-	4

Calculation of the reaction quantities (meq/L) for each ion :

Element	Eq (g)	r (meq/L)
Ca^{2+}	20	4
Mg^{2+}	12	1,5
K^+	39	0,064
Na^+	23	0,7
HCO_3^-	61	3,93

Element	Eq (g)	r (meq/L)
SO ₄ ²⁻	48	0,88
Cl ⁻	35	0,97
NO ₃ ⁻	62	0,065

2.3.2. Effective concentration (activity)

The effective concentration (A^+) is determined by the product of the actual concentration $[A^+]$ and the activity coefficient γ_i , which varies between 0 and 1. Thus, the relation can be expressed as $A^+ = \gamma_i \times [A^+]$.

The activity coefficient is influenced by the concentration of all ions in the solution, specifically by the **ionic strength (μ)**, which is defined as $\mu = 1/2 \sum Z_i^2 \times C_i$, where C_i represents the molar concentration and Z_i denotes the ionic charge.

The activity coefficient of each substance can be determined by the equation: $\log \gamma_i = -k Z_i^2 \sqrt{\mu}$.

*Illustration of ionic strength calculation: Consider a solution consisting of 0.10 mol/L KCl, 0.05 mol/L Ca(NO₃)₂, and 0.02 mol/L Na₂SO₄:

$$K^+ : (1)^2 \times 0,10 = 0,10$$

$$Cl^- : (-1)^2 \times 0,10 = 0,10$$

$$Ca^{2+} : (2)^2 \times 0,05 = 0,20$$

$$NO_3^- : (-1)^2 \times (2 \times 0,05) = 0,10$$

$$Na^+ : (1)^2 \times (2 \times 0,02) = 0,04$$

$$SO_4^{2-} : (-2)^2 \times 0,02 = 0,08$$

$$\text{Total: } 0,10+0,10+0,20+0,10+0,04+0,08=0,62$$

$$\mu = 0,62 / 2 = 0,31$$

2.4. Chemical Attacks: Hydration, Hydrolysis, Oxidation and Reduction.

2.4.1. Hydration

Definition and Mechanism

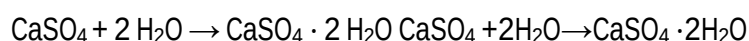
Hydration refers to the incorporation of water molecules into the crystal structure of a mineral or chemical compound. This process changes physical characteristics such as volume and stability, which can lead to the creation of new hydrated minerals.

Environmental examples

Swelling of clays : Clays such as montmorillonite absorb water in their intersheets, causing significant swelling. This phenomenon depends on the type of cation present (Na⁺, Ca²⁺, etc.) and influences the permeability and stability of the soil.

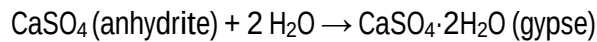
Hydration of minerals : For example, anhydrite (CaSO₄) is converted into gypsum (CaSO₄·2H₂O) by water absorption, which causes rocks to increase in volume and disintegrate.

The transformation of anhydrite into gypsum is written:



Hydration of iron oxides : The transformation of Fe_2O_3 into $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (limonite) colors soils and alters iron mobility.

Standard equation



Applications and Impacts

Geotechnics: Prediction of the swelling of clay soils.

Civil engineering: Durability of concrete structures (cement hydration).

Geomorphology: Alteration of rocks and formation of soils.

2.4.2. Hydrolysis

Definition and Mechanism

Hydrolysis refers to the process of breaking chemical bonds in the presence of water, resulting in the formation of new compounds. This process mainly involves the disintegration of covalent bonds present in minerals and organic molecules.

The equation required is written:



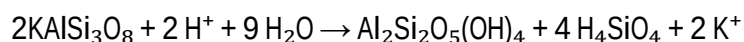
Environmental examples

Feldspar weathering : The hydrolysis of feldspars (KAlSi_3O_8) produces clays (kaolinite), silicic acid and dissolved ions, contributing to the formation of soils.

Pesticide degradation : Organophosphate pesticides decompose by hydrolysis, especially in basic environments.

Hydrolysis of polymers : Biodegradable plastics fragment under the effect of water, accelerated by pH and temperature.

Standard equation



(Hydrolysis of potassium feldspar to kaolinite)

Influencing factors

Temperature (higher = faster reaction)

pH (acidic or basic = accelerated hydrolysis)

Catalysts (metal ions, enzymes)

Applications and Impacts

Soil formation : Release of nutrients.

Pollutant degradation : Natural attenuation of pesticides and plastics.

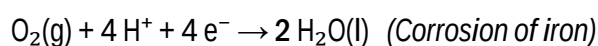
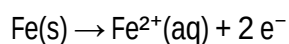
Element cycle : Transformation of minerals and mobility of ions.

2.4.3. Oxidation

Oxidation is the loss of electrons by a substance, often accompanied by the action of an oxidant such as oxygen, ozone or hydrogen peroxide. It is coupled with a reduction (redox reaction).

Environmental examples

Metal corrosion : Iron oxidizes in the presence of water and oxygen, forming rust (Fe^{2+} then Fe^{3+}).



Degradation of organic pollutants : Hydroxyl radicals (OHs) from advanced reactions oxidize pollutants in water.

Decomposition of organic matter : Microorganisms oxidize organic matter to CO_2 during aerobic respiration.

Atmospheric oxidation : Ozone and free radicals oxidize gases (SO_2 , NO_x), contributing to the formation of acid rain.

Applications and Impacts

Water treatment: Oxidation of pollutants.

Nutrient cycling: Transformation of nitrogen, sulfur, carbon.

Soil and water quality: Mobility of metals, bioavailability of elements.

2.4.4. Reduction

Reduction is the gain of electrons by a substance, usually under the action of a reductor (organic matter, H_2 , Fe^{2+} , etc.). It is coupled with oxidation in redox reactions.

Examples:

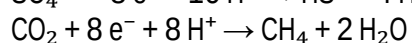
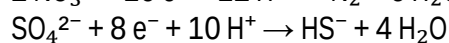
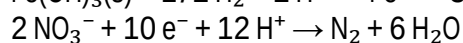
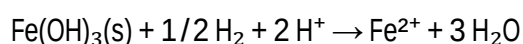
Metal reduction: In anaerobic environments, Fe(III) is reduced to Fe(II) by organic matter or hydrogen, often via bacteria.

Nitrate reduction: Denitrification converts nitrates (NO_3^{-}) into nitrogen gas (N_2), removing nitrogen from groundwater.

Sulfate reduction: Sulphate-reducing bacteria convert SO_4^{2-} into sulfides (HS^{-}), immobilizing certain metals.

Methanogenesis: In the absence of more favorable electron acceptors, CO_2 is reduced to methane (CH_4) by archaea.

Equation-type:



Applications and Impacts:

Element Cycle : Transformation and immobilization of nutrients and metals.

Pollutant mitigation : Reduction of toxic metals ($\text{Cr(VI)} \rightarrow \text{Cr(III)}$), degradation of organic pollutants.

Greenhouse gas production : Methanogenesis (CH_4), denitrification (N_2O).

Table 1. Summary table Processus.

Processus	Definition	Key example	Equation-type	Impact environnemental
Hydration	Incorporation of water into a structure	Swelling of clays, gypsum	$\text{CaSO}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Rock weathering, soil stability
Hydrolysis	Breaking of bonds by water	Alteration of feldspars	$2 \text{KAlSi}_3\text{O}_8 + 2 \text{H}^+ + 9 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4 \text{H}_4\text{SiO}_4 + 2 \text{K}^+$	Soil formation, degradation of pollutants
Oxidation	Electron loss	Iron corrosion, oxidation of pollutants	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^-$	Metal mobility, water treatment
Reduction	Electron gain	Denitrification, metal reduction	$2 \text{NO}_3^- + 10 \text{e}^- + 12 \text{H}^+ \rightarrow \text{N}_2 + 6 \text{H}_2\text{O}$	Pollutant mitigation, nutrient cycling

2.5. Chemical Composition of Natural Waters

2.5.1. The water molecule: structure and fundamental properties

2.5.1.1. Atomic structure of the water molecule

The chemical formula H_2O indicates that a water molecule is composed of two hydrogen atoms and one oxygen atom. However, this seemingly simple structure masks the remarkable complexity of its physicochemical properties.

Structure attributes:

- Binding angle H-O-H : $104,5^\circ$
- Link length O-H: $0,96 \text{ \AA}$
- Dipole moment: 1,85 debye
- Geometry: Angled (deformed tetrahedral).

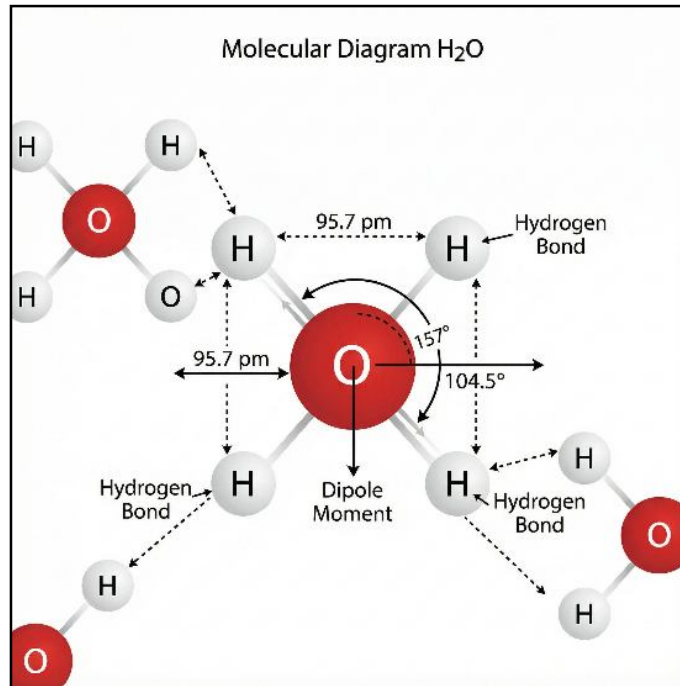


Figure 04. H₂O molecule.

The distinctive chemical and physical properties of water are attributable to hydrogen bonds. This predominant intermolecular bond, although weak (20 kJ/mol), gives water its characteristic properties.

2.5.1.2. Consequences of hydrogen bonds

High melting point and boiling.

High heat capacity.

Exceptional solvent power.

Tetrahedral structure in ice.

Water can be found in three states: liquid, solid and gaseous. Each state has specific characteristics.

Table 2. Specific characteristics of water.

Status	Temperature	Properties	Structure
Solid	< 0 °C	Densité = 0,92 g/cm ³	Hexagonal crystal lattice
Liquid	0-100 °C	Max density = 1,00 g/cm ³ à 4 °C	Fluctuating structure
Gaseous	> 100 °C	H ₂ O free molecules	Exact match to H ₂ O

Only the gaseous state corresponds exactly to the classical formula of the water molecule H₂O, because the intermolecular interactions are negligible.

2.5.2. Origin and genesis of chemical elements in water

2.5.2.1. Primary Sources of Chemical Elements

- Formation of meteoric water

The water cycle begins with the formation of raindrops within clouds, following the evaporation of surface water from oceans, seas, lakes and rivers. In this preliminary phase, a drop of water located in the heart of the clouds can contain various components, such as dust and dissolved substances, usually present in very low concentrations.

Air sources :

Marine aerosols: Na^+ , Cl^- , Mg^{2+} , SO_4^{2-}

Terrestrial particles: Ca^{2+} , K^+ , Al^{3+} , Fe^{3+}

Gaz dissous : CO_2 , SO_2 , NO_2 , NH_3

Anthropogenic activities: Industrial pollutants, agricultural pollutants.

-Average rainwater composition

According to global data, the average rainwater concentrations show an already significant composition:

Table 3.. Average composition of rainwater.

Element	Average concentration (mg /L)	Origine principale
Na^+	0,6	Marine aerosols
Ca^{2+}	0,4	Continental dust
Cl^-	1,0	Marine evaporation
SO_4^{2-}	1,4	SO_2 Oxidation
CID^*	0,8	CO_2 dissolved

*DIC = Dissolved Inorganic Carbon.

- Mineralization process during infiltration

* Water-soil-rock interaction

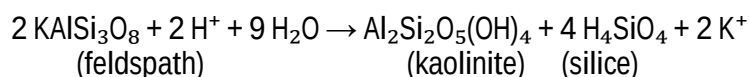
As water infiltrates the soil, it undergoes significant chemical transformations. These solutions, enriched with CO_2 and with acidity, participate in the hydrolysis and dissolution of the mineral constituents present in the rock, thus bringing cations, silica (SiO_2) and dissolved inorganic carbon (DIC) to rivers and groundwater.

The main mechanisms are as follows:

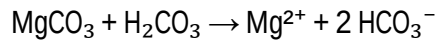
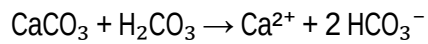
A) CO_2 dissolution and acidification

- $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$
- $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$
- $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$

B) Hydrolysis of silicate minerals



C) Dissolution of carbonates



2.5.2.2. Gradual geochemical evolution

These weathering processes control the chemical composition of inland waters and the consumption of atmospheric CO_2 . Enrichment is carried out according to a predictable geochemical sequence:

Steps of chemical enrichment:

1. Vadose zone (unsaturated):

Concentration of solutions by evapotranspiration

Selective precipitation of certain minerals

Ionic exchanges with clays.

2. Saturated zone (water table):

More stable thermodynamic equilibria

Extended contact time

Congruent dissolution of minerals.

3. Mixing and Emergence Zone:

Mixing different chemical facies

CO_2 degassing and precipitation

Modification of chemical equilibria.

2.5.2.3. Classification of Chemicals in Water

- Dissolved inorganic substances

* Major elements

The water present on Earth rarely exists in the form of a single chemical entity; Fresh water is often mineralized to varying degrees, while seawater has a high salinity. Even running water, coarsely filtered and of exceptional purity, is an aqueous solution that simultaneously constitutes a very dilute mixture of mineral salts, including cations such as sodium, potassium, magnesium and calcium.

Table 4. Classification according to abundance.

Category	Concentration	Typical elements	Main origin
Majors	> 1 mg/L	Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^-	Weathering of rocks
Minors	0,1-1 mg/L	SiO_2 , Fe, NO_3^- , F^-	Specialized Processes
Traces	< 0,1 mg/L	Heavy metals, rare earths	Contamination, geology

- Organic substances

* Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) represents a significant fraction of the dissolved matter in natural waters. Its origin can be:

Natural sources:

Decomposition of plant matter.

Root exudates.

Microbial metabolites.

Humic and fulvic substances.

Anthropogenic sources:

Urban and industrial discharges.

Agricultural leaching.

Pollution diffuse.

Geochemical role of the COD:

Metal complexation: Formation of organometallic complexes.

Element transport: Increased mobility of certain trace elements.

Redox reactions: Electron donor in an anoxic environment.

Sorption: Interactions with mineral surfaces.

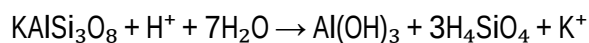
2.5.3. Mineralization and Enrichment Processes

2.5.3.1. Mechanisms of chemical spoilage

-Alteration of silicate rocks

The alteration of feldspars, the most abundant minerals in the Earth's crust, perfectly illustrates the mechanisms of genesis of chemical elements:

Example: Alteration of potassium feldspar



Products of the alteration:

Cations libérés : K^+ , Na^+ , Ca^{2+}

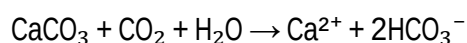
Dissolved Silica: H_4SiO_4

Secondary minerals: Clays, oxyhydroxides

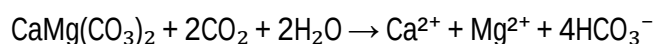
- Alteration of carbonate rocks

Limestones and dolomites are major reservoirs of alkalinity:

Dissolution of limestone:



Dissolution of the dolomite:



2.5.4. Evaporation and concentration processes

2.5.4.1. Simple Evaporation

In arid regions, evaporation gradually concentrates all dissolved elements according to a uniform concentration factor.

Precipitation sequence:

CaCO₃ (calcite) - factor 4-5

CaSO₄ (gypsum) - factor 8-10

NaCl (halite) - factor 80-100

K-Mg salts - factor >100

2.5.4.2. Evaporation with Fractional Precipitation

Selective precipitation of certain minerals changes the residual chemistry:

Example of chemical evolution:

Initial water (Ca-HCO₃) → Evaporation → Precipitation CaCO₃ → Residual water (Na-SO₄-Cl)

2.5.5. Factors controlling chemical composition

2.5.5.1. Lithological factors

- Type of bedrock

Each geological formation imprints its chemical signature:

Table 5. Chemical facies according to rock types.

Rock Type	Released Items	Typical chemical facies
Granites	K ⁺ , SiO ₂ , F ⁻	Potassium bicarbonate
Basalts	Ca ²⁺ , Mg ²⁺ , SiO ₂	Bicarbonaté calcico-magnésien
Limestone	Ca ²⁺ , HCO ₃ ⁻	Calcium bicarbonate
Evaporites	Na ⁺ , Cl ⁻ , SO ₄ ²⁻	Sodium chloride or sulfate
Shale	K ⁺ , SO ₄ ²⁻	Variable according to mineralogy

2.5.5.2. Mineralogy and weathering kinetics

The series of stability of minerals (from least stable to more stable) is as follows:

Olivine < Pyroxène < Amphibole < Biotite < Feldspath plagioclase < Feldspath-K < Muscovite < Quartz

Relative weathering rates:

Carbonates: 10⁶ times faster than silicates

Sulfates: 10⁴ times faster than silicates

Basic silicates: 10² times faster than acid silicates

2.5.6. Climatic Factors

2.5.6.1. Temperature

Temperature controls the reaction rates according to Arrhenius' law:

$$k = A \times e^{(-E_a/RT)}$$

Effects of temperature:

- Doubling of weathering rate for +10°C
- Inversely T° solubility for carbonates
- Directly T° Solubility for Silicates

2.5.6.2. Precipitation

- The rainfall pattern influences:
- Volume of leaching from soils
- Water-rock contact time
- Evaporative concentration
- Seasonal hydrogeochemical regimes.

2.5.7. Biological factors**2.5.7.1. Microbial activity**

- Microorganisms catalyze many reactions:

Major microbial processes:

Respiration: Biogenic CO₂ production

Denitrification: NO₃⁻ → N₂

Sulphate-reduction: SO₄²⁻ → H₂S

Fe/Mn oxidation: Redox state change

2.5.8. Vegetation

- Vegetation influences chemistry through:
- Selective nutrient pumping
- Release of rhizospheric organic acids.
- Soil CO₂ Modification
- Interception of precipitation.

2.5.9. Natural and spatial variability**2.5.9.1. Hadrochemical zoning****- Charging zone features**

- Low-mineral waters (< 500 mg/L TDS)
- Dominant calcium bicarbonate facies
- Equilibrium with soil CO₂

-Slightly acidic pH (6.0-6.8).

Dominant processes:

-Carbonate Dissolution

-Early hydrolysis of silicates

-Ionic exchanges with clays.

- Transit areas

Geochemical evolution:

Gradual increase in mineralization

Evolution towards mixed facies

Establishment of thermodynamic equilibria

pH tending towards neutrality (6.8-7.4).

-Discharge areas

Terminal features:

Strong mineralization (> 1000 mg/L TDS).

Sodium chloride or sulfate facies.

Evaporative concentration.

pH varies according to the process.

- Spatial heterogeneity

Examples of lithological variations:

Granitic zone → Water K-HCO₃ (100-300 mg/L TDS).

↓

Limestone zone → Water Ca-HCO₃ (300-600 mg/L TDS).

↓

Evaporitic zone → Water Na-Cl-SO₄ (1000-5000 mg/L TDS).

- Water mixtures

Mixtures of water from different origins create intermediate compositions:

Calculation of the binary mixture:

$$C_{\text{mélange}} = (Q_1 \times C_1 + Q_2 \times C_2) / (Q_1 + Q_2)$$

where Q = flow, C = concentration

2.6. Chemical analyses of water and limits of the methods used

2.6.1. Introduction to Chemical Water Analysis

2.6.1.1 .Definition and objectives

Chemical water analysis consists of evaluating the physico-chemical, microbiological and, sometimes, radiological composition of a water sample, taking into account both qualitative and quantitative aspects. These analyses allow us to:

Potability Assessment : Compliance with Quality Standards

Environmental Monitoring : Monitoring Pollution and Aquatic Ecosystems

Industrial control : Quality of process water and discharges

Scientific Research : Understanding Hydrogeochemical Processes.

- Classification of analytical parameters

* Basic physicochemical parameters

According to the technical guides, the basic parameters covered by the characterization of the initial state of surface water include:

Table 6. Different basic parameters.

Category	Parameters	Signification
Physical	Temperature, pH, conductivity, turbidity, color	General characterization
Major Chemicals	Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^-	Main mineralization
Nutrients	N, P, Si in different forms	Trophic status
Organic Matter	DOC, BOD ₅ , COD	Organic pollution

* Contamination parameters

Heavy metals : Pb, Cd, Hg, As, Cr, Cu, Zn.

Organic pollutants : Pesticides, PAHs, PCBs, solvents.

Emerging micropollutants : Pharmaceutical residues, hormones.

Microbiological parameters : Pathogenic bacteria, viruses, parasites.

2.6.2. Key Methods of Chemical Analysis

2.6.2.1. Field methods (in situ)

- Direct measurements

* Conductimetry

Principle: Electrical conductivity is a measure of the current conducted by aqueous solutions. This method allows a direct determination, with the help of a suitable instrument, of the electrical conductivity of aqueous solutions.

Materials required: Instrument for measuring electrical conductivity with electrode

Applications :

Quick estimate of total mineralization.

Water quality control ($\text{TDS} = \text{EC} \times 0.65$).

Point Pollution Detection.

Advantages:

Instant measurement.

Low cost.

Ease of use.

Limitations:

Aggregate information only.

Temperature sensitivity.

Interference from suspended solids.

-Other field measurements***pH-metry**

Principle: Potentiometric measurement with glass electrode.

Applications: Aggression assessment, treatment control.

Limitations: Electrode drift, ion interference.

***Oxygenometry**

Methods: Clark electrode, optical (luminescence).

Significance: Oxygenation status, biological processes.

Constraints: Frequent calibration, sensitivity to interference.

- Spectroscopic methods***UV-Visible Spectrophotometry***

Principle: Absorption of light by chemical species at specific wavelengths.

Tableau 7.Exemples d'applications courantes.

Parameter	Wavelength (nm)	Limit of detection	Main interferences
Nitrates	220	0,1 mg/L	Organic matter, nitrites
Nitrites	543	0,01 mg/L	Free chlorine, metals
Phosphates	880	0,05 mg/L	Silice, arsenates
Ammonium	655	0,1 mg/L	Metals, organic matter

Important limits:

Multiple spectral interferences.

Need for specific pre-treatments.

Sensitivity to suspended particles.

Atomic Absorption Spectroscopy (AAS)

Applications: Determination of metals (Ca, Mg, Fe, Mn, heavy metals).

Advantages:

Excellent elemental specificity.

Good accuracy (1-5%).

Broad area of concentration.

Technical limitations:

Single-element analysis.

Chemical interference (phosphates with Ca/Mg).

Important matrix effects.

High sample consumption.

-Chromatographic methods**Ion chromatography (IC)**

Principle: Ion separation on exchange resin followed by conductometric detection.

Applications: Simultaneous analysis of anions (Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , F^- , PO_4^{3-}) and cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+).

Major Benefits:

Multi-Elemental (6-8 ions simultaneously).

Excellent selectivity.

Full automation.

Low detection limits (0.01-0.1 mg/L).

Specific limitations:

High investment cost.

Sensitivity to complex matrices.

Need for systematic pre-filtration.

Retention Time Drift.

High-Performance Liquid Chromatography (HPLC)

Applications: Organic compounds (pesticides, PAHs, pharmaceutical compounds).

Advantages:

Very high resolution.

Accurate quantitation.

Coupling with mass spectrometry.

Limitations :

Complex sample preparation.

High analytical costs.

Need for technical expertise.

- Electrochemical methods**Selective electrodes****Main applications:**

Fluorides : LaF_3 electrode (limit: 0.1 mg/L).

Chlorides : Ag/AgCl electrode.

Nitrates : Liquid membrane electrode.

Advantages:

Ease of use.

Reduced cost.

Direct measurement in the matrix.

Critical Limits:

Ionic strength : Buffer adjustment required.

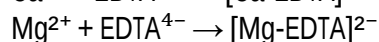
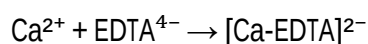
pH : Restricted operating range.

Interferences : Ions of similar charge.

Drift : Aging of membranes.

- Titrimetric methods**Complexometric Titration (EDTA)**

Application: Determination of total hardness ($\text{Ca}^{2+} + \text{Mg}^{2+}$).

Principle:**Advantages:**

Standard Reference Method.

Excellent accuracy ($\pm 2\%$).

Simple equipment.

Limitations:

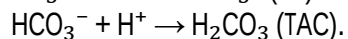
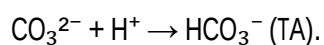
Interference by Fe^{3+} , Al^{3+} , Mn^{2+}

pH sensitivity (optimum: 10).

Time-consuming manual analysis.

Acid-base titration

Application: Alkalinity measurement (TAC, TA).

Reactions:

Accuracy: $\pm 5\%$ on TAC, $\pm 10\%$ on TA

2.6.3. Limitations of Analytical Methods**2.6.3.1. Limits of detection and quantification**

Table 8. Standard Definitions of Boundaries.

Parameter	Definition	Statistical calculation
Limit of Detection (LOD)	Lowest reliably detectable concentration	$\text{LD} = 3\sigma/S$
Limit of Quantification (LOQ)	Smallest concentration quantifiable with acceptable accuracy	$\text{LQ} = 10\sigma/S$

σ = standard deviation of the background noise, S = sensitivity of the method.

2.6.3.2. Examples of Limits by Method

Depending on the technical data, there are different measurement ranges for each use (between 0 and 60,000 mg/L) which ensure excellent quality of results, but with method limits of 5 mg/L for certain applications.

Table 9. Examples of limits by method.

Method	Parameter	LD (mg/L)	LQ (mg/L)	Linear domain
Spectrophotometry	NO ₃ ⁻	0,1	0,5	0,5-50 mg/L
Ion chromatography	Cl ⁻	0,01	0,05	0,05-100 mg/L
GET FLAMME	Ca ²⁺	0,01	0,05	0,05-100 mg/L
ICP-AES	Metals	0,001-0,1	0,005-0,5	Variable

2.6.3.3. Sources of error and interference

- Pre-analytical errors

A) Sampling and sampling

Technical recommendations: Ideally, measurements should be carried out continuously (except for alkalinity, which is measured by titration), in the middle of the current in the case of a river, or in a bucket placed at the pump discharge in the case of groundwater.

Essential precautions: Care must be taken not to aerate the water (risk of precipitation of elements in solution, oxygenation, etc.).

Common sources of error:

Cross-contamination : Insufficient flushing of equipment.

Sample evolution : Precipitation, degassing, oxidation.

Representativeness : Spatial or temporal heterogeneity.

Retention : Degradation during storage.

B) Preparation and storage

Table 10. Example of conservation.

Parameter	Optimal storage	Max duration	Key Risk
Dissolved metals	Filtration 0.45 µm + HNO ₃ (pH<2)	6 months	Adsorption, precipitation
Major anions	Filtration + 4 °C	48h	Microbial activity
Nutrients	Freezing (-18 °C)	Three months	Biological transformation
COD	H ₂ SO ₄ (pH<2) + 4 °C	28 days	Biodegradation

- Analytical interference

A) Spectral interference

Critical example - Nitrate assay at 220 nm:

Organic matter : Parasitic absorption (correction at 275 nm).

Nitrites : Spectral superposition (sulfonamide removal).

Turbidity : Light scattering (pre-filtration).

B) Chemical interference

Case of hardness by EDTA complexometry:

Iron and aluminum : Competitive complexation (triethanolamine masking).

Copper and zinc : Formation of stable complexes (calculation correction).

Organic matter : Interference on color toning.

- Instrumental limits

Sources of drift:

Thermal : $\pm 0.1^{\circ}\text{C} \rightarrow \pm 2\%$ on conductivity.

Electronics : Detector aging.

Mechanics : Pump wear, cell fouling.

Corrective Solutions:

Frequent automatic calibration.

Use of internal standards.

Systematic preventive maintenance.

2.6.4. Quality control and validation of results

2.6.4.1. Certified Reference Materials (CRMs)

Table 11. Types of RCMs available.

Type of CRM	Matrix	Certified parameters	Application
NIST 1643e	Freshwater	Trace elements	Metal calibration
BCR-610	Groundwater	Key elements	Routine control
IAEA-W4	Lake water	Nutrients	Environmental Monitoring

2.6.4.2. Acceptability criteria

Calculation of bias:

$$\text{Bias (\%)} = \frac{|\text{Measured Value} - \text{Certified Value}|}{\text{Certified value}} \times 100$$

Validation criteria:

Major elements : Bias < 10%

Minor items : Bias < 20%

Trace elements : Bias < 30%

-Analytical and control blanks

White hierarchy

Reactive White : All reagents without sample.

Method blank : Complete analytical procedure on pure water.

White Field : Pure Water Treated as Real Sample.

White transport : Assessment of contamination during transport.

Quality criteria

White method < LD/3.

Difference between duplicates < 10% (major elements).

Difference between duplicates < 20% (trace elements).

2.6.4.3. Consistency of Results

* Ionic balance

Fundamental principle: Electro-neutrality of aqueous solutions

Calculation formula:

$$\text{Erreur (\%)} = \left| \sum \text{cations (meq/L)} - \sum \text{anions (meq/L)} \right| / \left[\sum \text{cations} + \sum \text{anions} \right] \times 100$$

-Acceptability criteria:

CE < 500 $\mu\text{S/cm}$: Error < 10%

EC 500-1500 $\mu\text{S/cm}$: Error < 5%

CE > 1500 $\mu\text{S/cm}$: Error < 2%

- Inter-parameter relationships

Theoretical vs. Measured Conductivity:

$$\text{CE calculée } (\mu\text{S/cm}) = \sum (C_i \times \lambda_i)$$

where C_i = molar concentration, λ_i = equivalent molar conductivity.

-Common conversion factors:

$$\text{TDS} \approx \text{CE} \times 0.65 \text{ (low mineralized waters)}$$

$$\text{French hardness} = 2.5 \times [\text{Ca}^{2+}] + 4.1 \times [\text{Mg}^{2+}] \text{ (concentrations in mg/L).}$$

2.6.5. Regulatory and Normative Aspects

2.6.5.1. French and European regulatory framework

- Water intended for human consumption

French regulations set quality thresholds for substances likely to pose a short- or long-term risk to public health when present in water. These thresholds mainly relate to microbiological parameters as well as to about thirty undesirable or toxic substances.

Key regulatory considerations:

It is essential to understand that an unpleasant taste in water does not compromise its drinkability. Water can taste undesirable while meeting established quality standards.

In general, undesirable tastes in the water are attributed to the chlorine used during the disinfection process.

Table 12. Examples of essential regulatory parameters.

Parameter	Quality limit	Reference method	Inspection frequency
Lead	10 $\mu\text{g/L}$	SAA ou ICP-MS	Monthly
Nitrates	50 mg/L	Spectrophotometry or IC	Monthly
Pesticides	0.1 $\mu\text{g/L}$ per substance	HPLC-MS ou GC-MS	Quarterly
Escherichia coli	0/100 mL	Culture on selective medium	Weekly

2.7. Interpretation of Chemical Analysis Results

2.7.1. Educational objectives

The student will be able to:

1. Correctly interpret the results of chemical analyses.
2. Assess the reliability and significance of analytical data.
3. Identify sources of error and uncertainty.
4. Apply the criteria for validating the results.
5. Effectively communicate analytical findings.

2.7.2. Foundations of Analytical Interpretation

2.7.2.1 Definition and Issues

What is analytic interpretation?

The interpretation of the results of chemical analyses consists of giving meaning to the numerical data obtained by analytical methods, taking into account:

The reliability of the measurements.

The uncertainty associated with the results.

The significance of the observed discrepancies.

The context in which the analyses are applied.

2.7.2.2. Objectives of interpretation

The purpose of the interpretation is to:

Validate the quality of the results obtained.

Compare values to standards and benchmarks.

Identify anomalies or non-conformities.

Propose corrective actions if necessary.

Communicate findings clearly.

2.7.2.3. Analytical Chain and Critical Points

- Stages of the analytical chain

Sampling → Preparation → Analysis → Raw Results → Processing → Interpretation → Communication.

Critical points of interpretation:

Representativeness of the sample.

Adequacy of the analytical method.

Quality of implementation.

Validity of the statistical treatment.

Table 13. Sources of error to consider.

Type of error	Origin	Impact on interpretation
Sampling	Representativeness, conservation	Bias on the study population
Preparation	Contamination, losses	Systematic discrepancy
Analytics	Instrument, method	Imprecision, inaccuracy
Calculation	Data processing	Error in conclusion

2.7.2.4. Analytical quality parameters

- Basic analytical limits: Limit of detection (LOD) and limit of quantification (LOQ)

Good analytical practice is that when analyzing samples, analytical results below the limit of quantification should be interpreted with greater uncertainty associated with the measurement.

Operational definitions:

Limit of Detection (LOD): The smallest concentration that can be reliably detected.

Limit of Quantification (LOQ): Smallest quantifiable concentration with acceptable accuracy.

Table 14. Interpretation of results according to limits.

Result	Interpretation	Recommended expression
< LD	Not detected	"< LD" or "Not Detected"
LD ≤ result < LQ	Detected but not quantifiable	"Traces" or "< LQ"
≥ LQ	Accurately quantified	Numerical value ± uncertainty

2.7.2.5. Accuracy and Fidelity

-Accuracy assessment

Accuracy: Closeness of agreement between the average value obtained and the true or reference value.

Calculation of bias:

$$\text{Bias (\%)} = [(\text{Measured Value} - \text{True Value}) / \text{True Value}] \times 100$$

Acceptability criteria:

Major elements : | Bias | < 10%

Minor elements : | Bias | < 20%

Trace elements : | Bias | < 30%

Fidelity: Closeness of agreement between the results of independent tests.

Coefficient de variation :

$$\text{CV (\%)} = (\text{Standard Deviation} / \text{Mean}) \times 100$$

Performance criteria:

Excellent : CV < 2%

Good : 2% ≤ CV < 5%

Acceptable : 5% ≤ CV < 10%

Poor : $CV \geq 10\%$

2.7.2.6 Statistical treatment of results

- Consistency testing

* Outlier detection

Grubbs test (suspicious value):

$$G = |x_i - \bar{x}| / s$$

Rejection criteria:

$$n = 3 : G > 1.15$$

$$n = 5 : G > 1.67$$

$$n = 10 : G > 2.18$$

Checking for normalcy

Shapiro-Wilk test (recommended for < 50).

Kolmogorov-Smirnov test (for $n > 50$).

Consequences:

Normal distribution $\rightarrow$ Parametric tests.

Non-normal distribution $\rightarrow$ Nonparametric tests or transformation.

- Comparisons and significance tests

* Comparison to a reference value

Student's t-test (single sample):

$$t = (\bar{x} - \mu_0) / (s / \sqrt{n})$$

Interpretation:

$|t| < t_{\text{critique}} \rightarrow$ No significant difference.

$|t| \geq t_{\text{critique}} \rightarrow$ Significant difference.

* Comparison between two sets of results

Test F (variance comparison):

$$F = s_1^2 / s_2^2 \text{ (with } s_1^2 > s_2^2 \text{)}$$

Test t (comparison of means):

Equal Variances : Classical Student's t

Unequal Variances : Welch's t

Evaluation of measurement uncertainty

* Classification of uncertainties

Type A uncertainties (statistical assessment):

Repeatability of measurements.

Sampling variability.

Fluctuations instrumentales.

Type B uncertainties (non-statistical assessment):

Instrument calibration.

Purity of reagents.

Environmental conditions.

***Propagation of uncertainties**

General Propagation Law:

$$u^2(y) = \Sigma[(\partial f / \partial x_i)^2 \times u^2(x_i)] + 2\Sigma[(\partial f / \partial x_i)(\partial f / \partial x_j) \times u(x_i, x_j)]$$

Common special cases:

Addition / Soustraction : $u(y) = \sqrt{u^2(x_1) + u^2(x_2)}$

Multiplication / Division : $u(y)/y = \sqrt{[(u(x_1)/x_1)^2 + (u(x_2)/x_2)^2]}$

***Expression of uncertainty**

Expanded uncertainty

Standard calculation:

$$U = k \times u(y)$$

where $k = 2$ for a 95% confidence level

***Expression of results**

Recommended format:

Result = (measured value $\pm$ extended uncertainty) unit

Example: $[Ca^{2+}] = (45.2 \pm 2.1) \text{ mg/L}$

Interpretation according to the context of application

- Regulatory compliance

Comparison to standards and thresholds

Simple decision rule:

Result + U < Threshold $\rightarrow$ Compliant

Result - U > Threshold $\rightarrow$ Non-Compliant

Intermediate case $\rightarrow$ Uncertainty about compliance

Example: Drinking water

Table 15. Example of lead (threshold = 10 $\mu\text{g/L}$).

Result ($\mu\text{g/L}$)	Uncertainty U ($\mu\text{g/L}$)	Interpretation
6.5 ± 1.8	1,8	Conform ($8.3 < 10$)
8.5 ± 2.5	2,5	Uncertainty ($6.0 < 10 < 11.0$)
12.1 ± 1.5	1,5	Non-compliant ($10.6 > 10$)

- Environmental monitoring

*** Temporal evolution**

Trend detection:

Mann-Kendall test (monotonous tendency).

Linear regression (quantitative change).

Breakout testing (behavior change).

***Spatial variability**

Geostatistical analyses

Variograms : Structure of variability.

Kriging : Optimal interpolation.

Cartography: Spatial representation.

2.7.2.7. Ion Balance

$$BI = \frac{|\sum r^+ - \sum r^-|}{|\sum r^+ + \sum r^-|} \times 100 (\%)$$

With: r : quantity in reaction in (meq/L), BI : ion balance in %

BI < 2 good analysis.

2% < BI < 5 acceptable analysis.

BI > 5 bad analysis.

2.7.2.8. Presentation and communication of results

- Presentation rules and significant figures

The number of significant digits reflects the accuracy of the

Uncertainty guides the number of decimal places to be kept

Consistency between displayed accuracy and uncertainty.

Examples:

Correct : 25,4 ± 0,3 mg/L

Incorrect: 25.437 ± 0.3 mg/L (false precision)

Results Tables

Table 16. Example of a recommended structure.

Parameter	Unit	Result	Uncertainty	Method	Detection limit
pH	-	7,2	± 0.1	NF T90-008	-
Conductivity	µS/cm	485	± 24	NF EN 27888	1
Calcium	mg/L	62,3	± 3.1	NF T90-016	0,1

- Contextual interpretation

*** Typical analysis report and recommended structure:**

Sample Information

origin, date of collection.

Storage conditions.

Laboratory reference.

Analytical results

Tables with uncertainties.

Comparison to standards.

Special observations.

Interpretation

Regulatory Compliance.

Evolution compared to previous analyses.

Possible recommendations.

*Note codes and alerts

The remark code of the physico-chemical analysis makes it possible to provide details on the result by indicating whether the result obtained is below a threshold, or that there are traces.

Common codes:

< LOD : Below Limit of Detection.

< LOQ : Below Limit of Quantitation.

Traces : Detected but not quantified.

! : Non-compliant result

Practical case studies: Tap water analysis

Parameters analyzed:

Chemicals : pH, residual chlorine, nitrates.

Microbiological : E. coli, enterococci.

Organoleptics : Colour, smell, flavour.

Interpretation of the results

Table 17.Example of results.

Parameter	Result	Quality limit	Interpretation
pH	7.8 ± 0.1	$6.5 \leq \text{pH} \leq 9.0$	Compliant
Nitrates (mg/L)	42 ± 4	≤ 50	Compliant but close to the limit
E. coli (/100mL)	0	0	Compliant
Chlorine residual (mg/L)	0.05 ± 0.02	$0.1 \leq \text{Cl}_2 \leq 0.5$	Non-compliant (insufficient)

Conclusion: Water generally compliant, but vigilance on nitrates and chlorination adjustment necessary.

*Computer tools and specialized software

- Statistical processing

Recommended software:

R/RStudio : Advanced Statistical Analytics

Excel/LibreOffice : Basic calculations, graphs

Minitab : Statistical Quality Control

XLSTAT , Statistica: Excel extension for advanced analyses.

- Analytics management

LIMS (Laboratory Information Management System) :

Sample traceability.

Automatic uncertainty calculations.

Automatic report generation.

Real-time control charts.

- Validation and computer storage

Accuracy of programmed calculations.

Traceability of changes.

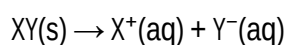
Data backup and security.

2.8 . Reconstitution in dissolved salts

2.8.1. Principle of dissolution and reconstitution

2.8.1.1. Dissolution mechanism

Upon contact with water, a crystalline salt undergoes dissolution and ionization, resulting in the formation of a cation, $X^+(aq)$, and an anion, $Y^-(aq)$. This phenomenon can be identified as follows:



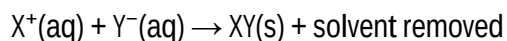
The resulting solution of this process is called an ionic solution because it contains ions and conducts electricity. This conductivity is due to the presence of ions, which are atoms or molecules that have lost or gained one or more electrons.

2.8.1.2. Principle of reconstitution

A-Definitions

Reconstitution is the opposite process of dissolution; It consists of recovering a solid salt from its ionic solution. This fundamental principle is based on the extraction of the solvent, usually water, in order to induce the recrystallization of the salt.

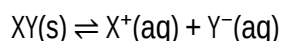
-General equation:



- Solubility balances

Solubility Product

For a poorly soluble salt XY, the dissolution equilibrium is written:



The solubility product K_s characterizes this equilibrium:

$$K_s = [X^+] \times [Y^-]$$

Influencing factors

Temperature: Solubility varies depending on the nature of the salt

***Endothermic salts :** Solubility increases with T.

***Exothermic salts :** Solubility decreases with T.

Common ion effect: The presence of a common ion decreases solubility.

Ionic Strength: Influences the activity of ions in solution.

B-Evaporative Reconstitution Methods

B-1. Simple Evaporation: Principle and Implementation

Experimental observations indicate that salt water is a homogeneous mixture composed of solid sodium chloride (salt) and liquid water; The recovery of dissolved salt requires the evaporation of water.

-Experimental procedure:

Heat the mixture to a boil in a saucepan on a sheet pan.

Observing the phenomena:

Appearance of small bubbles.

Release of "smoke" (water vapour).

Formation of large bubbles.

Decrease in water levels.

Salt appears little by little as it evaporates.

When the water is completely evaporated, a crackling sound is heard.

The salt recovered is fine.

-Yield and quality

Yield calculation

$$\text{Yield (\%)} = (\text{Mass of Salt Recovered} / \text{Mass of Initial Salt}) \times 100$$

Factors Affecting Quality

Evaporation temperature : Too high → decomposition

Evaporation Rate : Slow → larger crystals

Impurities : Concentration in the final residue.

B-2. Controlled Evaporation

-Vacuum evaporation

Advantages:

Lower temperature (product preservation).

Controlled evaporation rate.

Solvent recovery possible.

Industrial applications:

Concentration of saline solutions.

Production of pharmaceutical salts.

Seawater desalination.

B-3. Falling Film Evaporation

Principle: The solution flows in a thin film on a heated surface.

Advantages:

Short residence time.

Efficient heat exchange.

Suitable for temperature-sensitive products.

C. Crystallization and precipitation

C. 1. Cooling crystallization

- Mechanism

For salts whose solubility decreases with temperature:

Hot Dissolution : Preparation of a saturated solution.

Controlled Cooling : Decreased Solubility.

Supersaturation : Metastable state.

Nucleation and growth : Crystal formation.

-Crystallization control

Critical parameters:

Cooling Speed : Slow → Large Crystals, Fast → Small Crystals.

Agitation : Thermal and mass homogenization.

Seeding : Introduction of crystalline germs.

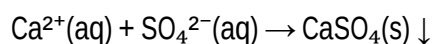
pH : Influence on crystalline form.

- Chemical precipitation

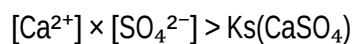
Reagent precipitation

Principle: Addition of a reactant forming a poorly soluble compound.

Example - CaSO₄ precipitation:



Precipitation conditions:



-Optimization of precipitation

Optimization factors:

Order of addition of reagents.

Concentration of solutions.

pH of the medium.

Precipitation temperature.

Precipitate maturation time.

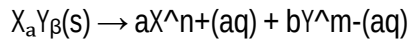
D. Reconstruction calculations and material balances

- Concentration of ionic solutions

* Relations concentration-dissolution

This relationship is essential to understanding the relationship between the amount of solute in a dissolved solid and the resulting concentration of chemical species present in the solution.

For a salt represented by X_aY_β , which dissolves according to the following rules:



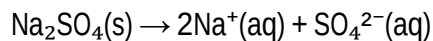
Relations de concentration :

$$[X^{n+}] = a \times C_{\text{mol}}(\text{sel})$$

$$[Y^{m-}] = b \times C_{\text{mol}}(\text{sel})$$

Example of Calculation

Dissolution of Na_2SO_4 :



$$\text{Si } [\text{Na}_2\text{SO}_4] = 0,1 \text{ mol/L} :$$

- $[\text{Na}^+] = 2 \times 0,1 = 0,2 \text{ mol/L}$
- $[\text{SO}_4^{2-}] = 1 \times 0,1 = 0,1 \text{ mol/L}$

Material balances in reconstruction

-Overall assessment

Mass of salt to be reconstituted:

$$m(\text{sel}) = C(\text{mol/L}) \times V(L) \times M(\text{g/mol})$$

Replenishment Yield:

$$\eta = (\text{Recovered mass} / \text{theoretical mass}) \times 100$$

Losses and optimization

Sources of losses:

1. Residual solubility in mother water.
2. Mechanical drive (projections, foams).
3. Thermal decomposition (evaporation).
4. Non-separable impurities.

Optimization strategies:

1. Crystal washing with cold solvent.
2. Recrystallization for purification.

3. Recycling of waters.

2.8.2. Applications industrielles et environnementales

2.8.2.1. Dessalement et production de sel

*** Dessalement d'eau de mer : techniques principales**

Multi-Effect Evaporation : Steam Reuse.

Instant Distillation (MSF - Multi-Stage Flash).

Compression de vapeur (VC - Vapor Compression).

Composition of seawater:

Total salinity : ~35 g/L

NaCl : ~27 g/L (77%)

MgSO₄ : ~3,2 g/L (9%)

MgCl₂ : ~2,4 g/L (7%)

Autres : ~2,4 g/L (7%).

*** Solar salt production**

Natural process:

Solar evaporation of seawater in shallow basins

Concentration progressive des saumures

Selective crystallization according to solubility:

CaCO₃ precipitates first.

NaCl then crystallizes.

Mg and K salts last.

2.8.2.2. Treatment of industrial effluents

*** Recovery of recoverable salts**

Electroplating Sector

Recovery of metal salts (CuSO₄, NiSO₄).

Reuse in electrolytic baths.

Reduced raw material costs.

*** Concentration of saline waste**

Objectives:

Reduction of the volume to be treated.

Facilitating storage or final processing.

Reusable water recovery.

Technologies used:

Industrial evaporators.

Vacuum crystallizers.

Reverse osmosis (prior concentration).

2.8.3. Advanced reconstitution techniques

2.8.3.1. Supercritical Water and Molten Salts

- Dissolution in supercritical water

Supercritical water conditions:

Temperature > 374 °C

Pressure > 221 bar.

Advanced research indicates that scientists use molten salts to dissolve various salts in supercritical water. This method facilitates the dissolution of all substances, thus allowing them to interact in the field of material recycling.

- Innovative applications

Recycling of composite materials:

Separation of metal components.

Selective recovery of rare earths.

Electronic waste treatment.

2.8.3.2. Assisted crystallization

- Ultrasonic crystallization

Effects of ultrasound

Cavitation-induced nucleation.

Improved crystallization kinetics.

Crystal size control.

- Crystallization in the presence of additives

Additives used:

Surfactants : Modification of surface tension.

Polymers : Control of crystal morphology.

Inhibitors : Preventing clumping.

2.8.4. Quality control and characterization

2.8.4.1. Analysis of reconstituted salts

- Chemical purity

Methods of analysis

Titrimetric Assay: Determination of the main grade.

Ion chromatography : Analysis of ionic impurities.

ICP-AES / MS : Trace Metal Elements.

Karl Fischer : Residual water content.

- Physical characterization

Properties to be checked

Particle size : Crystal size distribution.

Morphology : Crystalline shape and habitus.

Specific Area : BET Measurement.

Bulk Density : Handling Properties.

2.8.4.2. Process control

- Tracking settings

Critical variables:

Concentration of solutions (refractometry, conductometry).

Temperature (thermo-coupling, infrared).

pH (specific electrodes).

Evaporation rate (heat balances).

-Continuous optimization

Performance indicators:

Energy Efficiency = Theoretical Energy / Energy Consumed.

Selectivity = Main Product / Total Products Formed.

Productivity = kg product / (m³ reactor × h).

2.8.4.3. Energy and economic aspects

A- Energy consumption

Thermal evaporation: calculation of evaporation energy

$$Q = m \times \Delta H_{\text{vap}}$$

where $\Delta H_{\text{vap}} = 2260 \text{ kJ/kg}$ (pure water at 100°C)

-Optimization technologies

Multi-effect evaporation : 3-7 effects → 60-85% saving

Mechanical vapor compression : COP = 15-25

Heat pumps : Waste heat recovery

-Alternative techniques

Crystallization by cooling:

Cooling Energy << Evaporation Energy

Applicable if solubility decreases with T°

Heat recovery possible

B- Economic analysis

- Production costs

Cost structure (e.g. desalination):

Energy : 40-60%

Equipment depreciation : 25-35%

Maintenance and operation : 10-15%

Chemicals : 5-10%

- Valorisation of co-products

Additional sources of revenue:

Specialized salts (pharmaceutical, food).

Concentrated brines (chemical industry).

Purified water (industrial reuse).

Waste heat (district heating).

2.8.5. Environmental impact and sustainability

2.8.5.1. Effluent management

- Reduction of discharges

Zero liquid discharge (ZLD) strategies:

Preconcentration by reverse osmosis.

Evaporation of concentrates.

Crystallization of residual salts.

Solids recovery or storage.

Minimizing impact

Integrated approaches:

Use of renewable energies (solar, wind).

Heat recovery from industrial processes.

Systematic recovery of by-products.

Optimization of consumption (water, energy).

Applications to the circular economy

Material recycling: application sectors

Batteries : Recovery of Li, Co, Ni.

Solar panels : Ag, In, Ga extraction.

Catalysts : Precious metal recovery.

Electronics : Rare Earths and Critical Metals.

Industrial symbiosis

Principle: Waste from one process becomes raw materials for another Examples :

Desalination brines → Soda ash production.

Metallurgical residues → Industrial salts.

Pharmaceutical Effluents → API Recovery.

2.8.5.2. Examples of Studies:

***recovery of table salt**

Problem data

Situation: NaCl recovery from 1 L of seawater.

Initial concentration: 35 g/L of total salts.

NaCl content: 27 g/L.

Method: Complete evaporation.

Calculations and results

Theoretical mass of NaCl:

$$m(\text{NaCl}) = 27 \text{ g/L} \times 1 \text{ L} = 27 \text{ g}$$

Energy required to evaporate water:

$$Q = 1000 \text{ g} \times 2260 \text{ kJ/kg} = 2260 \text{ kJ}$$

If recovery efficiency = 95%:

$$\text{Mass recovered} = 27 \times 0.95 = 25.65 \text{ g}$$

***Optimization of an industrial crystallizer**

Operating Parameters

Sodium Sulfate Crystallizer:

Feed rate: 10 m³/h

Inlet concentration: 300 g/L Na₂SO₄

Output concentration: 100 g/L Na₂SO₄

Crystallization temperature: 10°C.

Balance sheets and performances

Crystal Production:

$$\text{Crystal flow rate} = 10 \times (300 - 100) = 2000 \text{ kg/h}$$

Crystallization efficiency:

$$h = (300 - 100) / 300 \times 100 = 66.7\%$$

To conclude this section, dissolved salt reconstitution is an essential area of technology that combines:

Thermodynamic Principles : Solubility Equilibria and Crystallization.

Kinetic aspects : Nucleation rates and crystal growth.

Process Engineering : Energy and Economic Optimization.

Environmental issues : Reduction of discharges and recovery.

Contemporary applications

Current developments include:

Energy sector:

Molten Salt Thermal Storage.

Lithium recovery for batteries.

Autonomous solar desalination.

Chemical industry:

Zero liquid discharge processes.

Selective recovery of rare earths.

Production of ultra-pure salts.

Environment:

Treatment of saline effluents.

Rehabilitation of saline soils.

Upgrading of industrial brines.

Future challenges

The challenges for the future relate to:

Energy efficiency : Reduction of consumption through innovative processes.

Selectivity : Specific separation of salts into complex mixtures.

Integration : Coupling with renewable energies and storage.

Automation : Intelligent control of crystallization processes.

Sustainability : Circular economy and systematic recovery.

Understanding the replenishment of dissolved salts is essential to address the challenges related to the energy transition, the sustainable management of mineral resources and the treatment of industrial wastewater. This field requires a multidisciplinary approach combining chemistry, thermodynamics, process engineering and environmental sciences.

2.9. Facies modifying phenomena

2.9.1. Pedagogical objectives

- Define and identify the different hydrochemical facies.
- Understanding the modifying mechanisms of chemical facies.
- Analysing the spatial and temporal evolution of facies.
- Interpreting hydrochemical classification diagrams.
- Plan for facies transformations according to the conditions.

2.9.1.1. Introduction to facies and their classification

A. Definition of chemical facies

Chemical facies refers to the dominant ionic composition of water, characterized by the majority ions. Inspired by geology, this concept facilitates the classification of waters according to their chemical signature, thus making it possible to understand their origin and evolution. The Piper diagram uses the key elements to illustrate the different groundwater facies and also offers a way to track the transformation of water from one facies to another through temporal analyses.

B. Classification of the main facies

-Facies according to the dominant anions:

Bicarbonate (HCO_3^-): Young waters, with little mineralization.

Sulphate (SO_4^{2-}): Evaporite dissolution, sulfide oxidation.

Chloride (Cl^-): Ancient waters, evaporation, marine influence.

-Facies according to the dominant cations:

Calcium (Ca^{2+}): Carbonate dissolution, calcium silicates.

Magnesian (Mg^{2+}): Mafic alteration, dolomites.

Sodium (Na^+): Ion exchange, evaporation.

Potassic (K^+): Alteration of potassium feldspars (rare).

C. Representation Tools

C. 1. Piper diagram

-Triangular structure:

Triangle des cations : Ca^{2+} , Mg^{2+} , $\text{Na}^+ + \text{K}^+$

Triangle of anions : $\text{HCO}_3^- + \text{CO}_3^{2-}$, SO_4^{2-} , $\text{Cl}^- + \text{NO}_3^-$

Central diamond : Synthesis of the two triangles.

-Classification of facies:

Calcium bicarbonate: Zone 1 (young water).

Sodium bicarbonate: Zone 2 (ion exchange).

Sodium chloride : Zone 3 (advanced waters).

Calcium chloride : Zone 4 (very old waters).

Calcium sulphate : Zone 5 (evaporitic influence).

Mixed facies : Intermediate zones.

C. 2. Stiff Diagram

Polygonal representation.

Direct visualization of concentrations.

Easy comparison between samples.

C. 3. Schoeller-Berkaloff diagram

Logarithmic scales.

Temporal evolution.

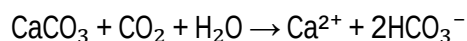
Geochemical processes.

2. 9.1.2. Natural Modifying Processes

Rock weathering and dissolution

- Carbonate dissolution

Fundamental mechanism:



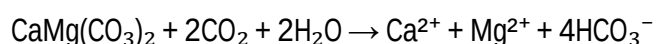
Evolution of the facies:

Origin : Pure water (no defined facies).

Evolution : Calcium bicarbonate facies.

Control factors : PCO_3 , temperature, pH.

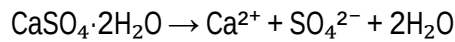
Case of dolomite:



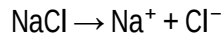
Modification: Transition to calcico-magnesium bicarbonate facies.

-Dissolution of evaporites

Gypsum:



Halite:



Impact on facies:

Gypsum : Evolution towards calcium sulphate facies.

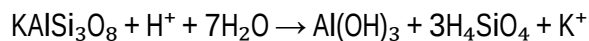
Halite : Evolution to sodium chloride facies.

Mixed Evaporites : Multi-ionic Complex Facies.

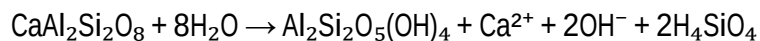
- Alteration of silicates

Hydrolysis of feldspar

Potassium feldspar:



Calcium plagioclases:



Facies modifications:

Libération de cations : Ca^{2+} , Na^+ , K^+

Acidity consumption : Increased pH

Clay Formation : Modification of Porosity.

-Alteration of mafic minerals

Olivine:



Pyroxenes:



Impact : Evolution towards magnesian bicarbonate facies.

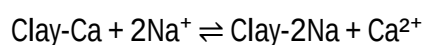
2.9.1.3. Exchange and transformation process

A. Ion exchanges

Mechanism on clays

Clays can exchange cations according to their cation exchange capacity (CEC).

$\text{Ca}^{2+} / \text{Na}^+$ exchange:



Favorable conditions:

High ionic strength : Promotes exchanges.

High $[\text{Na}^+]/[\text{Ca}^{2+}]$ ratio: Shift to the right.

Long Contact Time: Balancing.

B. Consequences on facies

-Typical evolution

Calcium bicarbonate facies → Sodium bicarbonate facies.

Exchange indices:

Schoeller index : $IS = (\text{Cl}^- - \text{Na}^+)/\text{Cl}^-$

Exchange index : $r(\text{Na}^+ - \text{Cl}^-)/r(\text{SO}_4^{2-})$.

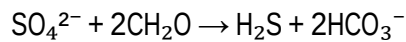
Interpretation:

$IS > 0$: $\text{Ca}^{2+} \rightarrow \text{Na}^+$ exchange

$IS < 0$: Échange $\text{Na}^+ \rightarrow \text{Ca}^{2+}$

- Redox process

Sulfate reduction In anaerobic conditions:



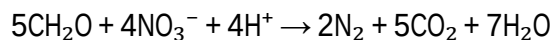
Modification of the facies:

Decrease $[\text{SO}_4^{2-}]$

Increase $[\text{HCO}_3^-]$

Evolution : Sulphate → Bicarbonate

Nitrate reduction ,Denitrification:



Limited impact on facies (NO_3^- generally minority).

C. Secondary precipitation and dissolution

C.1. Carbonate precipitation

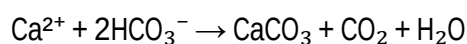
Precipitation conditions:

CO_3 degassing : Decrease in acidity

Evaporation : Concentration of ions..

pH Increase : Shift Balance.

Reaction:



Impact : Change in $\text{Ca}^{2+}/\text{HCO}_3^-$ ratio

C.2. Formation of authigenic minerals

Specific conditions:

Zeolites : Alkaline waters rich in Si

Chlorites : Reducing Conditions, Mg, Fe

Smectites : Weathering in hot climates.

D. Modifying Physical Processes

D.1. Water Mixing

- Binary Mix

Law of Mixing:

$$C_{\text{mélange}} = (Q_1 \times C_1 + Q_2 \times C_2) / (Q_1 + Q_2)$$

Graphical representation:

Piper's Diagram : Aligned Points.

Binary Diagram : Linear Relationships.

- Identification of mixing poles

Methods of analysis:

Principal Component Analysis (PCA).

Ionic correlation diagrams.

Inverse Mix Models.

Typical example:

Groundwater + Surface Water = Mixed Water

$(\text{HCO}_3\text{-Ca}) + (\text{SO}_4\text{-Ca}) = (\text{HCO}_3\text{-SO}_4\text{-Ca})$.

D.2 Evaporation and concentration

-Simple evaporation

Process:

Uniform concentration of all ions

Concentration factor = Initial volume / Final volume.

Evolution of the facies:

Preservation of relative proportions.

Modification possible by selective precipitation.

-Evaporation with precipitation

Precipitation sequence:

CaCO₃ (factor 4-5)

CaSO₄ 2H₂O (factor 8-10)

NaCl (factor 80-100)

K-Mg salts (factor >100).

Evolution of the facies:

$\text{HCO}_3\text{-Ca} \rightarrow \text{SO}_4\text{-Ca} \rightarrow \text{Cl-Na} \rightarrow \text{Cl-K-Mg}$

E .Temporal and spatial control factors

E .1. Temporal evolution

- Process kinetics

Relative speeds:

Carbonate Dissolution : A few hours to days.

Ionic exchanges : Days to months.

Silicate weathering : Months to years.

Redox evolution : Years to decades.

- Evolutionary sequences

Meteoric water → Groundwater:

1. Dissolution $\text{CO}_2 \rightarrow$ Acidification
2. Carbonate attack $\rightarrow \text{HCO}_3\text{-Ca}$
3. Ion exchanges $\rightarrow \text{HCO}_3\text{-Na}$
4. Dissolution evaporites $\rightarrow \text{Cl-Na}$ or $\text{SO}_4\text{-Ca}$
5. Redox Process $\rightarrow$ Secondary Changes.

E. 2. Space controls

-Geochemical zoning

Flow zones:

Recharge zone : Calcium bicarbonate facies.

Transit zone : Gradual evolution.

Discharge zone : Advanced facies (Cl-Na).

Lithological control:

Geological formations:

Limestone : $\text{HCO}_3\text{-Ca}$ facies.

Evaporites : $\text{SO}_4\text{-Ca}$ or Cl-Na facies.

Crystalline rocks : Variable facies according to mineralogy.

Clay formations : Modifier by exchange.

F. Anthropogenic modifiers

F.1. Pollution et contamination

-Sources of change

Agricultural pollution:

Nitrates : $\text{NO}_3\text{-Ca}$, $\text{NO}_3\text{-Na}$

Sulfates : Potash fertilizers.

Chlorides : Spreading of salt.

Industrial pollution:

Heavy metals : Changing equilibrium.

Acids : Change in pH, mobilization of elements.

Solvents : Complexation, co-solvent effects.

- Impact on facies

Example :P nitrate ollution

Natural facies: $\text{HCO}_3\text{-Ca}$

Polluted facies: $\text{NO}_3\text{-HCO}_3\text{-Ca}$ or $\text{NO}_3\text{-Ca}$

F. .2. Human activities

- Intensive pumping

Consequences:

Drawdown of the aquifers.

Inversion of hydraulic gradients.

Mixing of water from different origins.

Saline intrusion (coastal areas).

- Injection and artificial recharging

Direct Change:

Dilution of background concentrations.

Introduction of new facies.

Modification of geochemical equilibria.

2.9.2. Study and monitoring methods

2.9.2.1. Analytical Approaches

- Classic analytics

Essential Parameters:

Major ions : Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^-

Physical parameters : pH, conductivity, temperature

Trace elements : Process indicators.

-Specific trackers

Natural tracers:

Stable isotopes : $\delta^{18}\text{O}$, δD (origin of water).

Carbon isotopes : $\delta^{13}\text{C}$ (origin of dissolved carbon).

Sulphur isotopes : $\delta^{34}\text{S}$ (origin of sulphates).

Anthropogenic tracers:

CFC : Age of recent waters.

^3H : Thermonuclear marker.

Pesticides : Agricultural pollution.

-Geochemical modeling

*** Calculation codes**

PHREEQC:

Thermodynamic equilibria.

Reaction kinetics.

Responsive transport.

MINTEQ:

Ionic speciation.

Mineral saturation.

Surface adsorption.

*** Applications**

Inverse modeling:

Process identification.

Quantification of transfers.

Validation of hypotheses.

2.9.2.2. Case studies and examples

- Evolution along a flow

Geological context: limestone aquifer

Upstream : Massive limestone.

Median : Marls and evaporites.

Downstream : Alluvium.

Table 18. Example of facies evolution.

Position	Facies	Dominant Process
Upstream	HCO ₃ -Ca	Calcite Dissolution
Midway	SO ₄ -HCO ₃ -Ca	Gypsum Dissolution
Downstream	Cl-SO ₄ -Na	Ion exchange, evaporation

-Seasonal change

Alluvial aquifer

Factors of variation:

Winter Recharge : Dilution.

Summer low water level : Concentration.

River Connection : Variable Mix.

- Cyclical evolution

Wet period:

Dilute Facies: HCO₃-Ca (low mineralization).

Dry period:

Concentrated facies: SO₄-Cl-Ca-Na (strong mineralization).

Practical applications

*** Resource management**

-Identification of origins

Differentiation of sources:

Rainwater : Very low mineralization.

Surface water : HCO₃-Ca generally.

Deep Groundwater : Evolved Facies.

Marine water : Cl-Na dominant.

- Mixture detection

Mixing indicators:

Aligned Points on Binary Diagrams.

Intermediate facies on Piper.

Linear relationships between conservative elements.

***Environmental Monitoring**

- Early detection

Red flags:

Abrupt change of facies.

Appearance of unnatural ions.

Changing Ionic Ratios.

-Effectiveness monitoring

Decontamination:

Evolution of facies to natural state.

Decrease in specific concentrations.

Restoration of geochemical balances.

3. Chapter 2 (Thermodynamics of aqueous solutions)

3.1. Introduction

Thermodynamics studies the relationships between temperature variations within systems and changes in the physical state of matter. This discipline aims to understand the principles that govern the transfer of thermal energy and its conversion, particularly into other forms of energy such as mechanical and chemical energy. His objective was the exhaustive study of all energy transformations – chemical, nuclear, mechanical and thermal – with a particular interest in the conversion of heat into work and the reverse process (Rougier, 1918).

3.2. Fundamentals

3.2.1. Systems in thermodynamics

In thermodynamics, understanding the macroscopic characteristics of a system – namely temperature, volume, pressure and composition – is essential. A system is characterized as a mixture or a solution, its nature being determined by the proportions of its constituents. A mixture refers to a phase (liquid, gaseous or solid) that includes several substances in comparable quantities and is considered uniform. This principle applies, for example, to systems with only two main components.

Different categories of systems are identified:

An open system allows the transfer of matter and energy between itself and its environment.

A closed system interacts only by exchanging energy with its environment, while prohibiting any transfer of matter.

An isolated system does not exchange heat or matter with its environment (Bouasse, 1913). In thermodynamics, it is essential to identify the macroscopic characteristics of a system: temperature,

volume, pressure and composition. A system is defined as a mixture or solution, the proportion of the constituents determining its nature. A mixture is a phase (liquid, gas, solid) containing several substances in comparable quantities and treated in a similar way. This applies, for example, to systems with only two main components.

There are several types of systems:

- The open system allows an exchange of matter and energy with the surrounding environment.
- The closed system only exchanges energy with its environment, without transferring matter.
- The insulated system does not carry out any exchange, either of heat or matter, with the outside (Bouasse, 1913).

Note: In conventional terms, a system that absorbs energy or matter is assigned a positive sign, while the loss of energy or matter is assigned a negative sign.

A system reaches equilibrium when all its variables remain unchanged over time and at all points in the system.

3.2.2. System Transformations

Switching from one state to another requires the modification of one or more parameters. Here are the different categories of transitions:

- a) Isotherm: this process takes place at a uniform temperature.
- b) Isochore: the volume is maintained at a constant level.
- c) Isobaric: the pressure is maintained at a constant level.
- d) Adiabatic: the system is characterized by the absence of heat transfer to the external environment.
- e) Reversible: This transition can be reversed and passes through an infinite set of intermediate states of equilibrium, illustrated by infinitely progressive processes, such as the ideal boiling of water.
- f) Irreversible: This process takes place in a single direction and does not allow a return to the initial state of equilibrium without external intervention (such as an explosion).

3.2.3. Change in physical condition

Matter can exist in three distinct states: solid, liquid or gaseous. Generally, a change in state occurs at constant temperature and pressure. This transition involves an exchange of energy called latent heat. When the temperature increases, the vapor pressure of a liquid also increases. Therefore, when a liquid is heated until its vapor pressure reaches atmospheric pressure, gas bubbles are formed; This phenomenon is called boiling. Evaporation, an endothermic process, indicates that the energy supplied to the liquid facilitates its transformation into a gas. This energy, called enthalpy of vaporization (ΔH_v), must be delivered consistently throughout the boiling process to maintain this transition.

Concept of heat (Q)

- The transfer of heat between a system and its environment results in either a change in temperature or a change in state. For minor variations, the amount of heat exchanged (ΔQ) during heating or cooling processes can be determined using the following formula:
- The change in heat, ΔQ , is equal to the product of the heat capacity, C, and the change in temperature, dT.

- In this context, ΔT represents the temperature change, while C denotes the mass heat capacity measured in joules per kelvin (J K^{-1}). This value is called elemental heat.

- Mass heat capacity can be represented by specific heat (C in $\text{J K}^{-1} \text{kg}^{-1}$), depending on the circumstances, and the total heat is then expressed as follows:

- The change in heat energy, represented by ΔQ , is equal to the mass (m) multiplied by the specific heat capacity (C) and the change in temperature (dT).

- The specific molar heat capacity (C , measured in $\text{J K}^{-1} \text{mol}^{-1}$) is calculated as follows:

- The change in heat, ΔQ , is expressed as the product of the number of moles, n , the specific heat capacity, C , and the change in temperature, dT .

The Q symbol denotes the specific type of reaction.

- $Q < 0$ indicates that the system emits heat, characteristic of an exothermic reaction, such as the dissolution of sodium hydroxide (NaOH).

- $Q > 0$: The system absorbs heat, as seen in endothermic reactions such as the dissolution of KNO_3 .

- $Q = 0$: There is no heat transfer; The reaction is classified as athermal, as seen in the case of esterification equilibrium.

Latent heat

Latent heat is the energy that a system gains or loses when it moves from one state to another – such as from solid to liquid – without the temperature changing at all (Brunet and al., 2019).

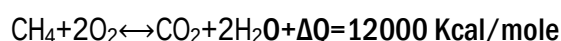
Basically, for a change of state, L is the amount of energy needed to transform a mole (or a kilo) of matter from one phase to another.

Some concrete examples:

- To melt ice into water, it takes about 80 calories per gram ($L_f = 80 \text{ cal/g}$).
- To spray water, it goes up to 2256 kJ/kg, or 539 kcal/kg (L_v).

A quick note: it's a bit like reaction heat, which measures the energy released or absorbed during a chemical reaction. For example: $\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O} + \Delta Q = 12,000 \text{ kcal/mol}$.

Example :



3.2.4. Heat exchange between two bodies

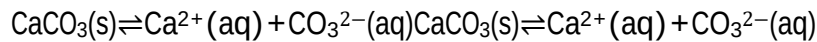
According to the principle of conservation of energy, all the heat that is lost in one system necessarily ends up in another. So, when two objects exchange heat and a chemical reaction occurs in one, you only need to check the rise or fall in temperature of the other to accurately calculate the amount of heat involved.

3.3. State of equilibrium (water-minerals in solution: fundamental relationships)

The equilibrium state between a solid mineral and an aqueous solution is governed by the fundamental laws of thermodynamics. At equilibrium, the chemical potential of the constituent in the solid is equal to

that in the solution. This results in an equality relationship of chemical potentials, which makes it possible to predict the direction of the exchange of matter between the mineral and the solution.

Example of a mineral dissolution: dissolution of calcium carbonate



At equilibrium, the product of the ionic activities of the dissolved species is constant and equal to the solubility product (K_s) = $a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}$ where a denotes the activity, which takes into account non-ideal interactions in solution

Thermodynamic equilibrium criterion: For a system with constant temperature and pressure, the equilibrium state is reached when the Gibbs free energy (G) is minimal. Any spontaneous evolution of the system tends to decrease G , and to equilibrium $dG = 0$

Ionic activity product and saturation index: The ionic activity product (Q) is defined as:

$$Q = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}$$

- If $Q < K_s$: the solution is unsaturated, the mineral can dissolve.
- If $Q = K_s$: the solution is in equilibrium with the mineral.
- If $Q > K_s$: the solution is supersaturated, the mineral may precipitate

$$SI = \log \left(\frac{Q}{K_s} \right)$$

The saturation index (SI) is defined by:

- $SI < 0$: dissolution possible
- $SI = 0$: equilibrium
- $SI > 0$: Possible precipitation.

3.4. Ionic Interactions in Solution

In aqueous solution, ions interact with each other and with water molecules. These interactions change the behavior of the ions compared to an ideal solution (where each ion would be independent).

Types of interactions:

- Electrostatic interactions: Ions with opposite charges attract each other, those with the same charge repel each other.
- Solvation effect: The ions are surrounded by water molecules, which stabilizes their presence in solution.
- Ionic force effect: The higher the total ion concentration, the greater the interactions, which changes the properties of the solution

Consequence: The effective concentrations of ions (activities) differ from their actual concentrations. We then introduce the activity coefficient (γ):

$$a_i = \gamma_i \cdot [i] \text{ where } i \text{ is the concentration of the ion } i.$$

3.5. Thermodynamic modelling of ionic interactions (calculation of saturation indices)

To take into account ionic interactions, thermodynamic models are used to calculate the activity coefficients.

a) Debye-Hückel law (for dilute solutions): This law relates the activity coefficient to the ionic strength (I) of the solution: $\log \gamma_i = -A z_i^2 \sqrt{I}$ where:

- A is a temperature and solvent dependent constant,
- z_i is the charge of the ion,
- $I = \frac{1}{2} \sum c_j z_j^2$ is the ionic strength, c_j being the concentration of each ion.

b) Calculation of the ionic activity product (Q) and the saturation index (SI): For a dissolution reaction:

$$Q = a_{A_n} \cdot a_{B_n} \dots$$

Each activity is calculated from the concentration and the activity coefficient: $a_i = \gamma_i \cdot [i]$

We then compare Q to the thermodynamic equilibrium constant (K) to obtain the saturation index: $SI = \log(Q/K)$. This calculation makes it possible to predict whether a mineral will dissolve or precipitate in a given solution.

c) Advanced models: For more concentrated solutions, more complex models (extended Debye-Hückel, Pitzer, etc.) are used that take into account the specific nature of ions and their interactions at short distances.

Examples:

Example 1: Dissolution of halite (NaCl)

At equilibrium, the chemical potential of a constituent is the same in all phases in which it is present. For a mineral in contact with an aqueous solution, this means that the tendency to dissolve or precipitate depends on the comparison between the ionic activity product in solution and the solubility constant of the mineral.

The dissolution reaction is: $\text{NaCl(s)} \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

At breakeven:

$$K_s = a_{\text{Na}^+} \cdot a_{\text{Cl}^-}$$

If we dissolve 1 mole of NaCl in 1 L of pure water, we initially obtain 1 mol/L of each ion. But, because of ionic interactions, the activities are slightly lower than the actual concentrations.

Saturation index (SI) calculation:

Suppose that in natural water, we measure:

- $[\text{Na}^+] = 0.01 \text{ mol/L}$
- $[\text{Cl}^-] = 0.01 \text{ mol/L}$
- $K_s = 0.0063$ (typical value at 25°C)

We assume that the activity coefficients are close to 1 (very dilute solution), therefore:

$$Q = [\text{Na}^+] \cdot [\text{Cl}^-] = 0.01 \times 0.01 = 0.0001 \quad Q = [\text{Na}^+] \cdot [\text{Cl}^-] = 0.01 \times 0.01 = 0.0001$$

$$SI = \log(Q/K_s) = \log(0.0001/0.0063) \approx -1.8$$

Interpretation: $IF < 0$, the solution is unsaturated, the halite can dissolve.

Example 2: Effect of ionic strength on activity coefficients

The ions in solution interact with each other, which changes their behaviour compared to an ideal solution. These interactions are mainly electrostatic and depend on the ionic strength of the solution.

Consider a solution containing:

- $[Na^+] = 0.1 \text{ mol/L}$
- $[Cl^-] = 0.1 \text{ mol/L}$

The ionic strength I is: $I = \frac{1}{2} \sum c_i z_i^2 = 0.5(0.1 \times 1^2 + 0.1 \times 1^2) = 0.1$

With Debye-Hückel's law (simplified for dilute solutions):

$$\log \gamma_i = -0.509 \cdot z_i^2 \cdot \sqrt{I}$$

For Na^+ and Cl^- ($z=1$)

$$\log \gamma = -0.509 \cdot 1 \cdot \sqrt{0.1} \approx -0.161 \quad \gamma \approx 10^{-0.161} \approx 0.69$$

Therefore, the actual activity of each ion is:

$$a_{Na^+} = 0.1 \times 0.69 = 0.069 \quad a_{Cl^-} = 0.1 \times 0.69 = 0.069$$

Example 3: Calcite saturation ($CaCO_3$)

To predict the precipitation or dissolution of a mineral, activities (not concentrations) must be used in the calculation of the ionic activity product.

Suppose:

- $[Ca^{2+}] = 2 \times 10^{-4} \text{ mol/L}$
- $[CO_3^{2-}] = 2 \times 10^{-4} \text{ mol/L}$
- $\gamma_{Ca^{2+}} = 0.5 \quad \gamma_{CO_3^{2-}} = 0.5$
- $K_s = 4.8 \times 10^{-9}$ at $25^\circ C$

Calculation of activities:

$$a_{Ca^{2+}} = 2 \times 10^{-4} \times 0.5 = 1 \times 10^{-4} \quad a_{CO_3^{2-}} = 2 \times 10^{-4} \times 0.5 = 1 \times 10^{-4}$$

$$Q = a_{Ca^{2+}} \cdot a_{CO_3^{2-}} = (1 \times 10^{-4})^2 = 1 \times 10^{-8} \quad SI = \log(1 \times 10^{-8} / 4.8 \times 10^{-9}) \approx \log(2.08) \approx 0.32$$

Interpretation: $IF > 0$, the solution is supersaturated, the calcite can precipitate.

4. Chapter 3 (Ionic strength and chemical activity)

4.1. Introduction

Actual electrolyte solutions deviate from ideal behavior because ions interact with each other and with the solvent, changing their "chemical efficiency" or activity relative to their actual concentration. To take these effects into account, we introduce the activity coefficient, denoted γ_i , which relates activity a_i to concentration c_i by the relationship $a_i = \gamma_i c_i$.

In highly dilute solutions, $\gamma_i \approx 1$ and the solution approaches the ideal behavior, while at higher concentrations $\gamma_i < 1$, indicating significant attractive ionic interactions. Debye-Hückel theories and

its extensions (approximations and empirical laws) make it possible to relate these activity coefficients to the ionic strength of the solution.

4.2. Ionic strength and chemical activity

Ionic strength I is a quantity that condenses the overall effect of all ions present in solution as a function of their charge and concentration. It is defined by:

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

where c_i is the concentration of the ion i and z_i its charge.

The chemical activity of a solute i is defined by:

$$a_i = \gamma_i c_i$$

in molar concentration (or $a_i = \gamma_i m_i$ molality), where γ_i is the individual activity coefficient. For an electrolyte $A_\nu B_\mu$ giving ν cations and μ anions, the ionic mean $\gamma_\pm$ defined by :

$$\gamma_\pm = (\gamma_+^\nu \gamma_-^\mu)^{1/(\nu+\mu)}.$$

The deviation from ideality translates thermodynamically into an excess contribution to the chemical potential, usually expressed as a function of $\ln \gamma_i$ or $\log_{10} \gamma_i$. Theoretical electrolyte models aim to relate these coefficients to the structure of the solution (charge distributions, Debye length, dielectric constants, etc.).

4.2.1. Debye-Hückel theory: principles

Debye-Hückel's theory describes dilute electrolyte solutions by taking into account the electrostatic attraction between a given ion and the opposite-sign ion cloud around it. This approach is based on the linearized Poisson-Boltzmann equation, in the approximation of dilute solutions and a continuous solvent of dielectric constant. ϵ

The main hypotheses are as follows.

- Ions are considered to be point charges immersed in a dielectric continuum (continuous medium model).
- The interactions considered are purely Coulombian, with ionic size contributions appearing only in later extensions.

-The solution is generally electrically neutral, and the distribution of ions obeys linearized Boltzmann statistics.

The theory introduces the Debye length, κ^{-1} which characterizes the thickness of the screening ionic layer around a given ion. This length is related to the ionic strength of the solution, and the more concentrated the solution (high ionicity), the κ^{-1} smaller (more efficient screen).

4.2.2. Debye-Hückel Limit Model (DHL)

Mathematical expression

Within the limit of highly dilute solutions (weak ionic strength), the theory leads to the Debye-Hückel limit law, which relates the average activity coefficient of an electrolyte to the square root of the ionic force. In decimal form, we can write for an ion i : and for the ionic mean of an electrolyte:

The constant A depends on the temperature, the permittivity of the solvent and its density; for water at 25 °C, in molar units. This law is called "limiting" because it is strictly valid only for, typically for mol·

Scope of Validity and Interpretation

The limit law applies to solutions that are sufficiently dilute that finite ion size and short-range correlation interactions can be neglected. In this regime, $\log \gamma_i$ varies linearly with $\sqrt{I}$, which allows the law to be verified experimentally by activity measurements (potentiometry, osmosis, solubility, etc.) Physically, the more the ionic strength increases, the more the electrostatic interactions are "screened", which reduces the free energy associated with the solitary ion and therefore decreases below unity. However, the limit law is insufficient to correctly describe multivalent ion solutions or concentrations above a few millimoles per liter.

4.2.3. Debye-Hückel Extended Formula (DHE)

4.2.3.1. Motivation and general form

For higher concentrations, the finite ion size and volume exclusion become important, and the limiting law must be changed. Debye and Hückel, and then Hückel alone, proposed "extended" expressions incorporating an ionic size parameter a in the denominator. A commonly used form of the extended Debye-Hückel formula (in decimal notation) is:

$$-\log_{10} \gamma_i = \frac{Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}}$$

Where A and B are solvent- and temperature-dependent constants, and a is an effective ionic size parameter. A similar form can be written for the mean coefficient by replacing with and using an appropriate size parameter.

4.2.3.2. Parameters and validity

For water at 25 °C, the constants A and B take approximate values and. The ionic size parameter is usually on the order of a few angstroms and can be adjusted to better reproduce the experimental data.

The extended equation is generally considered reliable up to ionic forces of the order of mol·L approximately, beyond which more sophisticated models (Pitzer, SIT, etc.) become necessary. However, it is a useful compromise between analytical simplicity and acceptable precision for many applications in solution chemistry, analytical chemistry and hydrogeochemistry.

4.2.4. Approximation de Güntelberg (AG)

4.2.4.1. Basic Idea

The Güntelberg approximation is a simplified variant of the Debye-Hückel theory, often formulated as part of the "charging process", where the work required to gradually charge an ion in an electrolytic medium is considered. This approach allows to obtain approximate expressions of activity coefficients from integrations of charge contributions as a function of ionic strength. In the Güntelberg approximation, some contributions (e.g. longer-range correlations or size corrections) are treated more coarsely in order to obtain an analytically usable relationship. Conceptually, it lies between the limit law and more complete models such as the theory of the spherical mean medium or modern developments of charging processes.

4.2.4.2. Role and limitations

The Güntelberg approximation is mainly of theoretical interest to understand how activity models can be derived by successive financial load processes (Debye vs Güntelberg) and to compare different formulations of the same underlying physics. Recent work has shown the links and differences between these two types of charging processes, highlighting the conditions under which Debye and Güntelberg formulations are equivalent or divergent. For practical calculations in aqueous solution, the extended Debye-Hückel and Davies equations are the most accurate and best parameterized.

4.2.5. Debye-Hückel Extended Formula (DHE)

4.2.5.1. Motivation and general form

For higher concentrations, the finite ion size and volume exclusion become important, and the limiting law must be changed. Debye and Hückel, and then Hückel alone, proposed "extended" expressions incorporating an ionic size parameter a in the denominator. A commonly used form of the extended Debye-Hückel formula (in decimal notation) is:

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Where A and B are solvent- and temperature-dependent constants, and a is an effective ionic size parameter. A similar form can be written for the mean coefficient by replacing with and using an appropriate size parameter.

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For water at 25 °C, the constants A and B take approximate values and. The ionic size parameter is usually on the order of a few angstroms and can be adjusted to better reproduce the experimental data.

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4.2.6.1. Basic Idea

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The Güntelberg approximation is mainly of theoretical interest to understand how activity models can be derived by successive financial load processes (Debye vs Güntelberg) and to compare different formulations of the same underlying physics. Recent work has shown the links and differences between these two types of charging processes, highlighting the conditions under which Debye and Güntelberg formulations are equivalent or divergent. For practical calculations in aqueous solution, the extended Debye-Hückel and Davies equations are the most accurate and best parameterized.

4.2.7. Davies' Law

4.2.7.1. Empirical Formulation

Davies' law is an empirical extension of Debye-Hückel's theory to more accurately describe activity coefficients at moderate ionic forces. It is often written, for an ion i, in the following form at 25 °C.

$$\log_{10} \gamma_i = -Az_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0,3I \right]$$

where A has the same meaning as in the Debye-Hückel theory.

For the ionic mean of an electrolyte, an analogous expression can be used by replacing by. The presence of the linear term en (coefficient 0.3) allows a better representation of the experimental data at higher concentrations than those covered by the classical extended formula.

4.2.7.2. Scope of validity and use

Davies' law is generally considered reliable for ionic forces up to about $0.5 \text{ mol} \cdot \text{L}$ for electrolytes (NaCl, KCl, etc.), with deviations of the order of a few percent. For electrolytes with higher charges, the accuracy decreases, and more advanced models are often required.

This law is widely used in geochemistry, hydrogeology and environmental chemistry, as it offers a good balance between simplicity of implementation and acceptable accuracy over a wide salinity range (fresh to brackish water).

4.3. Comparison of the four approaches

The following table summarizes the main features of the Debye-Hückel boundary model, the extended formula, the Güntelberg approximation and Davies' law.

Table 19. Synthesis of ionic activity models Model.

Ionic activity models Model	Equation	Domain of validity (Ionic strength I)	Required parameters	Key features
Debye-Hückel limit law	$\log(\gamma_i) = -0.509 z_i^2 \sqrt{I}$	$I < 0.005$	None (only z_i charge).	-Fundamental theory based on Coulomb electrostatic interactions - Considers ions to be point charges -Accuracy limited to highly dilute solutions.
Debye-Hückel formula extended	$\log(\gamma_i) = -\frac{0.509 z_i^2 \sqrt{I}}{1 + 0.328 a \sqrt{I}}$	$I < 0.1$	Ionic size parameter a (in Å)	-Takes into account the finite radius of hydrated ions. -Significant improvement over the limit law -Parameter typically between 3 and 9 Å depending on the ion.
Approximation de Güntelberg	$\log(\gamma_i) = -\frac{0.509 z_i^2 \sqrt{I}}{1 + \sqrt{I}}$	$I < 0.1$	None (set to 3.0 Å)	-Simplification of the extended formula with $a = 3.0$ Å for all ions. -Avoids the need to know the specific ion diameter - For $I = 0.01$ M, $\gamma = 0.65$ (ion ²⁺) and 0.38 (ion ³⁺)

Davies' Law	$\log(\gamma_i)$ $= -0.509 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \right)$	$I < 0.5$	None	-Empirical extension with corrective term 0.3I - The only simple model reproducing the increase from γ_i to $I > 0.4$ - ~2% accuracy for 1:1 electrolytes at 0.1 M -Particularly useful for complex ions.
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4.4. Strategy for choosing the model in practice

In practice, the choice of model for the calculation of activity coefficients depends on the concentration, the nature of the ions and the precision required. A typical strategy can be summarized as follows.

1. Very dilute solutions ($I < 10^{-3}$ to 10^{-2}): use of the Debye-Hückel limit law, sufficient for most basic needs.
2. Dilute to moderate solutions ($I \approx 10^{-2} - 10^{-1}$): use of the extended Debye-Hückel formula with an appropriate ionic size parameter
3. Moderately concentrated solutions ($I \approx 0.1 - 0.5$): use of Davies' law, particularly for electrolytes
4. Concentrated or multivalent ion solutions: adoption of advanced models (Pitzer, SIT, MSA), beyond the scope of this course.

For bachelor's or master's level courses, these four approaches offer a progressive overview, allowing to move from a simple theoretical description to empirical models adapted to experimental data.

Additional Notes

Model convergence: The four approaches give similar results for $I < 0.01$ M, but diverge significantly beyond $I = 0.1$ M. The constant 0.509 in all equations corresponds to the Debye-Hückel parameter A for water at 25°C.

Common limitations: These models assume no ion pair formation and become inadequate for highly charged or asymmetric electrolytes at high concentrations. For $I > 0.5$ M, more sophisticated models such as Pitzer equations are needed.

5. Chapter 4 (Calco-carbonic equilibria and calculations of ionic speciations)

5.1. Definition and mechanisms of calco-carbonic equilibrium

The calco-carbonic system includes all chemical reactions involving carbon dioxide (CO_2), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and calcium (Ca^{2+}) ions in water. It governs a major part of the chemistry of natural waters and determines in particular their hardness, pH and buffering capacity with respect to acidic or basic inputs.

In the steady state, the different forms of inorganic carbon are connected by acid-base and dissolution/precipitation reactions. The calculation of ion speciation consists of evaluating the relative concentration of each species from the equilibrium constants and the pH, in order to predict, for example, whether calcium carbonate (CaCO_3) will dissolve or precipitate.

Calco-carbonic equilibrium occurs when the calcium, bicarbonate and carbonate contents remain stable in the water, due to a set of reactions involving dissolved CO_2 , carbonate forms and solid CaCO_3 . This system determines the quality of the water, its scaling or aggressive nature and its ability to dissolve or deposit calcium carbonate.

When natural water comes into contact with carbon dioxide, it dissolves, forms carbonic acid (H_2CO_3), and then dissociates into bicarbonate and carbonate as follows:

- $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$
- $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$
- $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$

At the same time, calcium carbonate present in rocks or in suspension can interact with these dissolved species:

- $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$

5.2. Factors influencing the calco-carbonic balance

Several parameters control the stability of this balance:

pH: A low pH promotes the dissolution of CaCO_3 , while a high pH induces its precipitation.

CO_2 content: A high concentration of dissolved CO_2 acidifies the environment and strengthens the dissolution of calcium carbonate.

Temperature: it modifies the solubility of carbonate species and calcium. · Hardness and alkalinity: Ca^{2+} concentration (hardness) and buffering capacity (alkalinity) contribute to the overall stability of the system.

Thus, the calco-carbonic balance makes it possible to anticipate whether water will tend to deposit limescale (scaling water) or, on the contrary, to dissolve existing deposits (aggressive water).

5-3. Calculation of ionic speciations

Ionic speciation consists of determining the distribution of the different forms present: dissolved CO_2 , HCO_3^- , CO_3^{2-} and Ca^{2+} , based on physicochemical data such as pH, temperature, hardness, alkalinity and CO_2 content. These calculations make it possible to predict the evolution of water quality and to adapt treatments (softening, remineralisation, management of limestone deposits).

5.4. Equations for gas, liquid and solid equilibrium

The calco-carbonic equilibrium results from a set of equations coupling CO₂ gas, dissolved carbonate species and solid calcium carbonate. This multiphase model describes the dynamics of carbonate dissolution and precipitation in natural waters.

5.4.1. Gas Phase: Henry's Law and CO₂ Exchanges

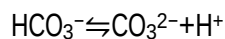
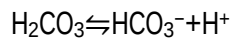
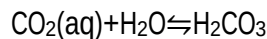
In the gas phase, carbon dioxide is considered to be present in the atmosphere or in a gaseous volume in contact with water. CO₂ dissolves according to Henry's law:

$$[\text{CO}_2(\text{aq})] = k_H \cdot p\text{CO}_2,$$

where k_H is Henry's constant and $p\text{CO}_2$ is the partial pressure of the gas. This gas-liquid exchange determines the quantity of carbonic acid formed and contributes to the stability of the calc-carbonic equilibrium.

5.4.2. Liquid phase: reactions in solution and successive dissociations

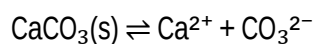
In water, the dissolved CO₂ hydrates and forms carbonic acid, which dissociates into bicarbonate and then carbonate:



All these species coexist in solution, and their proportions depend mainly on the pH and environmental conditions. The concentrations are related by the equilibrium constants K_1 and K_2 corresponding to the two dissociation steps.

5.4.3. Solid phase: deposition and dissolution of calcium carbonate

The solid phase essentially corresponds to CaCO₃ (and possibly other metal carbonates) that can precipitate or dissolve. The key equation is:



Controlled by the K_s solubility product of calcium carbonate. When the product $[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]$ exceeds K_s , precipitation is thermodynamically favored; below that, dissolution is preferred.

-Interfaces and transfer phenomena

Two main interfaces structure this system:

-Gas-liquid interface: ensures the transfer and balance of CO₂ between air and water.

- Liquid-solid interface: governs the dissolution and precipitation of CaCO₃ according to pH and ionic composition.

These interfaces influence the speed of reactions, mineralization and chemical stability of natural waters.

5.5. Different Acid Functions of CO₂, pH, pCO₂ and Alkalinity

Carbon dioxide (CO₂) plays a fundamental role in water chemistry, acting as a weak acid and influencing the pH, partial pressure (pCO₂) and alkalinity of the medium.

5.5.1. Acidic functions of CO₂

In both natural media and treatment processes, dissolved CO₂ is at the heart of many acid-base reactions. A colourless and odourless gas, it becomes the source of carbonic acid in solution, which gives the water a modular, crucial acidity for the stability of aquatic ecosystems and the quality of drinking or industrial water.

Within the carbon cycle, CO₂ is continuously exchanged between the atmosphere and waters through physical and biological processes. Once dissolved, it influences pH, ion speciation and buffering capacity, impacting the solubility of minerals and the functioning of aquatic life.

At acidic pH, the dissolved CO₂ form predominates.

At neutral or slightly basic pH, the majority form is HCO₃⁻.

At high pH, CO₃²⁻ ions become dominant.

5.5.2. Influence on pH and pCO₂

When CO₂ dissolves, it forms H₂CO₃ which releases H⁺ ions when it is dissociated, which lowers the pH and makes the water more acidic. As the dissolved CO₂ concentration increases, the pH decreases, while CO₂ degassing (by aeration, agitation, or photosynthesis) causes pH to rise.

CO₂ is thus a natural and technical tool for fine pH regulation, used in particular in the conditioning of drinking water. Charts relating pH, carbonate hardness (KH) and CO₂ content make it possible to quantify these relationships.

5.5.3. Role of CO₂ Partial Pressure (pCO₂)

pCO₂ refers to the partial pressure of CO₂ in the gas in equilibrium with water. It regulates the amount of CO₂ that can dissolve:

- High pCO₂ (such as in a confined atmosphere, or during intense organic decomposition) increases the dissolution of CO₂, increasing the acidity of the water.
- Low pCO₂ (well-ventilated medium, photosynthesis) promotes CO₂ degassing, thus a higher pH.

pCO₂ is a key indicator of the chemical balance between water and its gaseous environment, both for pH stability and for preventing corrosion or carbonate precipitation.

- Low pH → high proportion of dissolved CO₂, acidic water.
- Neutral pH → Dominant bicarbonates.
- High pH → Majority carbonates, basic water.
- Increase in CO₂ or pCO₂ → decrease in pH (acidification).
- Decrease in CO₂ or pCO₂ → Increase in pH (switch to alkalinity).

Understanding and manipulating the pH/CO₂/pCO₂ couple makes it possible to adjust the chemical quality of water, to influence biological balances and to prevent many natural or anthropogenic imbalances.

5.5.4. Alkalinity and buffering role

Alkalinity measures the ability of water to neutralize acids, in other words its buffering capacity against pH variations. This parameter is essential for the stability of aquatic systems, whether natural or man-made.

5.5.4.1. Origin and chemical roles of alkalinity

Alkalinity comes mainly from the HCO₃⁻, CO₃²⁻ and OH⁻ ions resulting from the dissolution of carbonate minerals or reactions involving CO₂. These ions consume the H⁺ brought to the medium, thus limiting the drop in pH. The higher the alkalinity, the more acidic input the water can absorb without significant pH fluctuations; conversely, low alkalinity makes the system vulnerable to rapid and potentially damaging fluctuations.

5.5.4.2. Operation of the buffer role

When an acid is introduced into alkaline water, the bicarbonates and carbonates react with the H⁺ to form less acidic species, which dampens the pH variation. This mechanism protects aquatic organisms and structures from the corrosive or toxic effects of acidification events.

5.5.4.3. Measurement and Quantitative Significance

In practice, alkalinity is determined by acid-base titration up to a pH close to 4.3, the threshold at which bicarbonates are converted to H₂CO₃. It is generally expressed in mg/L of CaCO₃ equivalent, which facilitates the comparison between different types of water.

5.6. Acidity and solubility of metals

The solubility of metals is highly dependent on pH and carbonate chemistry. In an acidic environment, protons promote the solution of metals in ionic form, whereas at higher pH, they frequently precipitate in the form of hydroxides or carbonates, reducing their concentration in solution.

5.6.1. Direct influence of pH on solubility

1. At low pH, metals such as Pb, Cu, Fe, or Zn readily remain in solution as ions, which can lead to high levels of contamination in acidified environments.
2. At high pH, these same metals tend to precipitate as poorly soluble hydroxides or carbonates, which decreases their mobility and potential toxicity.

5.6.2. Role of CO₂ in solubility

By changing the pH via the formation of carbonic acid, CO₂ indirectly influences the solubility of metal compounds. An increase in CO₂, and therefore acidification, promotes the dissolution of metal carbonates and hydroxides, while degassing or an increase in alkalinity leads to their precipitation.

5.6.3. Applications and Consequences

In water treatment, the pH is adjusted in a controlled manner to precipitate the metals in the form of hydroxides and facilitate their removal. In natural ecosystems, a decrease in pH increases the dispersion of metals, with significant consequences for biodiversity and water quality. Pourbaix diagrams make it

possible to visualize the stability domains of dissolved and precipitated species as a function of pH and oxidation-reduction potential.

Thus, acidity management and understanding of calc-carbonic balances are essential to control the mobility, precipitation and dissolution of metals in aquatic systems

CO₂ therefore indirectly influences the mobility of metals. An increase in pCO₂ in soil or groundwater tends to acidify the environment, dissolve more CaCO₃ and release associated metals. This behaviour partly explains the geochemistry of limestone water and the dynamics of metal pollutants.

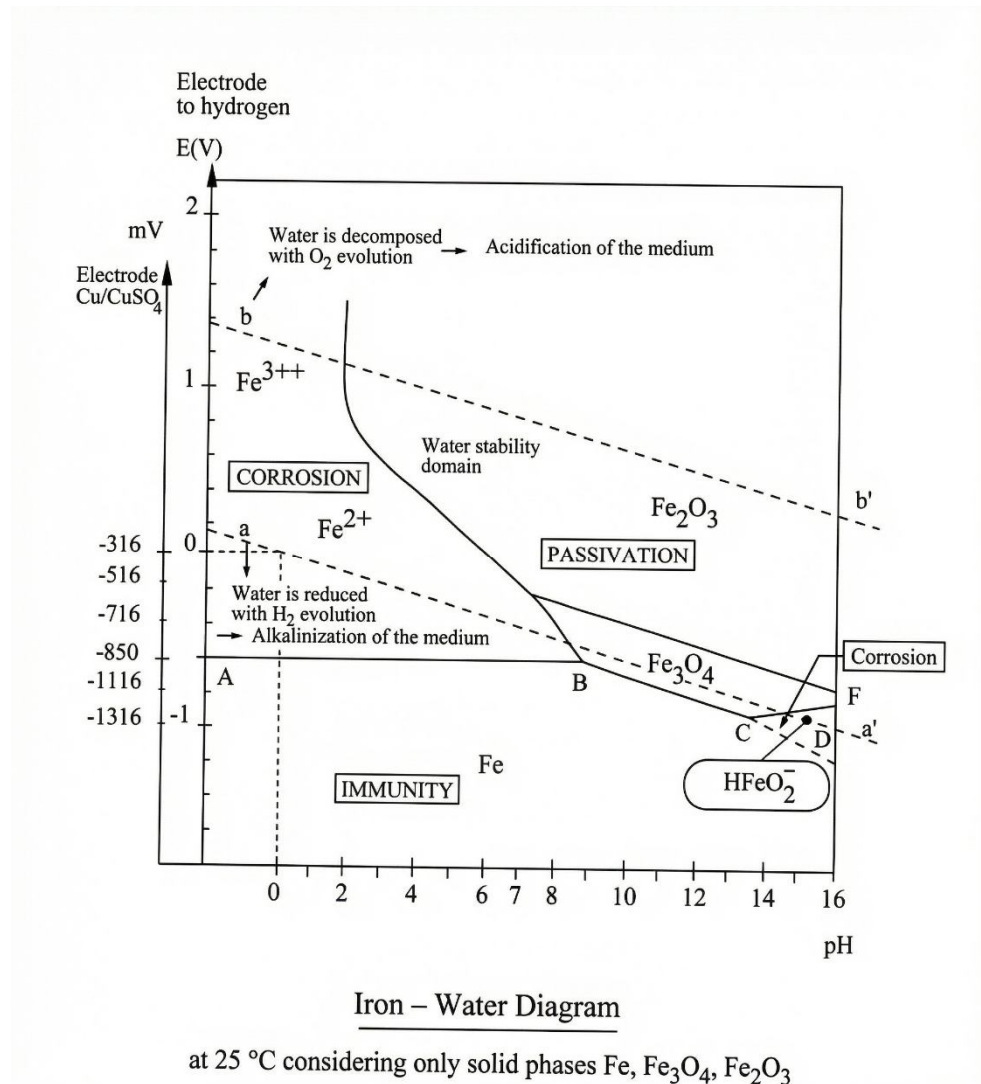


Figure. 5 Pourbaix Iron-Water diagrams: visualization of stability domains and dissolved and precipitated forms as a function of pH and oxidation-reduction potential.

6. Chapter 5 (Oxidation-reduction reactions in natural waters).

6.1. General Concepts and Case Study

A reducer refers to a chemical substance — whether it is an atom, an ion or a molecule — capable of yielding electrons; it therefore undergoes oxidation. For example:

$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$ (copper is oxidized). Reduction corresponds to a gain in electrons, while oxidation necessarily implies a loss of electrons. These two processes are always linked to each other. During an oxidation-reduction reaction, electron transfer can take place:

- either between a dissolved species and a metal electrode, which constitutes an electrochemical phenomenon,
- or between two chemical species in solution, which corresponds to a purely chemical reaction.

Each oxidation-reduction reaction is based on an exchange of electrons between an oxidant and a reductant. For each redox couple, the oxidizer and the reducer associated with it are precisely defined:

Examples of redox pairs:

- $\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+}$ \ Couple : $\text{Fe}^{3+} / \text{Fe}^{2+}$
- $\text{Fe}^{2+} + 2\text{e}^- \leftrightarrow \text{Fe}$ \ Couple : $\text{Fe}^{2+} / \text{Fe}$
- $\text{Cu}_2^{+} + 2\text{e}^- \leftrightarrow \text{Cu}$ \ Couple : $\text{Cu}_2^{+} / \text{Cu}$
- $\text{Cl}_2 + 2\text{e}^- \leftrightarrow 2\text{Cl}^-$ \ Torque: $\text{Cl}_2 / 2\text{Cl}^-$
- $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$ \ Couple : $2\text{H}^+ / \text{H}_2$

Notes:

1. The production of electricity in batteries, the determination of vitamin C by iodometry, the industrial manufacture of certain compounds such as dichlorine, soda or zinc, as well as phenomena such as corrosion or rust formation on metals, all illustrate oxidation-reduction reactions.

2. Among the elements of the periodic table, metals (such as copper, silver, iron or magnesium) are often found as reducing agents, as they usually occupy the left or central part of the table and tend to lose their electrons. Conversely, oxidants are frequently simple substances on the right side of the classification.

6.1.1. Oxidation-reduction potentials

The oxidizing or reducing power of a chemical species is measured by its standard potential, denoted E° . This potential, expressed in volts, makes it possible to evaluate the capacity of an oxidizer or a reducer under well-defined conditions: a temperature of 25 °C, a pressure of 1 atm, and standard concentrations. The standard potentials of the different redox pairs are always related to a common reference, which is the standard potential of the hydrogen electrode, denoted $E^\circ(\text{H}^+ / \text{H}_2)$.

Thus, each oxidizer/reducing pair, written in the form Ox/Red, has a standard potential value that allows their respective strength to be compared.

The Nernst equation then makes it possible to relate the potential of a redox pair to the real conditions of the system, taking into account the concentrations of the species present.

Example:

Redox couple	Fe ²⁺ /Fe	MnO ₄ ⁻ /Mn ²⁺	Fe ³⁺ /Fe ²⁺	Zn ²⁺ /Zn	Cu ²⁺ /Cu
E ⁰ (V/ENH)	-0,44	1,51	0,77	-0,76	0,34

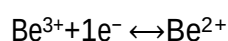
According to Nernst's law, the potential of an oxidizer/reducing pair in solution depends not only on E⁰ but also on the concentrations of the species involved. At 25 °C, the relationship is written:

$$E_{\text{ox/red}} = E_{\text{ox/red}}^0 + \frac{0,06}{n} \log \frac{[\text{ox}]^a}{[\text{red}]^b}$$

where a and b are the stoichiometric coefficients of the equation, n the number of electrons exchanged, and [ox], [red] the respective concentrations.

-Example application:

- For the Fe³⁺/Fe²⁺ pair:



$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + 0,06 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

6.1.2. Oxidation-reduction reaction

An oxidation-reduction reaction results from the transfer of electrons between several redox pairs. It is expressed by a global equation obtained by combining the corresponding half-equations. In general, the reducer of a first couple is combined with the oxidizer of a second pair to write the complete reaction.

Example: pairs Fe³⁺/Fe²⁺ and Sn⁴⁺/Sn²⁺.

In the representation of electronic transfers, it is necessary to balance the exchanges between the oxidizing/reducing couples. For example:

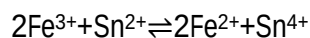
For the Iron⁺³/Iron⁺² pair:



For the pair $\text{Sn}(\text{Sn}^{2+})/\text{Sn}(\text{Sn}^{4+})$:



The overall reaction, after equalization of the electrons exchanged, becomes:



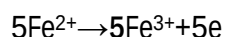
Each electron transfer is designated according to the couples involved: we then speak of the association between the oxidant of the first couple and the reducer of the second, as opposed to that between the reducer of the first couple and the oxidant of the second. An oxidation-reduction reaction therefore occurs when the best oxidizer reacts with the best reducer. This orientation is ensured if :

$E_0(\text{Ox1}/\text{red1}) > E_0(\text{Ox2}/\text{red2})$ (thermodynamic criterion based on standard potentials).

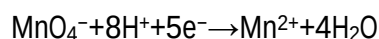
Example:

For couples:

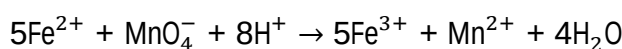
$\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E_0 = 0.77 \text{ V}$) and $\text{MnO}_4^-/\text{Mn}^{2+}$ ($E_0 = 1.51 \text{ V}$), since $E_0\text{MnO}_4^-/\text{Mn}^{2+} > E_0\text{Fe}^{3+}/\text{Fe}^{2+}$, the selected semi-oxidation is:



The reduction is:



or the overall reaction:



If we consider the couples, the reaction works in the direct direction.

6.1.3. Calculation of the equilibrium constant

To determine the equilibrium constant of a redox reaction, we use the difference in the standard potentials of the two pairs:

Let $\text{Ce}^{4+}/\text{Ce}^{3+}$ ($E_0 = 1.44 \text{ V}$) and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E_0 = 0.77 \text{ V}$). Since $E_0\text{Ce}^{4+}/\text{Ce}^{3+} > E_0\text{Fe}^{3+}/\text{Fe}^{2+}$

- Reduction half-reaction: $\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$
- Oxidation half-reaction: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
- Global reaction: $\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+}$

To evaluate the equilibrium constant, we use:

$$k_c = \frac{[\text{Ce}^{3+}][\text{Fe}^{3+}]}{[\text{Ce}^{4+}][\text{Fe}^{2+}]}$$

The two redox pairs considered, according to Nernst's relation:

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + 0,06 \log \left(\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right)$$

$$E_{\text{Ce}^{4+}/\text{Ce}^{3+}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + 0,06 \log \left(\frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \right)$$

Combining these two equations, we obtain:

$$E_{\text{Ce}^{4+}/\text{Ce}^{3+}} - E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + 0,06 \log \left(\frac{[\text{Ce}^{4+}][\text{Fe}^{2+}]}{[\text{Ce}^{3+}][\text{Fe}^{3+}]} \right)$$

At equilibrium, $\Delta E=0$, whence:

$$E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0,06 \log k_c$$

$$k_c = 10^{\Delta E^0 / 0,06}$$

In the example given, the potential difference is:

$$k_c = 10^{11,47} \approx 1,47 \times 10^{11}$$

Such a high constant implies that the reaction can be considered total.

Observations on the equilibrium constant and the evolution of the reaction

When the difference between the standard potentials $E_2^0 - E_1^0$ is 0.25 V, the equilibrium constant k_c is about 1.5×10^4 .

On the other hand, if this difference is -0.25 V, k_c is of the order of 6.8×10^{-5} .

In an initial situation where only the oxidizer of the second couple and the reducer of the first couple are present, several scenarios can arise:

1. If $E_2^0 - E_1^0 > 0,25$ V, then $k_c > 10^4$: the transformation is almost total.
2. If $E_2^0 - E_1^0 < -0,25$ V, then $k_c < 10^{-4}$: the reaction hardly takes place.

When the potential difference is between -0.25 V and 0.25 V, the reaction does take place, but it cannot be considered as totally quantitative. To anticipate the direction in which the reaction will evolve spontaneously and to estimate its degree of progress, it is therefore essential to know precisely the standard potentials of the species concerned (E_1 and E_2), and then to use the appropriate formula.

Note: The product $n_1 n_2$ corresponds to the least common multiple of the electrons exchanged in each half-equation, obtained by crossing the half-electron exchange equations (n_1 and n_2 representing the number of electrons transferred in each case). The general formula for the equilibrium constant is then written:

$$k_c = 10^{[n_1 n_2 (E_2^0 - E_1^0) / 0,06]}$$

6.1.4. Redox reactions in natural waters

Redox reactions play a key role in determining water quality, especially in groundwater. Unlike reactions involving carbonate species, redox processes are generally slow and often far from thermodynamic equilibrium, which complicates their consideration in models due to their particular kinetics. Acid-base reactions are involved in many of the phenomena observed in natural waters. Although some are influenced by biological activities, such as biologically induced alkalization, most remain abiotic in origin. Conversely, the majority of redox reactions are related to biological processes. Some, such as sulphate-reduction, can also have an impact on acid-base reactions. The level of redox in water depends on a balance between the rate at which oxygen (or other oxidizing agents) is consumed and the speed with which it diffuses into the aquatic environment. In aquatic environments, redox reactions are influenced by many factors, including the availability of oxidants and the presence of living organisms:

- **The presence of oxygen** (oxic or anoxic environment)
- **Organic matter** (source of electrons)
- **Microorganisms** (biological catalysts of reactions)
- **The redox potential (Eh)**, which measures the tendency of the medium to accept or donate electrons.

A. Role of biological activity

The activity of microorganisms is the main source of oxygen consumption in water. These organisms use oxygen, whether present in free form or in combination (such as in nitrates), to break down organic matter and extract the energy necessary for their development. Depending on the environmental conditions, they can release only carbon dioxide (CO_2) if the oxidation is complete, or CO_2 accompanied by organic anions when the degradation is only partial. In environments that are very low in oxygen, the production of methane (CH_4) can also accompany the production of CO_2 . Thus, an inverse relationship between the partial pressure of oxygen ($p\text{O}_2$) and that of carbon dioxide ($p\text{CO}_2$) in water is frequently observed.

B. Factors Influencing Oxygen Consumption

- **Temperature:**

The intensity of biological activity, and consequently the consumption of oxygen, increases with temperature. Conversely, when the water is cold, this activity slows down, causing the water to become less reductive.

- **Presence of organic matter and nutrients**

In environments where rocks contain little organic matter, such as some aquifers, microbial life remains limited, especially in the absence of photosynthesis. Conversely, in environments rich in organic matter or reducing compounds such as pyrite or ferrous ions, microbial activity and oxygen consumption are significantly greater. Thus, water tables located near the surface and in contact with layers rich in organic matter often have a very reducing character, with redox potentials close to zero, or even negative.

- **Type of organic matter**

The nature of organic compounds also influences their degradation. Substances with low polymerization are quickly consumed by microorganisms, which accelerates oxygen consumption. For example, simple sugars can be broken down to fermentation.

C. Degradation of organic matter and oxygenation of water

- **Nature of organic compounds**

Aliphatic organic substances, which consist of open chains of carbon and hydrogen that can be straight or branched, decompose much faster than aromatic compounds. Thus, when an organic source is mainly formed of aliphatic molecules, their rapid degradation favors the appearance of reducing conditions. In contrast, compounds rich in polymerized aromatic units, such as lignins, are much more resistant to decomposition. Their slow transformation therefore limits the development of these reducing conditions.

- **Factors influencing water re-oxygenation**

The renewal of oxygen in the water depends on several elements:

Aquifer type : Whether it is free or confined.

Water circulation speed : The faster the water in the aquifer or river circulates, the more effective the re-oxygenation.

Pore size in soil or rock : Porous materials facilitate the diffusion of oxygen.

Water dynamics : In stagnant environments (such as in a topographic depression), water renewal is slow, which promotes oxygen-poor or even anoxic conditions. Conversely, in areas where water circulates, even if the substrate is rich in organic matter, oxidizing conditions are observed.

Rate of waterlogging : The oxygen supply can vary according to the humidity and porosity of the environment, which explains the presence of very active areas ("hot spots") or periods of high activity ("flashes").

Variability of redox conditions

The balance between these different factors leads to strong variations in the oxygen level from one site to another, or even to the same place depending on the moment. Significant deviations can be observed over just a few millimeters or in the space of short periods, making the study of redox processes both more complex and richer.

6.1.5. The main redox processes that influence water quality

When water moves from a well-oxygenated environment to very oxygen-poor conditions, several main types of redox reactions come into play.

- **Aerobic respiration (use of oxygen)**

In a well-oxygenated environment, where oxygen is present either dissolved in water or in the air contained in soils or rocks, microorganisms use this oxygen primarily to degrade organic matter. This process releases carbon dioxide (CO₂), which then tends to accumulate in the medium. As a result, the partial pressure of CO₂ (pCO₂) in water becomes higher than that of air. When gas exchange with the atmosphere is easy, oxygen remains abundant (high pO₂) and CO₂ is removed, keeping pCO₂ low. If the soil is saturated with water, the circulation of gases slows down: oxygen becomes scarcer (pO₂ decreases) while CO₂ accumulates (pCO₂ increases).

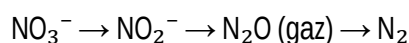
There is therefore often an inverse relationship between these two parameters. In very well-oxygenated environments, it is sometimes more relevant to monitor the evolution of CO₂ rather than that of oxygen, because a slight decrease in pO₂ (e.g. from 20% to 19%) is difficult to detect, while the increase in CO₂ (from 0.03% to 1%) is much more pronounced. Conversely, when water becomes low in oxygen (pO₂ of a few percent), it becomes crucial to accurately measure the amount of dissolved oxygen to fully understand the processes involved.

- **Oxygenated environment: rapid humification and mineralization**

When sufficient oxygen is available, the degradation and transformation of organic matter takes place rapidly. Recent organic residues, such as those from agricultural crops, decompose quickly: they become part of the humus and their visible fragments disappear in a short time.

- **Denitrification: a key process in the absence of oxygen**

When free oxygen is scarce, because it has been completely consumed, the microorganisms turn to other sources of oxygen to continue the oxidation of the organic matter. They then use the oxygen contained in the nitrates, a process called denitrification. This mechanism is particularly studied because it reduces the excess of nitrates in the water, thus contributing to depollution. Denitrification involves different microbial communities that carry out a succession of chemical reactions:



During these transformations, nitrous oxide (N₂O) can escape from the soil in gaseous form. This gas, which has a strong global warming power, gives denitrification a double effect: it purifies water, but can also contribute to the greenhouse effect. To better understand this phenomenon, researchers measure N₂O emissions by capturing gases escaping from the ground surface. Nitrite (NO₂⁻), which appears briefly during denitrification (but also during nitrification, another step in the nitrogen cycle), is rarely present in large quantities in water.

Its detection usually indicates that denitrification is in progress at the time of sampling.

In addition, microorganisms prefer the use of light nitrogen. Thus, as denitrification progresses, the nitrate concentration decreases.

Nitrogen cycling and associated oxidation-reduction reactions

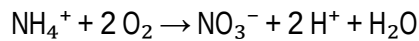
Nitrogen is a key element whose speciation is highly dependent on redox conditions:

- Oxidized forms: In oxidizing media, nitrogen is mainly found in the form of nitrate (NO₃⁻).

- Reduced forms: In reducing media, it is present in the form of ammonium (NH_4^+).

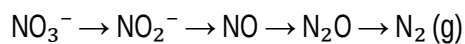
Main nitrogen oxidation-reduction reactions:

-Nitrification (oxidation of ammonium to nitrate):



This reaction occurs in the presence of oxygen and is carried out by nitrifying bacteria.

-Denitrification (reduction of nitrate into nitrogen gas):



This series of reactions occurs under anoxic conditions, thanks to denitrifying bacteria, and allows the return of nitrogen to the atmosphere.

-Ammonification (reduction of nitrogenous organic compounds into ammonium):



Influence du potentiel redox sur la forme de l'azote

-Potentiel élevé (milieu oxydant) : Favorise la présence de nitrates (NO_3^-).

-Potentiel faible (milieu réducteur) : Favorise la présence d'ammonium (NH_4^+) et la production d'azote gazeux (N_2) par dénitrification.

• Iron and manganese oxidation-reduction

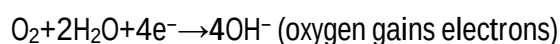
The displacement of iron in the soil, in connection with the presence of water, causes an uneven distribution of this element, which depends on the type and duration of waterlogging. For example, in areas where the water table rises and falls, especially on calcareous soils, water can stagnate seasonally for long periods of time without being permanently present. This situation leads to the formation of pseudogleys, recognizable by the presence of gray spots and traces of rust. The grey areas, which appear under reducing conditions, contain mixtures of iron oxides and hydroxides in different forms of oxidation (Fe^{2+} and Fe^{3+}). In acidic soils saturated with water, the places where water circulates promote the reduction, dissolution and then leaching of iron, which gives rise to very clear, even whitish areas, called iron removal zones.

When the soil remains saturated with water almost permanently, it takes on a characteristic grey hue, called gley. If the soil experiences short periods of dryness, local reoxidation occurs, especially around the roots, resulting in the precipitation of iron III hydroxides in the form of fine orange filaments in the grey-blue matrix of the soil. This phenomenon corresponds to the formation of an oxidized gley. Laboratory experiments show that, in soil with a high oxygen deprivation, the decomposition of organic matter remains incomplete: some organic compounds persist, particularly in the form of anions, which contribute to organic alkalinity. This alkalinity promotes the complexation of metal cations such as iron or manganese, thus increasing their solubility and mobility in the soil. Other metals can also be mobilized under these particular chemical conditions. The reduction and dissolution of iron and manganese oxides also leads to an increase in the alkalinity of the medium.

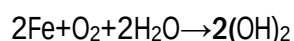
Iron oxidation:



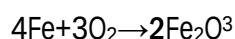
Oxygen reduction



Balanced global equation (to form iron(II) hydroxide):

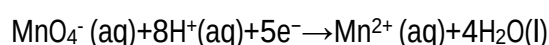


Formation of ferric oxide (rust):

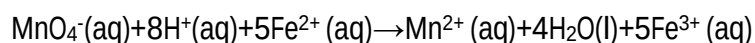


Reduction of permanganate to manganese (II) (Manganimetry)

Half-reaction (reduction):

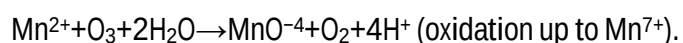


Reaction with iron ions (Fe^{2+}):



Oxidation of manganese (II) to manganese dioxide (MnO_2)

In an alkaline medium or with strong oxidants, Mn^{2+} can be oxidized to MnO_2 (brown), as illustrated by the following equation with ozone:



Interactions and environmental significance

- Iron and manganese are often found together in natural waters. Their behavior depends on the redox potential: iron reduces/oxidizes to higher potentials than manganese, which implies that iron precipitates or dissolves before manganese during variations in redox conditions.

- **Role of bacteria:** Many heterotrophic bacteria (e.g. Acinetobacter, Bacillus, Pseudomonas) catalyze the dissimilatory reduction of iron(III) and manganese(IV), promoting their solubilization under reducing conditions.

- **Consequences:** The solubilization of iron and manganese can lead to coloration, taste, and clogging problems in drinking water systems. Their precipitation, on the other hand, can form deposits in the pipes.

- The sulphur cycle and its oxidation-reduction reactions

Sulphur exists in water in different forms and oxidation states, mainly:

-Sulfates (SO_4^{2-} , S to +VI)

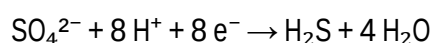
-Sulphites (SO_3^{2-} , S to +IV)

-Elemental sulphur (S^0)

-Sulphides (H_2S , S^{2-} , S to -II)

Reduction of sulphates (SO_4^{2-}) to sulphides (H_2S)

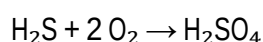
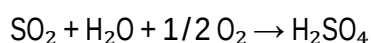
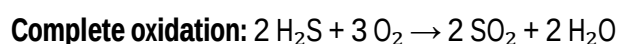
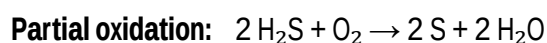
In an anaerobic (oxygen-poor) environment, some bacteria (sulphate-reducing) use sulphates as electron acceptors, thus reducing SO_4^{2-} to H_2S :



This reaction is coupled with the oxidation of organic matter or hydrogen. It is essential in sediments, wetlands and deep aquatic environments.

-Oxidation of sulphides (H_2S) to sulphates (SO_4^{2-})

In the presence of oxygen or oxidizing bacteria, H_2S can be oxidized to elemental sulfur (S^0) and then to sulfate:



These reactions are catalyzed by aerobic sulfur bacteria.

-Intermediate transformations and interactions with other cycles

-Formation of elemental sulphur (S^0): Sulphur can be an intermediate product during the partial oxidation of H_2S or the partial reduction of SO_4^{2-} .

-Precipitation of metal sulfides: H_2S reacts with dissolved metal ions (Fe^{2+} , Zn^{2+} , Pb^{2+} , etc.) to form insoluble sulphides (FeS , ZnS , PbS), which influences the mobility of metals in water.

-Role of microorganisms

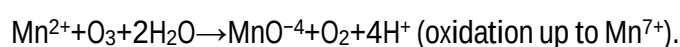
Bacteria play a key role in the sulfur cycle:

- **Sulphate-reducing bacteria:** reduce SO_4^{2-} to H_2S in the absence of oxygen.
- **Oxidizing sulfur bacteria:** oxidize H_2S to S^0 or SO_4^{2-} in the presence of oxygen.

Oxidation of manganese (II) to manganese dioxide (MnO_2)

In an alkaline medium or with strong oxidants, Mn^{+2} can be oxidized to MnO_2

(brown), as illustrated by the following equation with ozone:



Interactions and environmental significance

Iron and manganese are often found together in natural waters. Their behavior depends on the redox potential: iron reduces/oxidizes to higher potentials than manganese, which implies that iron precipitates or dissolves before manganese during variations in redox conditions.

- **Role of bacteria:** Many heterotrophic bacteria (e.g. *Acinetobacter*, *Bacillus*, *Pseudomonas*) catalyze the dissimilatory reduction of iron(III) and manganese(IV), promoting their solubilization under reducing conditions

- **Consequences:** The solubilization of iron and manganese can lead to coloration, taste, and clogging problems in drinking water systems. Their precipitation, on the other hand, can form deposits in the pipes.

The sulphur cycle and its oxidation-reduction reactions

Sulphur exists in water in different forms and oxidation states, mainly:

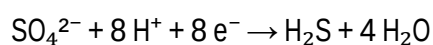
-Sulfates (SO_4^{2-} , S to +VI)

-Sulphites (SO_3^{2-} , S to +IV)

-Elemental sulphur (S^0)

-Sulphides (H_2S , S^{2-} , S to -II)

Reduction of sulphates (SO_4^{2-}) to sulphides (H_2S): In an anaerobic (oxygen-poor) environment, some bacteria (sulphate-reducing) use sulphates as electron acceptors, thus reducing SO_4^{2-} to H_2S :



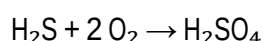
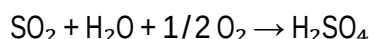
This reaction is coupled with the oxidation of organic matter or hydrogen. It is essential in sediments, wetlands and deep aquatic environments.

- Oxidation of sulphides (H₂S) to sulphates (SO₄²⁻)

In the presence of oxygen or oxidizing bacteria, H₂S can be oxidized to elemental sulfur (S⁰) and then to sulfate:

Partial oxidation: $2 \text{H}_2\text{S} + \text{O}_2 \rightarrow 2 \text{S} + 2 \text{H}_2\text{O}$

Complete oxidation: $2 \text{H}_2\text{S} + 3 \text{O}_2 \rightarrow 2 \text{SO}_2 + 2 \text{H}_2\text{O}$



These reactions are catalyzed by aerobic sulfur bacteria.

-Intermediate transformations and interactions with other cycles

*Formation of elemental sulphur (S⁰): Sulphur can be an intermediate product during the partial oxidation of H₂S or the partial reduction of SO₄²⁻.

*Precipitation of metal sulfides: H₂S reacts with dissolved metal ions (Fe²⁺, Zn²⁺, Pb²⁺, etc.) to form insoluble sulphides (FeS, ZnS, PbS), which influences the mobility of metals in water.

-Role of microorganisms

Bacteria play a key role in the sulfur cycle:

- **Sulphate-reducing bacteria:** reduce SO₄²⁻ to H₂S in the absence of oxygen.
- **Oxidizing sulfur bacteria:** oxidize H₂S to S⁰ or SO₄²⁻ in the presence of oxygen.

- Environmental Significance

- **Pollution control:** Sulphur redox reactions participate in the detoxification or mobilization of pollutants (heavy metals, organic matter).
- **Production of toxic gases:** H₂S is toxic and smelly, its formation or oxidation must be controlled in wastewater and natural water.
- **Coupling with other biogeochemical cycles:** Sulfur reactions are often coupled with carbon, nitrogen, and iron reactions.

6.1.6. Ionic exchanges between water and the clay complex – Hydrolysis of silicates

Interactions between water and clay minerals shape the chemical composition of soils and groundwater. The hydrolysis of silicates, a central process of chemical weathering, releases essential ions and shapes the ability of soils to retain or release nutrients and pollutants.

A. Structure of clay minerals: the basis of ion exchange

-Crystal clear organization

Clays are phyllosilicates with a laminated structure, composed of tetrahedral (SiO_4) and octahedral (AlO_6 , MgO_6) layers:

Kaolinite: 1:1 structure (one T layer + one O layer).

Smectite, Illite: 2:1 structure (two T layers framing one O layer).

Chlorite: 2:1:1 structure (addition of a brucitic layer).

- **Surface Loads and Exchange Sites**

Isomorphic substitutions (e.g., $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$) create permanent negative charges on the sheets.

Interlayer cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) compensate for these charges and are exchangeable with the ions in the solution.

Sites of exchange : mainly in the interleaf spaces (smectites, illites), but also on the edges of the sheets.

Table 20. Types of exchange of clay minerals.

Mineral	Structure	Major Exchanges	Cation Exchange Capacity (CEC)
Kaolinite	1:1	Edges (Low)	Low, pH-dependent
Smectite	2:1	Spacer (Strong)	High, Permanent
Illite	2:1	Divider (moderate)	Moderate, permanent

B. Principles of ion exchange in the clay-water system

Cation Exchange Capacity (CEC)

- **Definition:** The total amount of exchangeable cations that a soil or clay can hold at a given pH.
- **Origin:** Permanent charges (isomorphic substitutions) and variable charges (protonation/deprotonation of surface groups).
- **Dynamics:** The cations of the solution (Ca^{2+} , Mg^{2+} , K^+ , Na^+) exchange with those adsorbed on clays, without modifying the mineral structure.

Selectivity and influencing factors

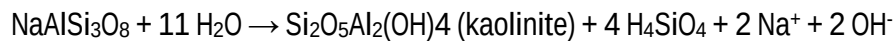
- **Selectivity:** Clays generally prefer divalent cations (Ca^{2+} , Mg^{2+}) to monovalent ones (K^+ , Na^+), depending on their charge, ionic radius, and hydration energy.
- **pH** : At high pH, CEC increases (more negative sites available).
- **Ionic strength:** A solution concentrated in ions reduces the range of electrostatic interactions and can change the exchange dynamics.

C. Silicate hydrolysis: mechanisms and reactions

Principle of hydrolysis

Hydrolysis is the reaction of water with silicates, leading to the release of ions and the formation of new clay minerals.

Example : (hydrolysis of albite, sodium feldspar):



Products: Clay (kaolinite), dissolved silica, Na^+ ions.

Kinetics and control factors

- **pH:** Hydrolysis is accelerated in an acidic (proton attack) or basic (OH^-) environment.
- **Temperature:** The higher the temperature, the faster the reaction.
- **Specific surface:** Finely divided clays react faster.
- **Presence of organic ions or ligands:** Some organic ions or molecules can accelerate or inhibit dissolution.

Balances and saturation

- Equilibrium constants: Each mineral has a solubility product (K_{sp}) that determines the maximum concentration of ions in solution.
- Saturation: As the solution approaches saturation, the rate of hydrolysis decreases.

Environmental consequences and applications

Impacts on water quality

- **Ion release:** Hydrolysis enriches water with cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and dissolved silica, changing the composition of groundwater and surface water.
- **Pollutant retention:** Clays adsorb and retain heavy metals and nutrients, acting as a natural filter.

Real-world applications

- **Clay barriers:** Used to contain waste, thanks to their low permeability and cation exchange capacity.
- **Water treatment:** Clays are used to trap contaminants in remediation processes.

Role in soil fertility

- **Nutrient retention:** A high CEC helps retain elements that are essential for plant growth.
- **Buffering effect:** Clays dampen pH variations and limit nutrient leaching.

7. Chapter 6 (Chemical tracers and markers in waters)

7.1. Definition of the Tracer in Hydrology-Hydrogeology

In hydrology and hydrogeology, it is fundamental to understand how water circulates in its environment. However, because water is a colorless, odorless, and tasteless liquid, it is often difficult to accurately track its movements. That's why tracers are used. These tools are used to "mark" water or to observe some of its properties, which makes it easier to analyze its paths, the duration of its passage through an environment, as well as its interactions with the environment. A tracer corresponds to a substance or signal, whether of natural origin or added by man, which makes it possible to follow the path of water or to study its exchanges between the different compartments of the hydrological cycle.

7.2. Hydrogeological Uses and Applications

In hydrogeology, tracers are valuable tools for analyzing groundwater behavior. In particular, they make it possible to measure the speed at which water circulates underground, to identify the link between different aquifer reservoirs, or to identify the origin of contamination. Trackers are useful in many areas, such as:

- Understand the speed and direction of groundwater flows.
- Check the interactions between rivers, lakes, groundwater and springs.
- Identify or locate potential pollution.
- Estimate the time it takes for water to pass through an aquifer.
- Study water exchange between saturated and unsaturated areas of the subsurface.

Example: Injection of a dye into a water table. By monitoring its appearance downstream or in a spring, we can calculate the flow velocity and understand the path of the water.

7.3. Different Types of Trackers

Tracers exhibit quantitative behaviour: they are not only used to detect their presence in the water, but also to measure their concentration. This characteristic makes it possible to evaluate the proportion of water from different origins within the same mixture.

In contrast, markers do not behave in a strictly conservative manner when moving. The amount of the water can vary due to physical or chemical processes, or because of differences in transport speed compared to water. Thus, the markers mainly provide qualitative information: their detection simply indicates that a passage has taken place, without making it possible to precisely quantify the fraction of water concerned.

7.3.1. Nature of tracers and markers: natural or artificial

Tracers and markers can also be classified according to their origin:

Natural: Some of these elements occur naturally in the environment, such as stable or radioactive isotopes of water (e.g. ^{18}O , ^2H , ^3H), as well as some dissolved ions such as chlorides, bromides, sodium or silicates.

Artificial: Other substances are intentionally added by humans, in controlled quantities. Examples of artificial tracers include tritium (^3H) or chloride, while fluorescein, a dye, is frequently used as a marker.

A-Stable or radioactive tracers

Tracers and markers can be made of stable elements or radioactive substances. Radioactive compounds are particularly valuable in determining the residence time or age of water in underground reservoirs.

However, due to the risks to the environment, the use of radioactive tracers is currently limited to very localized laboratory tests, where it is possible to recover and treat the water after the experiment. In the past, these tracers were sometimes injected directly into aquifers during field studies, but this method has been abandoned in favour of safer techniques.

An ideal tracer is a substance in which each particle behaves in the same way as those of the fluid or material under study, whether it is water, suspended particles, or moving sediments. This implies that the tracer must move at the same speed as water (kinematic condition) and not interact significantly with the other components present, at least during the duration of transport (biogeochemical condition).

When these criteria are met, the tracer makes it possible to obtain quantitative data: it then becomes possible to evaluate the proportion of water coming from different sources, to calculate transfer or residence times, etc.

Dyes, such as fluorescein (used in karst aquifers) or methylene blue (used in soils), can also be used as markers. Although they do not provide quantitative measurements, they are very effective in clearly demonstrating the contribution of a specific area to runoff or erosion, or in tracking the path of water.

B. Isotopic tracers

The isotopes present in the water molecule act as natural tracers, allowing them to perfectly track the movements of the water. Their use, whether naturally occurring or artificially produced, has improved the understanding of hydrological dynamics. For example, they made it possible to distinguish between water that has recently infiltrated during rainfall ("new water") and water already stored in soils or aquifers before the event ("old water"), thus highlighting the share of pre-existing water mobilized during rainfall.

However, even if isotopes faithfully follow the path of water, their use is hampered by the variability of their composition over time and space. If the isotopic signature of precipitation varies within the same episode or from one location to another, this complicates the analysis of the results. Rainwater can also have an isotopic composition very close to that of ancient water, which makes tracing difficult or even unreliable. In such situations, isotope-based estimates therefore remain uncertain.

7.4. Tracer Analysis Methods

A tracer test involves introducing a tracer, or a detectable substance, into a specific location in the aquifer (such as a well, loss, or piezometer). The evolution of its concentration in one or more sampling points (such as a well, a spring or a resurgence) is then monitored over time. The tracers used can be dyes (such as fluorescein or rhodamine), salts (e.g. chlorides or bromides), isotopes, or natural tracers such as temperature or conductivity.

Fluorescent dyes are the most frequently used, as they can be detected at very low concentrations and their analysis is facilitated by the use of fluorometers.

The experiment consists of regularly sampling water downstream of the injection point in order to measure the concentration of the tracer and to draw a restitution curve, which represents the evolution of this concentration over time.

The main parameters studied are the following:

Transit time: The time it takes for the tracer to travel the distance between the injection point and the detection point.

Flow velocity: determined from the transit time and the distance traveled.

Dispersion: measurement of the spread of the tracer, which gives information on the heterogeneity of the medium crossed.

Dilution: decrease in tracer concentration, related to the size and connectivity of the aquifer.

7.5. Application of tracers in different aquifer types

The use of tracers in hydrogeology is a fundamental approach to analyze the behavior of aquifers, understand groundwater circulation and highlight the links between different parts of the same aquifer system. Tracer tests can be used to determine the speed and direction of water flows, and sometimes to detect the presence of pollutants or contaminants.

-Karst aquifers

In karst environments, characterized by networks of cracks, galleries, losses and resurgences, tracing is particularly valuable for studying rapid and complex circulations. They are used to identify connections between losses and sources, to map underground networks and to assess the sensitivity of these environments to pollution.

-Porous aquifers

In aquifers made of porous materials, tracer tests measure the flow velocity, dispersion and dilution of water in generally more homogeneous environments. This information is essential for the sustainable management of water resources and the protection of catchment points.

-Fissured aquifers

For fissured aquifers, tracings help characterize the connectivity between different fractures and identify preferential water flow pathways.

7.5.1. Other uses of tracers in Hydrology-Hydrogeology

A. Exchanges between the aquifer and the river

The relationships between groundwater tables and rivers vary greatly, both over time and depending on the location. Thus, depending on the sector, a river can be fed by the water table (drainage role) or, conversely, contribute to the recharge of the water table (infiltration role). In addition, a section that drains the water table during periods of low water can become infiltrating during a flood.

The detailed understanding of these exchanges is therefore complex, which makes the use of tracers particularly valuable for their study. In addition to conventional chemical or isotopic tracers, additional information is provided by parameters such as CO₂ partial pressure or dissolved oxygen content, which differ significantly between surface water and groundwater.

Using these methods, it is possible to monitor the evolution over time of the proportion of groundwater and surface water in the total flow of the river.

Artificial tracing techniques are also used. For example, the injection of a tracer such as NaCl into a piezometer near the river, combined with the measurement of conductivity using electrodes placed around the injection point, makes it possible to determine the direction of water circulation in the piezometer, i.e. whether the local flow follows, converges or diverges from the river.

B. Differentiation between soil water and rainwater

The analysis of stable isotopes of water, in particular oxygen-18, is now commonly used to distinguish the origin of water that flows at the outlet of a watershed during a rainy event. This method makes it possible to show that the water collected at the outlet of the basin is not only made up of recent rainwater.

However, it remains difficult to accurately assess the proportion of water that comes from the ground. Even if the isotopic composition of the rain remains stable during the event, that of the soil water can vary greatly, both horizontally and vertically, sometimes by only a few centimetres at the surface.

C. Spatial origin of water in a watershed

Tracers are also widely used to determine the geographical origin of water at the outlet of a watershed. This approach makes it possible to differentiate the inputs of the various sub-basins and to analyse the spatial distribution of hydrological flows.

In this context, chemical tracers can sometimes offer a better ability to discriminate than isotopes, provided that the basin has marked chemical and geological contrasts between its different parts. However, this is not always the case, and the choice of tracer is an important constraint: one tracer can only distinguish two sources, two tracers three sources, etc. In addition, some chemical parameters are not suitable for this type of analysis, which limits the accuracy of spatial differentiation.

D. Confluence of flow lines and calculation of respective inputs

Tracing also makes it possible to quantify the contribution of each flow when several flows meet, by identifying the origin and proportion of each in the final mixture.

E. Flow estimation in torrential hydrology

In torrents, conventional methods of measuring flow, such as the use of a reel, are often unsuitable. Several factors explain this:

The cross-section of the torrent is very irregular and difficult to measure precisely.

The flow speeds are high, which makes it impossible to use the reel.

The flow splits into multiple arms between the boulders, creating a great heterogeneity of velocity and complicating the installation of instruments.

Under these conditions, it is not possible to measure the flow in a conventional way, even though this data is essential in hydrology. Artificial chemical tracing is then an effective alternative.

The method consists of injecting a tracer at a known flow rate (Q_1) and at a determined concentration (C_1) for a sufficient time. Downstream, the concentration of the tracer (C) in the torrent is measured. The flow rate (Q) is then calculated according to the following formula:

$$Q = (C_1 \times Q_1) / C$$

In addition to the flow rate, tracing makes it possible to determine the propagation speed of the chemical wave and the apparent coefficient of dispersion, two valuable parameters that only concern the actual flow rate at the time of tracing.

7.6. Tracer Selection and Interpretation of Tracer Tests

7.6.1. Selection of Tracers in Hydrogeology

7.6.1.1. The importance of the choice of tracer in hydrogeology

Selecting a suitable tracer is a decisive step in ensuring the reliability of a hydrogeological tracer test. This choice must take into account the geological context, the objectives of the study, as well as environmental and analytical constraints. Several essential criteria guide this selection, and certain types of tracers are preferred depending on the situation.

Criteria to consider when selecting a tracker:

a. Detectability and analytical sensitivity

The tracer must be able to be detected at very low concentrations, which makes it possible to limit the quantity injected and reduce the risks to the environment. Fluorescent tracers, such as fluorescein or rhodamine, are often chosen because they are detectable at very low levels, in the order of micrograms per litre.

b. Conservative behavior

It is essential that the tracer does not undergo any chemical or biological transformation during its journey. It must move like water, without being absorbed, degraded or precipitated in the medium through which it passes.

c. Environmental safety

The tracer selected must not present any danger to the environment, fauna, flora or human uses of the water. In hydrogeology, non-toxic and biodegradable substances, such as fluorescein, are generally preferred.

d. Absence of analytical interference

It is necessary to ensure that the tracer is not naturally present in the water, or in negligible quantities compared to the dose injected. When using several tracers simultaneously, it is essential to check that they do not interfere with each other during the analysis.

e. Ease of use and cost

The tracer must be simple to handle, inject and analyze. Coloured or saline tracers are often chosen for their ease of use and reasonable cost.

7.6.1.2 . Main types of tracers used

****Fluorescent Tracers:***

Fluorescein: Widely used, easily detectable, safe and biodegradable.

Rhodamine: close to fluorescein, but with different spectral properties, which allows them to be used together during multiple tracings.

****Saline tracers:***

Chlorides, bromides: suitable for simple tests, but their natural presence in water may limit their use.

****Natural tracers:***

Lycopodium spores: used in specific contexts.

****Emerging tracers:***

Specific substances or stable isotopes, reserved for advanced studies or specific contexts.

-Adapting the choice of tracker to the context.

-Karst environments.

Fluorescent tracers are preferred for their high sensitivity and their ability to follow rapid and complex circulations.

-Porous media

Saline or fluorescent tracers can be used, ensuring that their use is compatible with the natural composition of the water.

-Multi-tracing

It is possible to inject several different tracers to study several connections or flow directions. In this case, it must be ensured that each tracer can be detected separately, without interference.

Application examples:

For tracing in a karst aquifer, fluorescein is often chosen for its high visibility and easy detection.

When several losses are to be monitored simultaneously, both fluorescein and rhodamine can be used, each of which can be identified by its own spectral properties.

If groundwater naturally contains a lot of chlorides, it is best to avoid this tracer so as not to skew the results.

7.6.2. Interpretation of tracer tests

The analysis of trace tests is an essential step in understanding the behaviour of groundwater, how aquifers are connected to each other, and the transport mechanisms of dissolved substances. This interpretation is mainly based on the study of the restitution curves, obtained by following the evolution of the tracer injected at different points in the aquifer over time.

A. The restitution curve: the basis of the analysis

After injecting the tracer, its concentration is regularly measured at a checkpoint (such as a well or spring). These measurements are then graphically represented in the form of a restitution curve, which shows the evolution of the tracer concentration as a function of time.

Arrival time: This is when the tracer is first detected at the tracking point, which provides information on the speed of the groundwater flow.

Peak concentration: This point corresponds to the fastest passage of the tracer between injection and detection.

Tail of the curve: It reflects the dispersion and dilution of the tracer in the aquifer.

Examination of the shape of this curve makes it possible to obtain information on the speed of circulation, dispersion, dilution, and sometimes to identify the existence of several flow paths or areas where the tracer has been temporarily retained.

B. Hydrodynamic parameters obtained

The interpretation of tracer tests makes it possible to estimate several important parameters:

Flow velocity: Inferred from the time taken by the plume to travel the distance between the injection and the follow-up point.

Dispersion: The more spread the curve, the more dispersive the medium, which gives indications of the heterogeneity of the aquifer.

Dilution: A decrease in the maximum concentration of the tracer indicates that it has been diluted during transport.

Retention or temporary storage: A curve that stretches over time can reveal areas where the tracker was momentarily stored before being released.

C. Tools and methods of analysis

Interpretation can be done graphically or using specialized software, such as TRAC, which simulates the movement of the tracer and allows the model parameters to be adjusted to match the observations. These tools offer different analytical approaches adapted to the nature of the environment (porous, fissured, karstic, etc.) and facilitate the extraction of hydrodynamic parameters.

D. Limitations and Difficulties of Interpretation

Complexity of the environment: Heterogeneous or karst aquifers can produce complex curves, with several peaks or prolonged tails, which complicates the analysis.

Overlapping flows: The presence of multiple simultaneous flow paths can make interpretation more difficult.

Influence of external factors: Variations in flow, pumping or weather events can disrupt the results obtained.

E. Practical applications

The analysis of tracer tests makes it possible to:

Identify the connections between different points in an aquifer.

Assess the vulnerability of a catchment to potential pollution.

To design catchment or decontamination structures.

Understand the overall functioning of a hydrogeological system.

8. Chapter 7 (Reminders on the interpretation of chemical analysis results)

8.1. Water analysis and method of sampling.

8.1.1. Types of water testing measurements

There are two main categories:

- **Field measurements:** These are performed using portable devices (multi-parameter probes, colorimeters, field kits) to quickly obtain results for parameters such as pH, conductivity, temperature, dissolved oxygen, or turbidity. These measurements are essential for real-time monitoring and rapid detection of anomalies (Rodier et al., Dunod, 2009).

- **Laboratory analyses:** These require appropriate sampling, transport and storage. The analyses are more precise and make it possible to detect very low concentrations of contaminants (heavy metals, pesticides, pathogenic micro-organisms). Steps include sample preparation, assay, quality control, and interpretation.

8.1.2. Steps in the analysis

Different steps to obtain the result of an analysis. Of the previous steps, sampling and sampling are the most important and there is indeed a lot of risk of error.

8.1.2.1. Sampling and sampling

Sampling is a critical step, as it determines the representativeness and reliability of the results. Sampling errors are often more important than analytical errors.

- **Consistency and representativeness:** The sample must accurately reflect the composition of the water at the time and place of collection. Any physico-chemical changes (loss of dissolved gases, precipitation, adsorption on the walls) must be avoided.

- **Organization and methodology:** It is necessary to have trained staff, a methodology adapted to each case, a judicious choice of sampling points and appropriate equipment.

8.1.2.2. Sampling Equipment

The choice of equipment depends on the analyses to be carried out. The sampling equipment must satisfy the object of particular attention. The use of new glass bottles, preferably with Polyethylene (PE) or Teflon stoppers held for 1 hour in distilled water and then dried, is recommended, especially if it is a question of dosing volatile elements such as mercury (Hg).... At the time of sampling, for chemical analysis, the vials will be rinsed again three times with the water to be analyzed, then filled to the brim.

The cap will be placed in such a way that it does not have any air bubbles and is not ejected during transport. However, the ideal material does not exist and the use of one product rather than another depends on the nature of the elements to be dosed.

- **Glass bottles (new, PE or Teflon stoppers):** recommended for most chemical analyses, especially for volatile elements (e.g. mercury). The vials should be rinsed with distilled water and then three times with the water to be analyzed.

- **Quartz:** ideal for storing sensitive but fragile samples.

- **Glass/Pyrex:** suitable for major ions, but silica or boron dissolution must be attacked.

- **Polyethylene:** recommended for radionuclide analyses, but porous to gases, therefore to be avoided for samples rich in dissolved gases

8.1.2.3. Method of collection

The method of sampling varies according to the origin of the water and also according to the nature of the physico-chemical or bacteriological analyses.

**Surface water (rivers, lakes, reservoirs)*

1. Immerse the bottle 50 cm from the bottom and the surface, away from banks and obstacles.
2. Multiply the points and depths to take into account spatial heterogeneity.
3. Use depth-specific opening devices for deep sampling

**Tap water*

1. Let the water run for at least 10 minutes before sampling.
2. Volume of 2 to 5 liters depending on the analyses.
3. Some parameters (dissolved O₂, pH, turbidity) must be measured on site.
4. For heavy metals, let the water stagnate overnight and then take the first water in the morning.

8.1.2.4. Transportation and Conservation

After collection, the sample must be transported quickly to the laboratory, protected from light and at low temperature (usually 4°C). Preservative adjuvants (acids, bactericidal agents) may be added depending on the analyses to be performed.

• Modification risks: secondary precipitation, valence changes, wall adsorption, microbial biodegradation.

8.1.3. Information to be provided to the laboratory

1. Identity of the sampler.
2. Date and time of the collection.
3. Individual or authority requesting the analysis.
4. Reason for the request (initial analysis, periodic check, pollution, poisoning, epidemic...).
5. Use of water (drinking, washing, industry, etc.).
6. City or establishment supplied by the water.
7. Name of the water point and precise location.
8. Origin of water (spring, well, borehole, river, etc.).
9. Water temperature and atmospheric temperature (weather conditions).
10. Approximate flow rate (liter / minute).
11. Geological nature of the land crossed.

Water analysis requires methodological rigour at every stage, from sampling to interpretation, using standardized protocols and international guidelines to ensure reliability and comparability of results.

8.2. Physicochemical characteristics of natural waters

The study of groundwater chemistry completes any hydrogeological analysis. It is essential for determining the quality of water and its suitability for different uses (food, irrigation, industry, etc.). The ionic composition of groundwater depends on the chemistry of precipitation, surface water, soil properties and the lithology of the host rock. During their infiltration, the water is loaded with mineral salts (calcium, magnesium, sulphates, etc.) and metals (iron, manganese, etc.) by dissolving the soils and rocks through which it passes.

-Temperature (T): The temperature of the water directly influences the solubility of mineral salts and dissolved gases. For example, warmer water typically dissolves less oxygen, which can affect the redox chemistry of the water. The temperature varies according to the season, the ambient temperature and the depth of the water table. At depth, the temperature is more stable and generally higher than the surface temperature.

-pH: measures the acidity or alkalinity of water, expressed on a scale of 0 to 14, where 7 is neutral. The pH is influenced by the nature of the terrain crossed: carbonate rocks tend to increase the pH (alkaline water), while silicate or acidic soils can lower the pH. pH affects the solubility of metals and the chemical form of dissolved elements.

-Conductivity: measures the ability of water to conduct an electric current, which depends on the total concentration of dissolved ions (mineralization). It is expressed in micro-siemens per centimetre ($\mu\text{S}/\text{cm}$). High conductivity indicates water rich in dissolved salts, while low conductivity corresponds to water with low mineral content. Conductivity is a quick and simple indicator for tracking water quality.

Table 21. Determination of mineralization from conductivity.

Conductivity ($\mu\text{S}/\text{cm}$)	Mineralization (mg/L)
Conductivities <50	1.365079 x conductivities
50<Conductivities< 166	0.947658 x conductivities
166<Conductivities< 333	0.769574 x conductivities
333<Conductivities < 833	0.715920 x conductivities
833<Conductivities < 10000	0.758544 x conductivities
Conductivities >10000	0.850432 x conductivities

Table 22. Relationship between conductivity and mineralization.

Conductivity ($\mu\text{S/cm}$)	Mineralization (mg/l)
Conductivity <100	Very Low
100 < Conductivity < 200	Low
200 < Conductivity < 333	Medium
333 < Conductivity < 666	Medium to Stressed
666 < Conductivity < 1000	Important
Conductivity > 1000	High

-Turbidity: it reflects the presence of particles suspended in the water, such as clays, colloids, organic matter or plankton. It is measured in NEPUs (NTUs). High turbidity can indicate pollution or significant particle transport, which can affect potability.

-Dry residue: The dry residue corresponds to the total amount of dissolved and suspended solids in the water after evaporation. The measurement on unfiltered water gives the total content, while the measurement after filtration concerns only dissolved solids. The dry residue is an overall indicator of mineralization. (RODIER et al, 2009).

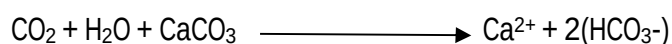
-Total hardness: Hardness is linked to the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, which come from the leaching of limestone and dolomite soils. It is expressed in French degrees ($^{\circ}\text{F}$), where 1°F corresponds to 10 mg/L of CaCO_3 . Hard water can cause limescale deposits in the pipes and reduce the effectiveness of soaps. (RODIER et al, 2009).

-Full alkali titer (TAC): The TAC expresses the total concentration of alkaline and alkaline earth bases in the form of hydroxides (OH^-), carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-). It is calculated by the formula: $\text{TAC} = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] + [\text{OH}^-]$

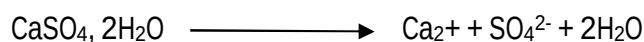
The TAC is important for assessing the buffering capacity of water, i.e. its ability to resist pH variations.

The major elements:

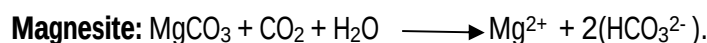
***Calcium (Ca^{2+}):** Calcium is abundant in carbonate rocks (limestone, marble) and gypsiferous rocks. Its dissolution is favored by the presence of CO_2 dissolved in the water, which forms carbonic acid, facilitating the dissolution of calcium carbonate according to the reaction:



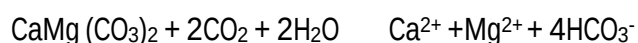
Calcium can also come from the dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) according to the following reaction:



***Magnesium (Mg²⁺):** Magnesium comes mainly from the dissolution of dolomitic rocks (CaMg(CO₃)₂) and ferromagnesian minerals. It dissolves more slowly than calcium, with the following reactions:



Dolomite dissolves according to:

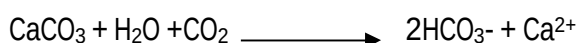


***Sodium (Na⁺):** Sodium comes from the leaching of evaporitic deposits, particularly halite (NaCl), as well as from the intrusion of seawater into coastal aquifers. The dissolution of the salt minerals takes place according to the following relationship:



***Potassium (K⁺):** Potassium is released by the alteration of potassium minerals (feldspars, micas), evaporites (sylvinite, KCl) and by the dissolution of chemical fertilizers used in agriculture.

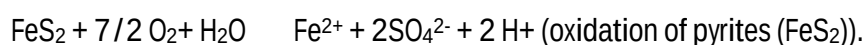
***Bicarbonates (HCO₃⁻):** Bicarbonates are formed when carbonates dissolve by CO₂-laden waters, playing a key role in the carbon cycle and pH regulation



***Chlorides (Cl⁻):** Chlorides have a natural origin (dissolution of NaCl, marine intrusion) and anthropogenic origin (fertilizers, industrial discharges). Their high concentration may indicate pollution or saline intrusion.

***Sulphates (SO₄²⁻):** come from natural and or anthropogenic origin. They exist in many minerals such as gypsum (CaSO₄.2H₂O), anhydrite (CaSO₄), barite (BaSO₄), celestine (SrSO₄) and epsomite (MgSO₄.7H₂O), they can also come from the oxidation of pyrite (FeS₂). The anthropogenic origins are the use of chemical fertilizers in agriculture.

Gypsum dissolution reactions are written:



Trace elements:

***Strontium (Sr²⁺):** Strontium is an alkaline earth metal. In nature, strontium is found mainly in volcanic and evaporitic rocks. It is found in the form of celestine (SrSO₄) and strontianite (SrCO₃). Celestine usually accompanies evaporitic formations associated with gypsum. Strontium can also substitute for Ca²⁺ in carbonate and sulfate rocks due to the similarity of their ionic radius.

***Barium Ba²⁺:** It comes mainly from the dissolution of barite: BaSO₄ or mixed sulfates of Ba and Sr. The solubility limit of BaSO₄ is 2.5 mg/L in pure water at 20°C.

***Silicon (Si):** Silica in nature is found in the form of SiO₂, of essentially natural origin, linked to silicate formations (clays, metamorphic formations). In cold shallow waters, the SiO₂ contents come largely from the soil where the clay weathering phenomena take place.

***Fluoride (F-):** Fluorine can be found in different minerals, such as in calcium fluorite (CaF₂), a mineral mainly bound to hydrothermal deposits, or in fluorine-apatites (Ca₅(PO₄)₃(OH, F, Cl)). Phyllosilicates, such as muscovite and illite, contain trace amounts of fluorine which they can release upon exchange or degradation (TRAVI, 1988).

Ionic balance:

The calculation of the ion balance allows the validity of the results to be tested, based on the principle of equilibrium of the charges of the cations and anions of the water. The ion balance (BI) of a water is determined by the following formula:

$$BI = \frac{|\sum r^+ - \sum r^-|}{|\sum r^+ + \sum r^-|} \times 100 (\%) \quad \text{With: } r: \text{quantity in reaction, in (meq/L)}$$

BI < 2 good analysis.

2% < BI < 5 acceptable analysis.

BI > 5 bad analysis.

The interpretation of the results of the physico-chemical analyses, taking into account the geological and hydrogeological context of the aquifer reservoir, will allow a better understanding of the mechanisms of acquisition of water mineralization, as well as its spatial and temporal evolution.

The physico-chemical analysis is completed by the bacteriological analysis to see the potability of the water, referring to the standards of drinkability.

8.3. Graphical representation of chemical test results

The graphical representation of hydrochemical data on the different interpretation diagrams is a very effective working tool for the interpretation of the properties of a water, as well as for making comparisons. It also makes it easy to see the behaviour and evolution of water over time in a given territory.

For the graphical representation of the water analysis, many methods were presented. Among the most commonly used methods are: bar chart, pie chart, rigid chart, triangular chart, vertical chart... etc.

❖ **Bar or column charts:** have been widely used because of their simplicity. The chemical composition may be expressed in mg/L, meq/L or % meq/L (Figure 6).

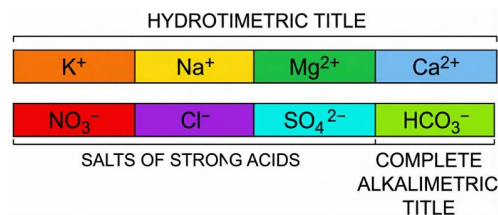


Figure 6. Bar chart.

❖ **The pie chart:** expresses the composition by means of a circle whose angles are proportional to the concentrations and their radii or diameters to the total dissolved solids, while the sum of the anions and cations is equal to 180° (Figure 7). This is one of the most useful methods for expressing the chemical composition of an area on the map.

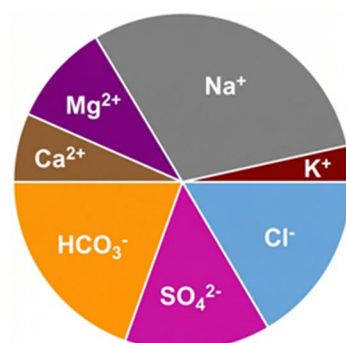


Figure 7. Pie chart.

❖ **The Stiff diagram:** uses a system of parallel horizontal axes and a vertical axis. A particular ion is placed on each of them. On the left axes, the concentrations (meq/L) of $\text{Na}^+ + \text{K}^+$, Ca^{2+} and Mg^{2+} ions from top to bottom and, in the same order, on the right axes, Cl^- , Ca^{2+} and Mg^{2+} ions. On the right-hand axes, the ions Cl^- , $\text{HCO}_3^- + \text{CO}_3^{2-}$, as well as SO_4^{2-} . The Stiff diagram makes it possible to read and recognize the major anions and cations in water (Figure 8).

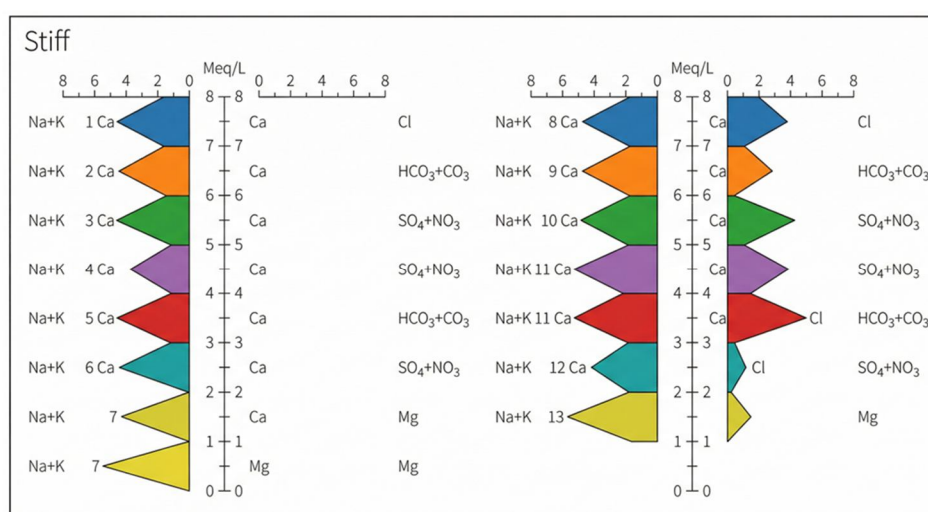


Figure 8. Stiff Diagram.

Another graphical method used for the representation of chemical water analyses is the triangular method. The simplest is to use two equilateral triangles, one for anions and one for cations, where each vertex represents 100% of a particular ion.

❖ **Piper's triangular diagram:** has the advantage, compared to the previous ones, of allowing the representation of a large number of samples in a single graph. In Piper's diagram, the anion and cation triangles occupy the lower left and right corners with their bases aligned. The central part of the diagram is in the shape of a diamond, and the points of each of the triangles are projected by a line parallel to the upper edge of the diamond. The intersection of these two lines represents the composition of water with respect to a given grouping of anions and cations. This diagram makes it possible to represent several water samples simultaneously. It is composed of two triangles representing the cationic and anionic facies of the waters and a lozenge synthesizing the overall facies (Figure 9).

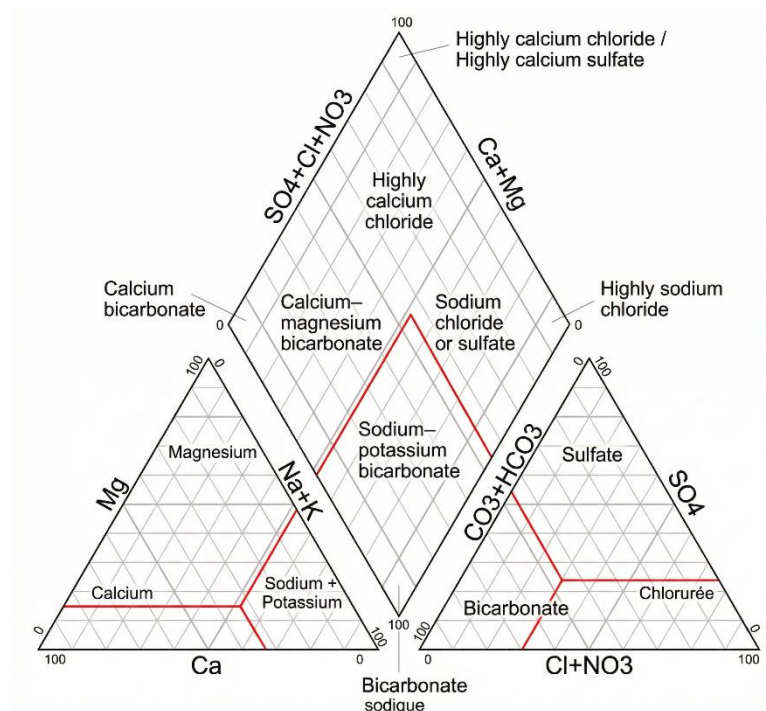


Figure 9. Piper diagram.

❖ **Schoeller-Berkaloff diagram:** It is worth highlighting the possibilities offered by vertical diagrams in the graphical representation of the chemical composition of a group of samples. In these diagrams, the concentration (in mg/L, meq/L or %) is placed on the y-axis and on the x-axis the different ions present. The most widely used is the variant proposed by Schoeller-Berkaloff, in which the chemical composition is expressed in logarithmic units (Figure 10).

The shape of the graph makes it possible to visualize the facies of the water analyzed. Indeed, the Schoeller-Berkaloff diagram indicates for each water analyzed the average content of major elements of these waters, and to establish the variations between the chemical elements. It has a maximum of 14 water samples to be represented.

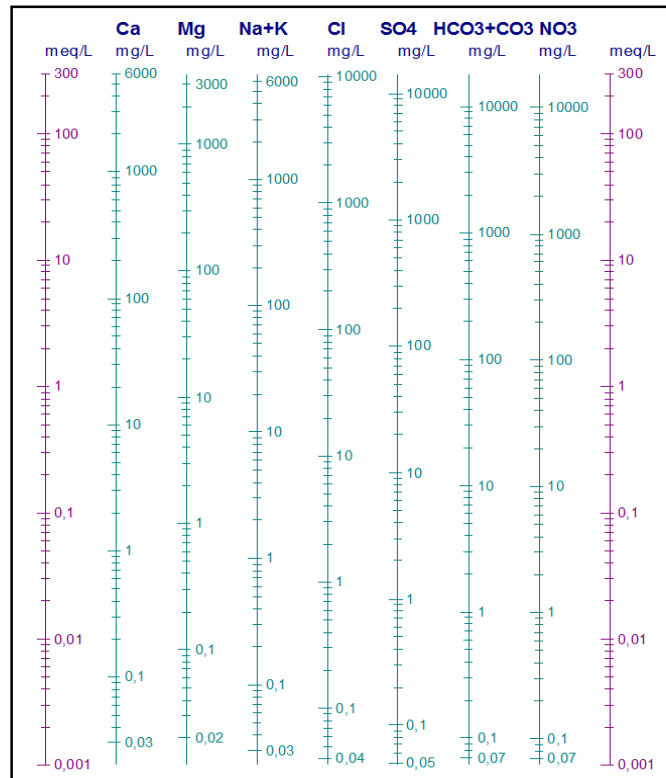


Figure 10. Schoeller-Berkaloff diagram.

❖ **Stabler diagram:** The Stabler diagram is used to quickly determine the different facies of a water. To do this, the concentrations in meq/L of anions and cations are reported on two separate bars or columns of the same length, the concentrations being reported in % (Figure 11). The determination of the different facies is visual.

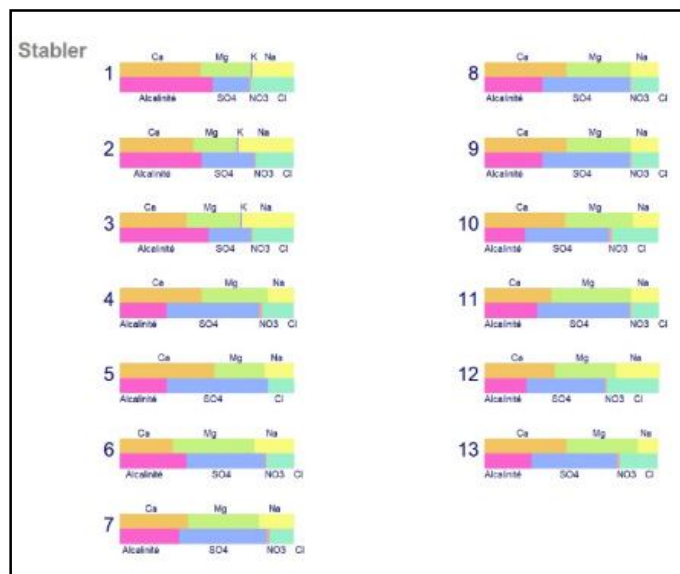


Figure 11. Stabler diagram.

❖ **Richards or Riverside or Wilcox diagram:** These diagrams are mainly used to assess the risk of soil salinization. They are based on the values of the SAR and the electrical conductivity of the ions contained in the water and the conductivity and percentage of sodium, in order to facilitate the characterization of the water and its suitability for irrigation.

The diagrams are divided into four salinity classes (C1,C2,C3,C4 x-axis) and four sodization hazard classes (S1,S2,S3,S4 y-axis) for Riverside (Figure 12) and 5 classes for Wilcox (Excellent, Good, Permissible, Poor and Poor) (Figure 13).

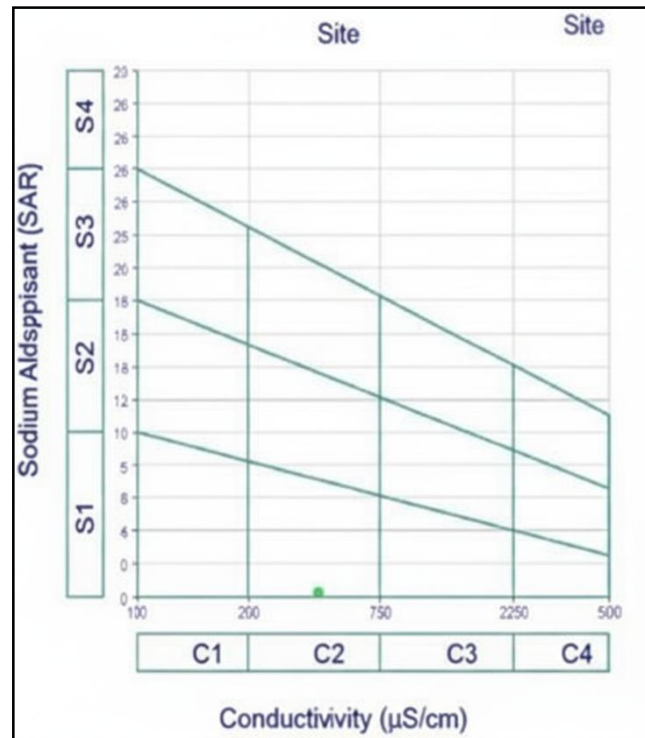


Figure 12 . Riverside diagram.

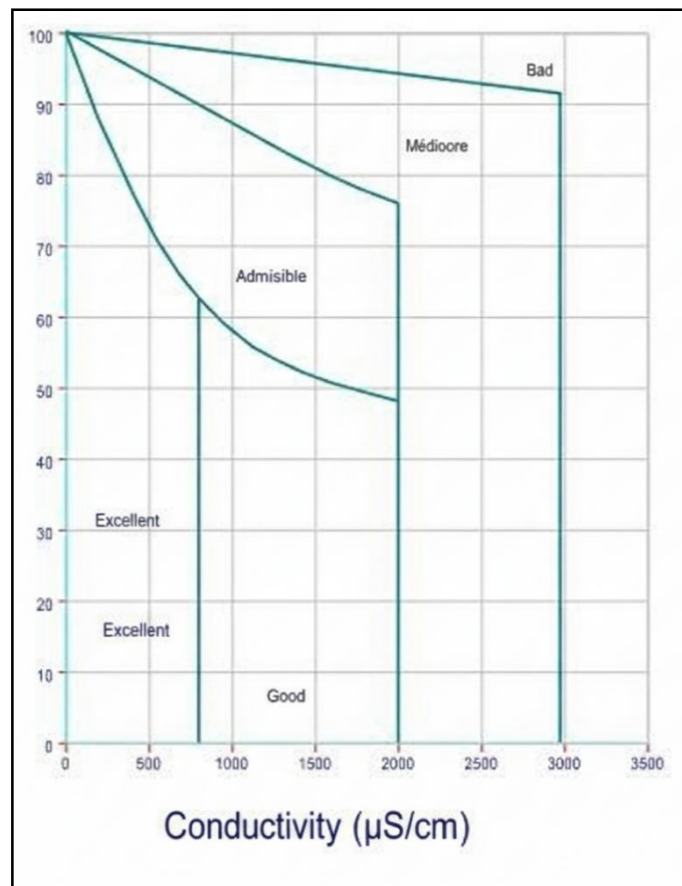


Figure 13. Wilcox diagram.

9. Chapter 8 (Water pollution)

Water resources are exploited for human consumption and for use in the agricultural and industrial fields. These waters are often threatened by contamination by pollutants of different kinds: biological, chemical or physical. Urbanization, the rise of industry and intensive agriculture have increased, chronically or accidentally, groundwater pollution. This chemical pollution comes from synthetic fertilizers and pesticides used by agriculture and toxic discharges from industrial and mining activities, among other things.

Prevention of groundwater pollution is an important step to which scientists are making an increasing effort. To be able to react effectively to this pollution and preserve water resources, a good knowledge of the nature of contaminants, their origin, their mode and their speed of propagation is a valuable asset.

9.1. The main sources of pollution

Water pollution is caused by discharges from domestic and urban, agricultural or industrial activities, for which water is the ideal vehicle for transport and dissemination (Castany, 1982).

9.1.1. Domestic pollution:

It comes from domestic and municipal wastewater discharges (street washing, watering). Household waste accumulated in illegal landfills that does not comply with standards releases pollutant-rich leachate that can be transferred to the water table. Domestic wastewater is generally loaded with organic matter, nitrogen and phosphorus, micro-organisms, etc.

9.1.2. Agricultural pollution:

Pollution is spread in space and time; It is chronic and affects large areas. It is mainly caused by the massive use of fertilizers and phytosanitary products and pesticides (Castany, 1982). The transfer of fertilizers and pesticides to the water table is done either by infiltration over the entire cultivated area, or by discharge into lost wells, chasms, etc. The practice of irrigation accelerates the transfer. These products used in agriculture are the source of the presence of nitrates and trace metal elements (Zn, Cu, Pb,...) in water.

9.1.3. Industrial pollution

It comes from industrial, thermal and chemical discharges (Castany, 1982).

This pollution is characterized by:

- organic matter and fats (agri-food industries)
- hydrocarbons (refineries)
- metals (metallurgical surface treatment)
- acids, bases and various chemical products (chemical industries)
- hot water (cooling circuits of thermal power plants)
- radioactive materials (nuclear power plants).

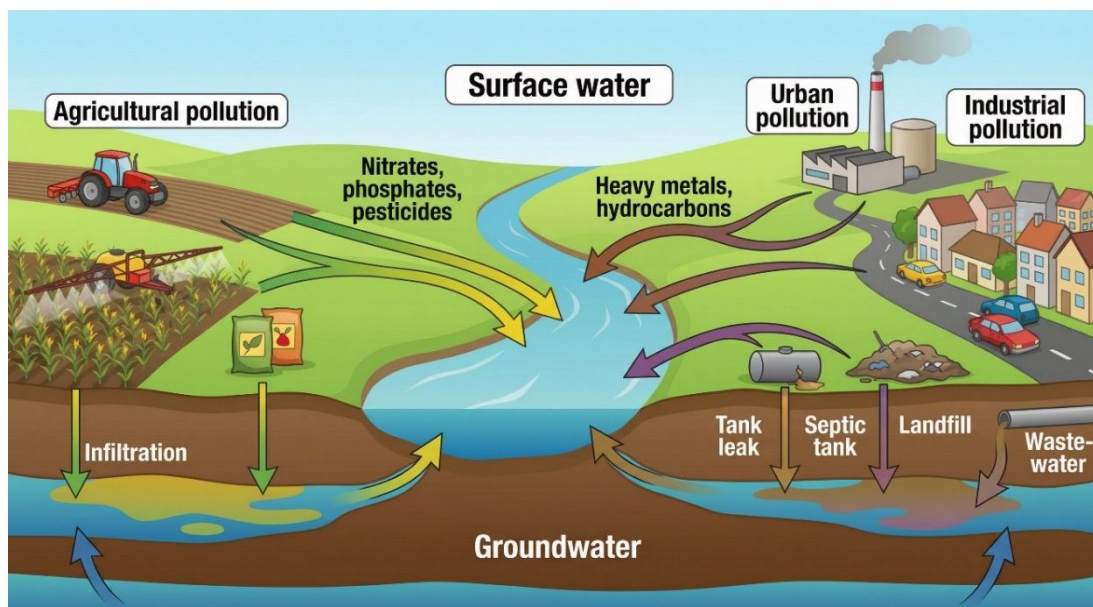


Figure14. The different sources of water contamination in urban areas.

This figure illustrates how different human activities pollute both surface water (rivers, lakes) and groundwater (groundwater and deep aquifers).

***Surface water:** Agricultural fields bring nitrates, phosphates and pesticides to the river and lake through rainwater runoff, which can cause eutrophication and toxicity to aquatic organisms. Urban and industrial areas release heavy metals, hydrocarbons and other pollutants via rainwater and sometimes poorly treated discharges, degrading the quality of surface water.

***Groundwater:** Groundwater is contaminated by the infiltration of pollutants through the soil, especially those from intensive agriculture, roads and urban areas. Deeper aquifers can also be affected in the long term when the protective layers are cracked or locally permeable, making pollution difficult to remove.

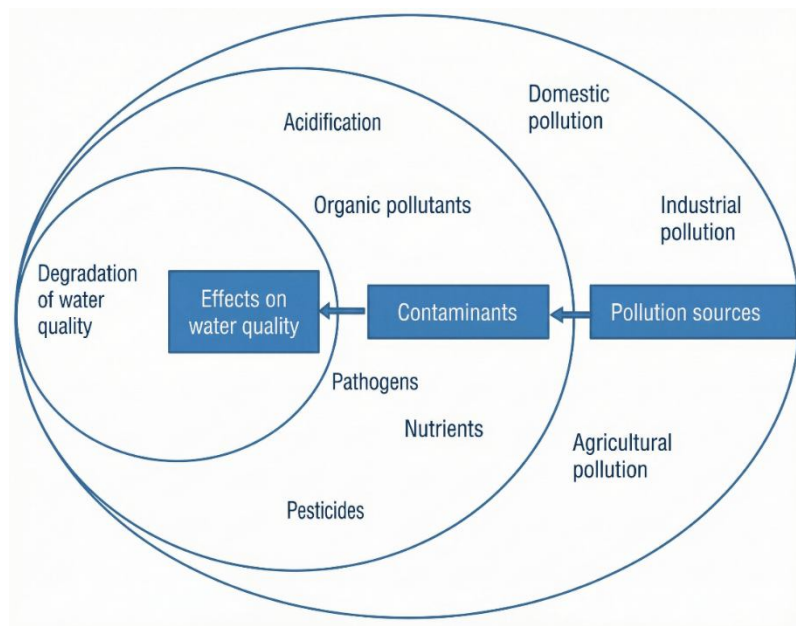


Figure15. Pollution sources, contaminants and their effects on water quality.

9.2. The main types of pollutants

9.2.1. Physical Pollutants

The three main physical agents of pollution are heat, the transport of suspended solids and radioactivity (Castany, 1982).

-Radioactive pollutants: Radioactivity is potentially the most dangerous physical pollutant (Castany, 1982). The sources of these radioactive isotopes come from nuclear power plants and reprocessing activities, largely from hospital wastewater.

-Suspended solids (TSS): Fine suspended particles are either of natural origin (soil erosion, dust carried away by the wind, etc.) or produced by the agri-food industry, the chemical industry, etc.

-Heat: The rise in temperature causes ecological effects on aquatic life (algae development). It decreases the solubility of oxygen (Castany, 1982). Thermal pollution can be natural, in the case of hot springs, or related to the use of water as a coolant in thermal and nuclear power plants.

9.2.2. Chemical pollutants

-Heavy metals: The heavy metals most often encountered in nature are: lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn). Some of these heavy metals are associated with natural processes (weathering of the parent rock), while others result from anthropogenic activities (metallurgical industrial waste, agricultural practices, etc.). Heavy metals are dangerous pollutants because they are toxic at low concentrations and in addition they are not biodegradable and they are bioaccumulative in soils and in the tissues of living organisms.

-Dissolved mineral salts: Their presence in groundwater is likely to make it unfit for human consumption nitrates (NO_3^-), nitrites (NO_2^-), phosphate (PO_4^{3-}), fluoride (F^-). These pollutants are not toxic, but present a danger to the environment (eutrophication) if they are used too intensively.

9.2.3. Organic pollutants

-Pesticides: phytosanitary products of mineral origin, synthetic organic plants, more commonly known as pesticides. The origin of these substances is mainly found in agricultural activities. Their evolution in the soil leads to toxic derivatives. Several scientists have shown that the biodegradation of these pollutants depends on soil temperature, soil horizon biological life, depth, and pH.

-Hydrocarbons: hydrocarbons come mainly from effluents from factories, the oil industry and petrochemicals. These products include various petroleum products (crude oil, refined oil, kerosene, petrol, fuel oil, lubricants, engine oils, etc.).

9.2.4. Microbiological pollutants

Microbiological pollution results from the presence in water of microorganisms that are carried by water and are responsible for many waterborne epidemic diseases. Bacteria, viruses and protozoa come mainly from septic tanks, landfills, wastewater spreading, and livestock farming.

9.3. Modes of Pollutant Transfer

9.3.1. Point Source Pollution

Groundwater contamination is said to be point contamination when the source of pollution is identifiable and contaminates only a limited area.

9.3.2. Pollution diffuse

It is caused by the diffusion of multiple pollutants in time and space. The most common examples are: industrial areas that release many pollutants into the atmosphere, agricultural activities that spread substances such as nitrates and pesticides over very large areas, and gases from motor vehicles. The mechanisms of transfer of these pollutants depend strongly not only on the characteristics of the product (doses, physico-chemical parameters, etc.) and the environment (soil type, microbial activity, etc.), but also on the climate and the period of application.

9.3.3. Temporary (accidental) pollution

It can be caused by the exceptional emission of polluting material following an incident during which hazardous materials are spilled (bad factory manoeuvre, traffic accident, etc.).

9.3.4. Chronic pollution

Is permanent pollution due to repeated or constant emissions of highly persistent pollutants (which persist after the source has disappeared). It is more insidious and more damaging, less spectacular and can go unnoticed (agricultural pollution by nitrates; contamination by hydrocarbons from polluted soils).

9.4. Pollutant Transfer Mechanisms

9.4.1. Physical transfers

-Volatilization: This is the passage of a substance into a gaseous state that reduces the concentration of the contaminant in the environment. Organic molecules are likely to volatilize. When the product is pure, this volatilization is calculated from the saturation vapor pressure describing the equilibrium between the gas and liquid phases. Highly volatile substances, such as gasoline, benzene and chlorinated hydrocarbons, can preferentially escape from contaminated soil into the soil air and the free atmosphere.

-Dispersion: This is a mixing phenomenon essentially linked to the heterogeneity of microscopic velocities within the porous medium. It is characterized by a change in the direction and speed of a particle, often related to the movements of the water table and the heterogeneity of the porous medium. The process of hydrodynamic dispersion of pollutants thus contributes to their spread over time and in the three-dimensional space of the aquifer. There are two mechanisms of dispersion:

Mechanical dispersion: depends on the characteristics of the medium: pore size, heterogeneity, particle size, etc. The dispersion process causes the concentration and transfer time of contaminants to decrease, while the contaminated volume increases.

Molecular diffusion: (of a solute) occurs under the effect of concentration gradient: The substance migrates from an area of high concentration to an area of low concentration. In the aquifers, convective dispersion predominates.

-Filtration: The effect of filtration by soils and rocks is a complex physical and chemical phenomenon. It includes the removal of larger particles by mechanical deformation, and the adsorption of smaller suspended particles (bacteria, iron hydroxide flakes, etc.). The transport of suspended particles can be mechanically limited by pore size and microorganism or particle size.

-Dilution : The dilution of the solute with groundwater reduces the concentration of the pollutant, and therefore its harmfulness. Dilution is a function of water inputs or renewal (Castany, 1982). For example, drainage between two aquifers or hydraulic relations with a watercourse located in the vicinity of the pollution plume.

9.4.2. Chemical Transfers

-Dissolution-Precipitation: Along the groundwater flow path, dissolved solids can be precipitated when evaporation and transpiration increase their concentrations beyond saturation limits or when groundwater of different chemical compositions is mixed. The capacity of water to dissolve substances

is increased by inorganic and organic acids as well as by the increase in temperature. The evolution of the reaction equilibrium is a function of many parameters (respective concentrations in the aqueous phase, soil composition, temperature, pH, pressure,...).

-Adsorption: Adsorption is the property of certain solid bodies to retain the molecules of other bodies (in a gaseous or liquid state) on their surface. There are two mechanisms of adsorption: Physical adsorption, which is the result of reactions involving low-energy physico-chemical bonds (ion exchange), and chemical adsorption, which involves high-energy chemical bonds (covalent bonds). The soil constituents most likely to be involved in the process are those with a large specific surface area (in the case of clays) or highly reactive sites on which various substances can attach (in the case of organic matter).

9.4.3. Biological transfers

The biodegradation of an organic compound under aerobic (O_2 present) or anaerobic (absence of oxygen) conditions can be defined as a biologically catalyzed reduction reaction. It frequently leads to the conversion of an organic compound into an inorganic product. Such conversion is called mineralization. This process is destructive, which is particularly interesting for natural attenuation; provided that the neoformed products (metabolites) have less toxicity, which is not always the case.

9.5. Pollution Indicators

9.5.1. Suspended solids (TSS)

Suspended solids include all insoluble mineral and/or organic matter that is suspended in water. They include clays, sands, silts, low-dimensional organic and mineral matter, plankton and other water microorganisms (Rodier and al, 2009). They depend on the nature of the land crossed, the season, rainfall, discharges, and the development of microorganisms.

9.5.2. Dissolved Oxygen

The quantity of oxygen in solution in a water governs the redox reactions and shows an identical evolution to that of the redox potential. The solubility of oxygen is a function of atmospheric pressure, temperature and salinity: O_2 saturation decreases as temperature and altitude increase. This parameter is used mainly for water; Water that is very aerated is generally supersaturated with oxygen, while water laden with organic matter that can be degraded by microorganisms is poor.

9.5.3. Biochemical oxygen demand (BOD_5)

BOD_5 measures the amount of oxygen needed to oxidize biodegradable organic matter (bacteria), this analysis is carried out at a temperature of $20^\circ C$ for 5 days in the dark. It is expressed in $mg\ O_2/L$. The BOD_5 parameter is used to establish a qualitative ranking of water and to define the alteration of the environment by biodegradable organic matter (Rodier and al, 2009).

9.5.4. Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is the amount of oxygen required for the chemical degradation of all biodegradable or non-biodegradable organic matter in water using potassium dichromate ($K_2Cr_2O_7$) at 1500C, in an acidic environment and in the presence of silver sulphate (Ag_2SO_4) acting as an oxidation catalyst and mercury sulphate ($HgSO_4$) to complex chloride ions. Excess potassium dichromate is measured by iron ammonium sulphate ($FeSO_4(NH_4)_2SO_4, 6H_2O$) (Eckenfelder, 1982). It is expressed in $mg\ O_2/L$.

*Biodegradability

The combination of the 2 global pollution parameters COD and BOD_5 allows a good approach to biodegradability, which reflects the ability of an effluent to be decomposed or oxidized by micro-

organisms involved in the biological water purification process. The COD/ BOD_5 ratio gives an initial estimate of the biodegradability of the organic matter of an effluent. The following limitations are generally agreed upon (Rodier and al, 2009).

$COD / BOD_5 < 3$ readily biodegradable effluent.

$3 < COD / BOD_5 < 5$ moderately biodegradable effluent.

$COD / BOD_5 > 5$ effluent that is difficult to biodegrade or even non-biodegradable.

9.5.5. Nitrates (NO_3^-)

Nitrates (NO_3^-) represent the final oxidized form of nitrogen after the nitrification step corresponding to the transformation of NO_2^- into NO_3^- . In groundwater, nitrates come mainly from the application of nitrogen, chemical or organic fertilizers. A significant amount of NO_3^- also comes from the natural biological cycle of nitrogen, either by the decomposition of organic matter or by the active production of certain plants.

9.5.6. Nitrites (NO_2^-)

Nitrites, or nitrous nitrogen, represent a less oxygenated and less stable form. It's a passage between nitrates and ammonium, it's a toxic form.

9.5.7. L'ammonium (NH_4^+)

Ammonium (NH_4^+) is the most toxic form of nitrogen. Its presence in water usually reflects a process of incomplete degradation of organic matter. Ammonium (NH_4^+) is a good tracer of domestic pollution (human discharges).

9.5.8. Phosphates (PO_4^{3-})

Phosphorus can be found in different oxidized forms; in the acid form, we find the meta(HPO_3), pyro ($H_4P_2O_7$) and ortho (H_3PO_4) acids (Debieche, 2002). At the pH of natural waters (between 7 and 8) ortho-phosphates are mainly in the $H_2PO_4^-$ and HPO_4^{2-} forms.

9.6. Water pollution by trace metal elements (TME)

9.6.1. Definitions and Classification

Trace metal elements, commonly known as heavy metals, are a group of naturally occurring metallic elements present in very low concentrations in the environment. Their definition varies according to the criteria used: density, atomic number, atomic weight, chemical properties or toxicity. This diversity leads to a certain ambiguity in the classification. For example, some toxic metals such as zinc are not particularly heavy, while some toxic elements such as arsenic are not metals but metalloids. For this reason, the scientific community now favours the term "trace metal elements" (TME) to refer to these substances (INERIS, 2010).

The European Union has proposed a regulatory definition specifying that heavy metals include antimony, arsenic, cadmium, hexavalent chromium, copper, lead, mercury, nickel, selenium, tellurium, thallium and tin, in their metallic or compound forms, as long as they are classified as hazardous substances (European Directive, 2006).

9.6.2. Properties and toxicity

ETMs are characterized by their non-degradability in the environment, their persistence, their toxicity at low concentrations and their ability to bioaccumulate in living organisms. The chemical form of metals (ionic, organic, complex) strongly influences their toxicity, as does the dose and duration of exposure (Alloway, 2013).

9.6.2.1. Health impacts of the main ETMs

Arsenic (As): Arsenic is a highly toxic metalloid with atomic number 33 that has been regulated in Europe since 2005. Acute exposure to inorganic arsenic causes severe gastrointestinal disturbances (nausea, vomiting, hemorrhage, abdominal pain) as well as delayed neurological and dermatological effects (INERIS, 2010).

Cadmium (Cd): A metal with atomic number 48, cadmium is a major industrial contaminant, particularly from metallurgical activities and the manufacture of nickel-cadmium batteries. Acute poisoning by ingestion causes gastrointestinal and muscle disorders, while inhalation can lead to severe chemical pneumonia with a mortality rate of 15-20% (Bliefert and Perraud, 2009; INERIS, 2011).

Chromium (Cr): Chromium, element 24, occurs naturally in some minerals and is concentrated in industrial areas such as tanneries. Ingestion of hexavalent chromium salts causes inflammation and extensive necrosis of the gastrointestinal tract, which can progress to coma and death with mass exposure (Attia, 2005; INERIS, 2005).

Nickel (Ni): Metal 28, nickel is used in the manufacture of stainless steel, batteries and catalysts. Nickel tetracarbonyl is particularly toxic, causing neurological, respiratory, and dermatological symptoms, including contact dermatitis, the most common manifestation in the general population (INERIS, 2006; Rodier and al., 2009).

Lead (Pb): Metal 82, lead is a major environmental contaminant, particularly from car emissions. It is toxic even in low doses, affecting the digestive, renal, central nervous and hepatic systems. Early

symptoms include colic, abdominal pain, and vomiting, with the risk of serious injury that can be fatal (INERIS, 2003; Bliefert and Perraud, 2009).

Zinc (Zn): Metal 30, zinc is naturally present in the form of sulphides. Mining and industrial activities are increasing its concentration in the environment. Inhalation of zinc vapours can cause "foundry fever", characterized by respiratory and systemic symptoms, and in some cases, fatal pulmonary fibrosis (INERIS, 2005; Rodier and al., 2009).

9.6.3. Environmental impact of OTEC

OTEC are naturally present in trace amounts in soils, water and sediments. However, their concentration can increase significantly as a result of human activities such as mining, metallurgy, intensive agriculture and urbanization. These elements are transferred to the environment via rainfall, irrigation, runoff and percolation into soils. Their mobility depends on the physicochemical properties of the soil (pH, permeability, organic matter) and the chemical form of the metals (Alloway, 2013).

Unlike organic pollutants, OTEC does not degrade and can accumulate in sediments, water and living organisms, generating persistent and often irreversible pollution (Salvárredy Aranguren, 2008).

In conclusion: trace metals represent a major threat to human health and the environment because of their toxicity, persistence and accumulation capacity. Their rigorous monitoring, based on precise scientific and regulatory criteria, is essential to limit their impact. A thorough understanding of their sources, chemical forms and transfer mechanisms is essential for developing effective management and remediation strategies.

10. Conclusion

The entire document on the hydrochemistry of natural waters is presented as a complete course, from the fundamental basics of water chemistry to the most operational applications in the management and protection of water resources. As the chapters progress, it becomes clear that the chemical composition of water is neither fortuitous nor fixed: it is the result of a chain of physicochemical, geological, climatic and biological processes, which take place throughout the hydrological cycle, from meteoric waters to groundwater and surface water. By first laying the theoretical foundations (structure of the water molecule, solutions, ions, acid-base and redox equilibria, concentrations and activities), the book gives the reader the conceptual tools necessary to understand the behaviour of chemical species in solution and to interpret the analytical data rigorously.

The part devoted to the genesis of dissolved elements and the processes of chemical alteration highlights that water is at the same time an agent of erosion, a vector of material transport and a reaction medium. By describing in detail the mechanisms of hydration, hydrolysis, oxidation and reduction, as well as the dissolution of silicate, carbonate or evaporitic minerals, the paper shows how the chemical characteristics of different waters are gradually constructed. The notion of hydrochemical facies then takes on its full meaning: calcium bicarbonate, magnesium bicarbonate, sulfate or sodium chloride, each facies testifies to a lithological context, a degree of geochemical evolution and often specific anthropogenic influences. The reader learns to consider the chemical composition of water as integrative information, which records the memory of water-rock interactions, climatic conditions, biological activity and land uses.

A major contribution of the document lies in the close articulation it establishes between geochemical theory and analytical practice. The chapters devoted to analysis methods – in situ measurements, spectrophotometry, atomic absorption, ion chromatography, HPLC, electrochemical and titrimetric methods remind us that any solid hydrochemical interpretation is based first and foremost on reliable data. By insisting on the principles of each technique, its areas of validity, its possible interferences, its detection and quantification limits, the course makes the reader aware of the need to master the measurement chain as a whole. The use of ion balance, quality control (blanks, duplicates, reference materials) and verification of the consistency of the results underlines that hydrochemistry is not only a science of interpretation, but also a science of measurement, where metrological rigour conditions the relevance of the conclusions. |

The normative and applied dimension also occupies an important place, which gives this document a scope that goes beyond the academic framework alone. By bringing the concepts of hydrochemistry closer to regulatory requirements for the quality of water intended for drinking, irrigation, or other uses, the book shows how analytical parameters translate into issues of public health, environmental protection, and resource management. Discussions on permissible thresholds, monitored parameters (nitrates, metals, pesticides, microbiological indicators), measurement uncertainty and conformity assessment highlight the responsibility of the water specialist: his analyses and interpretation can guide decisions on the treatment, restriction of use or protection of structures and aquifers.[AB1]

Graphical interpretation tools, such as Piper, Stiff or Schoeller-Berkaloff diagrams, are another highlight of the document. They make it possible to visually synthesize chemical information, compare several samples, monitor the spatial or temporal evolution of facies and highlight trends or anomalies. Their use, placed in the broader context of the geochemical processes presented in the course, helps the reader to move from a purely descriptive approach to the data to an explanatory approach, where each diagram becomes a reasoning support on the origin, the path and the degree of evolution of the waters studied.

At the end of the reading, it appears that this document fulfils a double function: it is both a training manual and a methodological guide. As a textbook, it provides a body of fundamental and applied knowledge for students in earth sciences, hydrogeology, environment, civil engineering and related disciplines, and provides them with the necessary foundation to tackle more specialized work or field studies. As a guide, it provides practitioners (engineers, technicians, managers) with a frame of reference for developing sampling strategies, choosing analytical methods, controlling data quality, and interpreting results in an operational context.

The general conclusion that emerges from the whole is that the hydrochemistry of natural waters, as presented in this document, is not an accumulation of abstract concepts, but a real language for describing and understanding the functioning of hydrosystems. Mastering this language means being able to link a chemical composition to processes, to identify pollution signatures, to diagnose malfunctions, but also to recognize situations of equilibrium and good condition. In a context where water resources are increasingly coveted, vulnerable and at the centre of sustainable development policies, this knowledge is becoming strategic. By providing a solid conceptual framework, proven measurement and interpretation tools, and an openness to regulatory and industrial applications, the document empowers the reader to move from analysis to action, and to put water chemistry at the service of responsible and informed management of aquatic environments.

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12. List of Abbreviations

➤ General chemistry and units

- H_2O → Water molecule.
- NaCl → Sodium chloride.
- Na^+ → Sodium ion.
- K^+ → Potassium ion.
- Ca^{2+} → Calcium ion.
- Mg^{2+} → Magnesium ion.
- Cl^- → Chloride ion.
- SO_4^{2-} → Sulfate ion.
- HCO_3^- → Bicarbonate ion.
- CO_3^{2-} → Carbonate ion.
- NO_3^- → Nitrate ion.
- NO_2^- → Nitrite ion.
- SiO_2 → Silica (silicon dioxide).
- DOC → Dissolved Organic Carbon.
- DIC → Dissolved Inorganic Carbon.
- CO_2 → Carbon dioxide.
- O_2 → Molecular oxygen.
- H^+ → Hydrogen ion (proton).
- OH^- → Hydroxide ion.
- mg/L → Milligrams per liter.
- g/L → Grams per liter.
- mol/L → Moles per liter (molarity).
- mol/kg → Moles per kilogram (molality).
- meq/L → Milliequivalents per liter.
- $\mu\text{S/cm}$ → Microsiemens per centimeter (electrical conductivity).
- NTU (NEPU) → Nephelometric Turbidity Unit.

➤ Thermodynamics, kinetics, activities

- E_i → Ionization energy.
- Ox/Red → Oxidized / Reduced form in a redox couple.
- k → Rate constant.
- A (in $k = A e^{(-E_a/RT)}$) → Pre-exponential (frequency) factor.
- E_a → Activation energy.
- R → Universal gas constant.

- T → Absolute temperature.
- I (ionic strength) → Ionic strength of the solution.
- γ_i → Activity coefficient of species i.
- **Water analysis and quality indicators**
 - TDS → Total Dissolved Solids.
 - TAC (titre alcalimétrique complet) → Total alkalinity.
 - TH (total hardness, expressed in °F) → Total hardness of water.
 - °F (French degree) → French degree of hardness (10 mg/L CaCO₃).
 - LOD → Limit of Detection.
 - LOQ → Limit of Quantification.
 - CRM → Certified Reference Material.
- **Analytical methods**
 - UV-Vis → Ultraviolet–Visible spectrophotometry.
 - AAS (or SAA) → Atomic Absorption Spectrometry.
 - ICP-AES → Inductively Coupled Plasma – Atomic Emission Spectrometry.
 - ICP-MS → Inductively Coupled Plasma – Mass Spectrometry.
 - IC → Ion Chromatography.[1]
 - HPLC → High-Performance Liquid Chromatography.
 - GC-MS → Gas Chromatography – Mass Spectrometry.
 - EDTA → Ethylenediaminetetraacetic acid (complexometric reagent).
- **Hydrochemistry, facies, diagrams**
 - EC (or CE in French tables) → Electrical Conductivity.
 - T (for water) → Temperature.
 - BI → Ionic balance.
 - Ca–HCO₃ facies → Calcium–bicarbonate hydrochemical facies.
 - Na–Cl facies → Sodium–chloride hydrochemical facies.
 - Piper diagram → Piper trilinear diagram (hydrochemical classification plot).
 - Stiff diagram → Stiff diagram (polygonal hydrochemical diagram).
 - Schoeller-Berkaloff diagram → Schoeller-Berkaloff semi-logarithmic diagram.
- **Tracers and hydrology**
 - Sr²⁺ → Strontium ion.
 - Ba²⁺ → Barium ion.
 - PAH → Polycyclic Aromatic Hydrocarbons.
 - PCB → Polychlorinated Biphenyl

Biography

Sabrine Guettaia is a lecturer and researcher in hydrogeology and hydrochemistry at the Abou Bekr Belkaid University in Tlemcen, where she has been working as a class A lecturer in water sciences. She teaches hydrochemistry, fundamental hydrogeology, Hydrodynamics, hydrogeological modelling, hydrogeology of Algeria and water management and treatment, with a strong focus on the management and protection of water resources. She is part of the "hydrogeochemistry and water pollution" team of Laboratory n°25 "Promotion of Water, Mineral and Soil Resources, Environmental Legislation and Technological Choices", dedicated to the study of water quality, soil and environmental impacts. His research focuses on aquifer hydrochemistry, geochemical facies and contamination by irrigation water or nitrates in semi-arid environments, particularly in the Tlemcen region, Maghnia and Hennaya plain and Oued Righ valley. She is the author or co-author of several scientific works on groundwater quality, the evolution of physico-chemical parameters and the use of advanced statistical tools to analyze pollution processes and sources, and regularly participates in national and international programs and seminars on water resources.