



# **CERI MATERIAUX ET PROCEDES DEPARTEMENT DE GENIE CIVIL ET ENVIRONNEMENT**

## **SURICATES (NWE462): SEDIMENT USES AS RESOURCES IN CIRCULAR AND TERRITORIAL ECONOMIES**

DELIVERABLE T2.2.1 – SEDIMENT AS A POZZOLANIC MATERIAL : FORMULATION AND  
LAB TESTS OF ECO-SOLUTIONS REPORT



Client: Interreg NWE

File Ref: NWE462/SURICATES/ DT2.2.1

Issue:

Date:

Prepared by:

# TABLE OF CONTENTS

## **TABLE OF CONTENTS**

<b>INTRODUCTION.....</b>	<b>3</b>
<b>CHAPTER 1 : CONTEXTUALIZATION, OBJECTIVES AND METHODOLOGY</b>	
1.1 INTRODUCTION.....	4
1.2 CHALLENGES AND STRATEGIES.....	6
1.2.1 Environmental and health issues.....	7
1.2.2 Regulatory issues.....	7
1.2.3 Socio-economic issues.....	8
1.3 OBJECTIVES AND METHODOLOGY.....	9
1.4 AIMS OF THIS REPORT.....	9
1.5 METHODOLOGY.....	10
1.6 MATERIALS.....	11
1.7 SEDIMENT TREATMENT.....	12
1.8 FORMULATION.....	12
1.9 CHARACTERIZATION - ANALYSIS AND OPERATION.....	13
<b>CHAPTER 2 : DREDGED SEDIMENTS AND CEMENTITIOUS MATRICES</b>	
2.1 DREDGED SEDIMENTS.....	14
2.1.1 Definition.....	14
2.1.2 Origin.....	15
2.1.3 General composition.....	16
2.1.4 Particle size composition.....	18
2.1.5 The fine fraction - Clay fraction.....	18
2.1.6 Water.....	19
2.1.7 Pollutants.....	21
2.1.8 Organic Matter.....	23
2.1.9 Pretreatment and Treatment.....	25
2.1.10 Chemical methods.....	33
2.1.11 Sediment Regulations.....	34

## TABLE OF CONTENTS

---

2.2	CEMENTITIOUS MATERIALS.....	41
2.2.1	Cement and its manufacture.....	41
2.2.2	Cement Hydration.....	42
2.2.3	Porosity in Cementitious Matrices.....	47
2.2.4	The matrix-aggregate interface.....	49
2.3	CONCLUSION.....	51

### **CHAPTER 3 : MATERIALS AND METHODS**

3.1	CEMENT.....	52
3.2	MINERAL ADDITIONS.....	53
3.2.1	Dredged sediments.....	53
3.3	PHYSICAL AND CHEMICAL CHARACTERISTICS OF MATERIALS USED .....	54
3.4	PREPARATION OF MORTARS.....	54
3.5	SETTING TIME.....	55
3.6	MECHANIC PERFORMANCES.....	55
3.7	MERCURY POROSITY.....	55

### **CHAPTER 4 : RESULTS AND ANALYSES**

4.1	THERMO GRAVIMETRIC ANALYSIS (TGA).....	56
4.2	PHYSICAL CHARACTERISATION.....	57
4.3	DIFFRACTION ANALYSIS (XRD).....	59
4.4	THERMOGRAVIMETRIC ANALYSIS (TGA).....	59
4.5	SITTING TIMES.....	61
4.6	MECHANICAL PERFORMANCE.....	62
4.6.1	Compressive strength of mortars.....	62
4.6.2	Flexural strength of mortars.....	63
4.7	MERCURY POROSITY.....	63
4.8	CONCLUSIONS.....	64

### **BIBLIOGRAPHICAL REFERENCES**

### **APPENDICES**

# INTRODUCTION

In France, construction sector annual needings for granular materials are close to 400 million tons, of which 96% are natural in origin. Thus, it becomes necessary to find alternative solutions, particularly in the valorization of industrial by-products (IBP) such as dredging sediments. Marine sediments are designated as a secondary raw material in this study. However, the latter may present varying levels of pollution, with the presence of organic matter (5% to 30%), high water content (50% to 200%) and a fine granulometry ( $6300\text{ }\mu\text{m}$ ). Currently, research targets to use them as supplementary mineral addition in concrete after efficient methods of treatment that improve some Physico-chemical properties.

The problem of dredged sediments is part of a broader environmental issue. At the dawn of the 21st century, the environment is now considered to be of major importance (COP 21, Paris, 2015). Currently, the need to find alternative solutions for the preservation of the environment and resources are more than necessary: it is vital. In this context, the substitution of natural materials by recycling materials is at least a partial solution to this socio-economic and environmental challenge. Now, the 3 R law "Reduce, Recycle, Reuse" [1][2] (Fig. 1.2) seems to prevail in many sectors and sustainable waste management is more strongly encouraged, if not required (EU Directive 2008/98/EU, Energy Transition Act (2015), etc.) [3]. This principle constitutes an articulation and synergy between current and potential future resources.

Sediment is made up of a combination of smaller or larger particles or Precipitated materials having separately undergone a certain transport [4]. In France, approximately 50 million  $\text{m}^3$  of sediments is dredged annually, stored, treated and/or released at sea [5]. Sediments, according to their degree of pollution (heavy metal content, hydrocarbons: HAP, PCB, TBT, etc.), can be considered to be waste and pose a risk to the environment. Then the problem of what to become of them. Several treatments and therefore valorization channels are now being explored. Among these, the valorization in road technology as a base layer or form layers [6][7], the manufacture of building bricks [8], the establishment of landscape bumpers [9], and their use as materials substitution of cement and/or sand in concrete [10] [11] [12] [13] [14] [15].

In some countries, they are used in the following important structures: Port of Rotterdam, Palm Island in Dubai, National Theatre in London, or the artificial island of Chek Lap Kok

where the Hong Kong airport is located, etc. [16]. According to San Nicolas [17], the industrial cement production is particularly polluting (1 T Clinker / 1 T CO<sup>2</sup>), costly in energy (8000 Joules / 1 T Clinker) and relatively expensive (150 €/ 1 T Clinker) [18]. For Meyer [19], the cement industry, somewhat a victim of its success produces around 7% of the world's CO<sup>2</sup> emissions [20]. In the construction sector, the aggregate requirements were 349 million tons in France in 2014, 96% of which are of natural origin [21] [22]. The turnover of the sector reached 3664 million euros [21] and that of ready-mixed concrete (BPE) stood 3664 million euros [22]. Cement consumption in France amounted to almost 15.6 million tonnes in 2015. This represents a substantial financial windfall and weight for the environment [23].

Because of these economic and ecological issues, sediments are potentially recoverable as construction materials. Sediments are effective as a substitute for concrete [24] [10]. Indeed, faced with declining natural resources and increasingly restrictive environmental regulations, the use of these materials in the construction sector is a relevant solution [25]. Moreover, the solutions initially envisaged are the storage or release at sea. These are governed by the Order of 09 August 2006 fixing the reference values for dumping and the Order of 28 October 2010 relating to the storage of inert waste. Also, the recycling and use of sediments as a resource advocated in more and more European projects (Usar, Setarms, etc.), can be considered very appropriate in a common ambition of sustainable development. However, several scientific obstacles need to be removed. Among these, the possible content of sediments in mineral pollutants such as heavy metals (Lead, Iron, Chromium, etc.), salts, cyanides. But also organic pollutants such as hydrocarbons, HAP, PCB, TBT, etc. [26]. Our study will focus exclusively on the formulation of mortars. It will consequently be necessary to deal with the problem of the optimal dosage of sediments, that of water due in particular to the fineness of the material ( $D_{50} < 100 \mu\text{m}$ ), but also the durability of the cementitious matrices produced.

The objective of this report is therefore to the treatment of dredged sediments in the sense of their valorization in cementitious matrices. The scientific line adopted is as follows: sediments are properly treated to increase their effectiveness as a mineral addition to improve the mechanical characteristics of mortars or concrete. Physical and chemical modifications about the treatment will be assessed and quantified (shape, texture, reactivity, etc). Finally, it will be a question of assessing the environmental impact matrices produced and aspects related to their durability.

This report aims to establish a synthesis of the scientific and experimental work carried out within the framework of this report. First, it will recall the problem raised earlier, the issues,

as well as the legislative and normative context. Then it will be declined the specifications setting the objectives a bibliographical synthesis relating to the various scientific and technical aspects addressed as well as the application of the treatment methods, and the scientific methodology used (characterization methods). Then, the application of the treatment methods, and to present the materials used and their likely impact. Finally, the conclusion will highlight the strongest results of this work, the contributions of the thesis and the perspectives, thus offering a projection on future research avenues.

# CHAPTER

# 1

## CONTEXTUALIZATION, OBJECTIVES AND METHODOLOGY

---

1.1	INTRODUCTION .....	4
1.2	CHALLENGES AND STRATEGIES.....	6
1.2.1	Environmental and health issues .....	7
1.2.2	Regulatory issues.....	7
1.2.3	Socio-economic issues.....	8
1.3	OBJECTIVES AND METHODOLOGY .....	9
1.4	AIMS OF THIS REPORT .....	9
1.5	METHODOLOGY .....	10
1.6	MATERIALS.....	11
1.7	SEDIMENT TREATMENT.....	12
1.8	FORMULATION .....	12
1.9	CHARACTERIZATION - ANALYSIS AND OPERATION.....	13

---

### **1.1 INTRODUCTION**

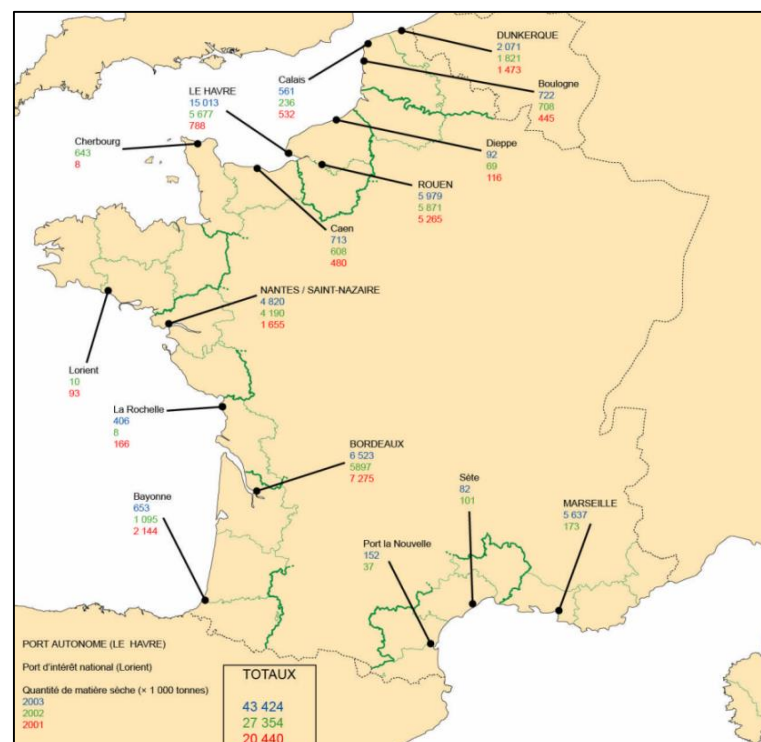
The sediments come from dredging operations on the seabed and rivers in general. These dredging operations are necessary for the smooth flow of people, goods, etc., in France, there are six autonomous ports, the dredging operations generate annually 30% of the 50 million m<sup>3</sup> of dredged material at the national level (see Fig 1.1). Dredging is also carried out in waterways and rivers 25,000 km long. The table below represents a non-exhaustive list of key figures giving an overview of the problem at the European level.

The problem of dredged sediments requires a multi-scale and complex analysis. It requires the use of artificial technical devices, and ecological awareness, in particular by respecting the regulations, but also the socio-economic aspect [\[27\]](#). It should be noted that, within the meaning of article L541-1-1 of the Environment Code, the recovery of waste is relative to the whole operations involving the use of products, materials or substances to a specific application. There are many different issues exist. This is due in particular to the economic, health and environmental impact that can be caused by the management of dredging

sediments. As mentioned above, the aim is to find an efficient socio-economic and environmental agreement between available resources and the current needs (Fig. 1.2).

**Table 1. 1 :** Dredged sediment volumes in Europe (CEDA 1, 2008).

Country	Sediment (Mm <sup>3</sup> )		Totals	
	Marins	Continental	Volumes (Mm <sup>3</sup> )	Rates (%)
Belgium	5	9.2	14.2	7.2
Danemark	4.5	...	4.5	2.27
France	50	6	56	28.5
Germany	41	5	46	23.2
Ireland	0.8	...	0.8	0.4
Italy	4	...	4	2.0
Netherlands	19	9	28	14.1
Portugal	4	...	4	2.0
Spain	...	8.5	8.5	4.3
Sweden	1.38	0.1	1.5	0.7
Great Britain	30	0.7	30.7	15.5
	168.2	30.8	198.2	100
<b>Total</b>	84.9 %	15.1%	100%	



**Figure 1. 1 :** Quantities of dredged material in the various French ports [28].



## 1.2 CHALLENGES AND STRATEGIES

This project aims at finding innovative and sustainable solutions for the valorisation of dredged sediments in civil engineering fields. This is a common desire around which several industrial (Eqiom, Colas, Edf, Neo-Eco, Arf, Boulonnais quarries), regional and administrative (GPMD: large seaport of Dunkerque, the Hauts de France region, Lille métropole), research and institutional (Douai mining school, dreal, vnf: voies navigables de France) partners are working together.

In addition, the use of sediments as a secondary raw material in cement matrices requires several scientific and technical prerequisites. The authors have already widely conducted product characterization studies. Others have studied the treatment of the latter [30] [31] as well as durability [32]. For us, it will be a question of going further in the Physico-chemical characterization, the efficient treatment and the valorization as a mineral additive. Initially, several treatment options will be identified. The mechanical behaviour of mortars based sediment will then be studied.

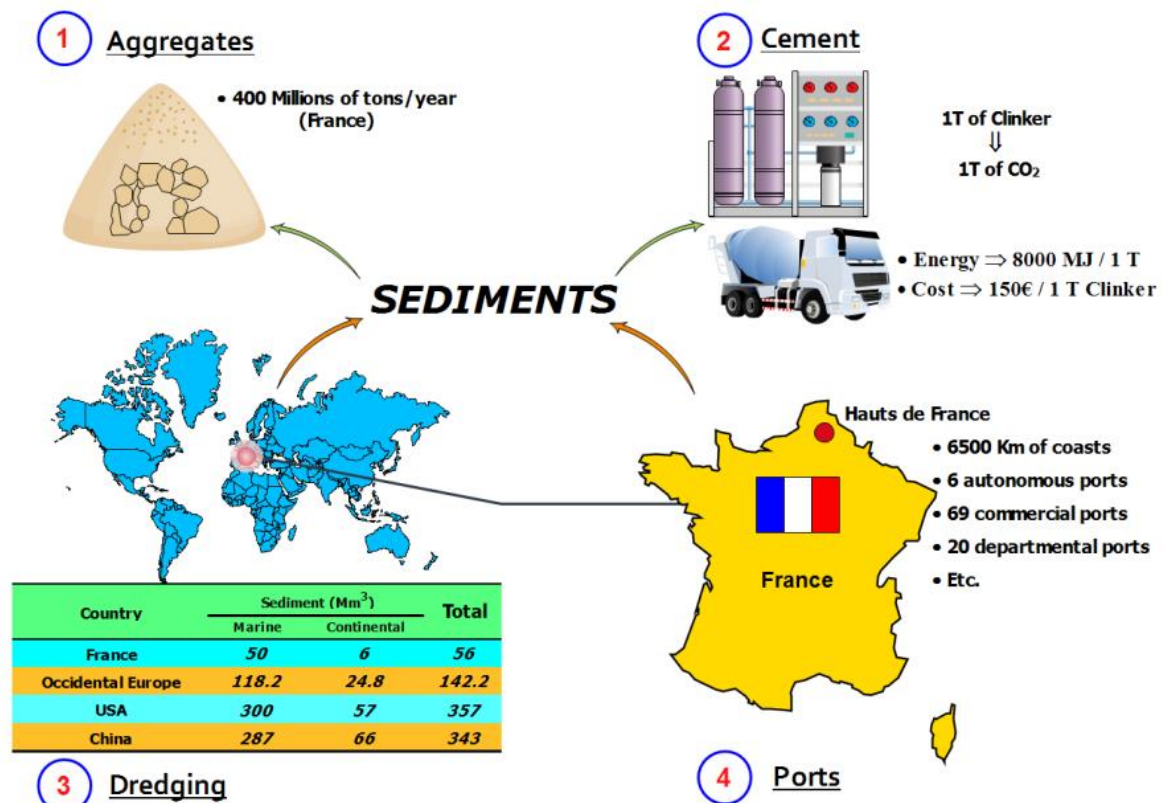


Figure 1. 2 : Diagram of interactions within the framework of the 3Rs principle [33].

### 1.2.1 Environmental and health issues

Sediments from dredging operations are materials that can be considered inert, non-dangerous or dangerous depending on their degree of pollution or toxicity. As a result of a collective awareness of the environment, regulations have gradually emerged. At first sight, sediments, whatever their degree of pollution, are considered a priori as waste to decree n° 2002-540 of 18 April 2002. The axes mentioned below justify the relevance of using sediments as secondary raw material to preserve the environment and natural resources: the environmental weight of civil engineering materials, natural origin of sediments (river bottoms), etc. However, the opening of new quarries in Europe is now subject to very strict regulations, notably through Article R515 of the Environmental Code, which places a very large category of quarries under the heading of installations classified for environmental protection (ICPE). Submerged sediments can also cause many eco-toxicological problems.

Concerning their degree of pollution, sediments can promote dysfunction of aquatic balances which are often fragile. Moreover, it is no less relevant to recall that according to CEREMA, about 91% of the volumes of dredged sediments are immersed in the sea, thus a significant burden for the environment. Finally, it is useful to recall the Grenelle of the environment and the sea, which is part of a synchronised and coherent policy for the implementation of commitments aimed at protecting the environment and enhancing biodiversity. Among the commitments recommended in this national project is the establishment of a strategic framework for the protection of marine environments, in accordance with Article L 219-6 of the Environment Code. There is also the drafting of guides and monitoring databases contributing to the proper management of sediments on land and at sea (geode, meeddm guides, sedimaterials, etc.).

### 1.2.2 Regulatory issues

Under their regular functions, the state and regional authorities are responsible for dredging operations and sediment management. Consequently, within a national and a European legislative framework, many rules of good management have been put in place. The following regulations are worth remembering for this purpose:

- The OsPar Convention (1992): It aims to set guidelines for the protection of the sea in the North Atlantic.
- The Barcelona Convention (1976, amended in 1995): gives guidelines for protection in the Mediterranean area through the application of the principles precaution, polluter-pays, impact studies, interstate cooperation, etc.

- The London Protocol (1996): is an updated version of the so-called London convention and aims to prevent marine pollution.

There are also many measures at both Community and national level. These all aim at the legislator's determination to preserve the environment by implementing protective and preventive measures. They, therefore, govern dredging and dumping operations, according to the common principle of prohibiting elements that hurt the marine ecological balance. These include the following:

- ➡ The Waste Framework Directive 2008/98/EC of 19 November 2008
- ➡ The Marine Strategy Framework Directive 2008/56/EC of 17 June 2008;
- ➡ The Water Framework Directive 2000/60/EC of 23 October 2000
- ➡ Articles L. 214-1 to 6 of the Environment Code
- ➡ Circular No. 2000-62 of 14 June 2000
- ➡ The decree of 9 August 2006 as amended;
- ➡ The H14 protocol of October 1st 2009 [\[34\]](#)
- ➡ The decree of 28 October 2010
- ➡ The decree of 12 March 2012 setting the thresholds for the storage of non-hazardous waste
- ➡ The decree of 10 October 2012 setting the thresholds for the storage of hazardous waste

### 1.2.3 Socio-economic issues

The valorised sediments are likely to be used as granular material for civil engineering applications. This will not be without socio-economic consequences through the development of eco-industrial sectors with high potential. According to Alzieu [\[35\]](#), there are several types of dredging: hydraulic dredging, mechanical dredging, rotodredging, etc. Maintenance dredging is a dredging operation necessary for the proper functioning of ports. The sedimentation process leads to a silting phase making the waterways shallower. This can potentially penalise maritime and river activity; and also pose a public health threat (flooding, floods, etc.). Due to restrictions on salting-out or storage operations, sediment treatment systems are now at the research or exploitation stage. Ramaroson [\[31\]](#) cited the following methods: desorption, pyrolysis, incineration, etc. Other methods include cycloning,

bioleaching, phosphatization and calcination, etc [30]. These processes can represent a significant economic burden.

It is also necessary to note the various channels of sediment valorization, namely: applications in road engineering [36] [37], they have also been used for the realization of bricks [38], also in the formulation of concretes and mortars [39]. In these sectors, sediment is used as a partial substitute for cement and/or sand and therefore appears to play an important role from an economic point of view. As an example, optimization tools such as the operational optimization software developed within the framework of an inter-European project called Prisma [40] can also be mentioned. The latter brings together several actors, aims in the context of sediment recovery, to set up management and economic optimisation tools: from dredging to effective recovery.

### 1.3 OBJECTIVES AND METHODOLOGY

The purpose of dredged sediments, considered in many regulations as waste is a major problem. Both environmental issues (pollution), economic (saturation of waterways) but also safety (floods). Among the avenues being explored is the recovery of dredged sediment in the construction industry. Our study will, therefore, focus on the mechanical and environmental characterization of cementitious matrices based on sediments. Which, by the way, is a sort of propaedeutic because of the mechanical aspect, as we conceive it, has been very little addressed by previous authors.

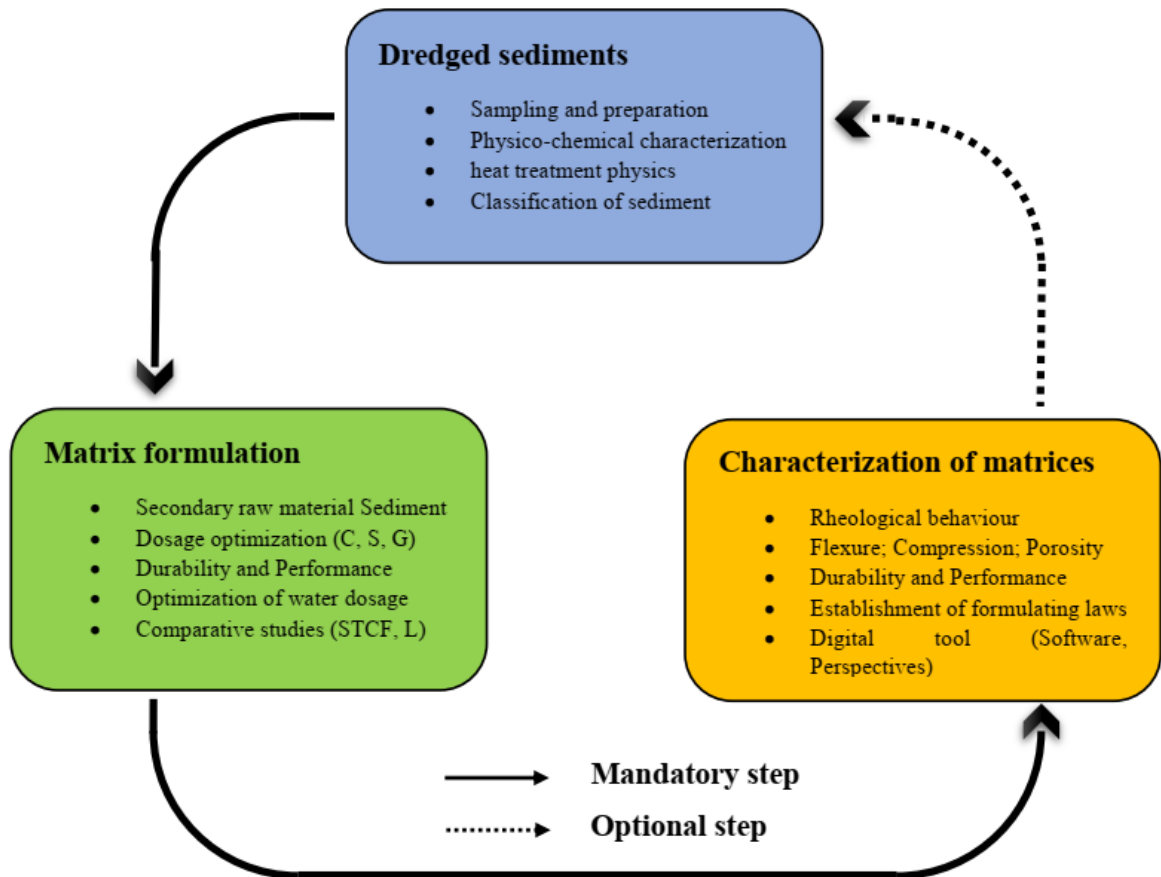
To achieve the expected objective, the scientific approach adopted will be based on the following three components: A theoretical phase, an experimental phase and consolidation by validation.

### 1.4 AIMS OF THIS REPORT

The overall objective of our work is the treatment and valorization of dredged sediments as secondary raw material in cementitious materials. To effectively achieve this aim, it will be necessary to consider multiple parameters. These parameters include the initial physicochemical characteristics of the sediment, the implementation of suitable treatment processes, the effective recovery of sediments in cementitious materials, particularly by quantifying the activity (pozzolanicity), the mechanical strength of the mortars produced, and finally, taking into account the environmental aspect.

## 1.5 METHODOLOGY

The working methodology adopted is described in the diagram below (Fig1.3). It is articulated on three axes: materials, formulation and characterization.



**Figure 1. 3 :** Methodological scheme of work adopted.

C=cement; S=sand; G=aggregate; STF=dredged sediment; L=slag.

The characterization of materials in general and sediments, in particular, is carried out according to the methodological approach detailed in Figure 1.4. This makes it possible to determine the main characteristics of the materials to better identify their likely impact when used as additions in cementitious matrices.

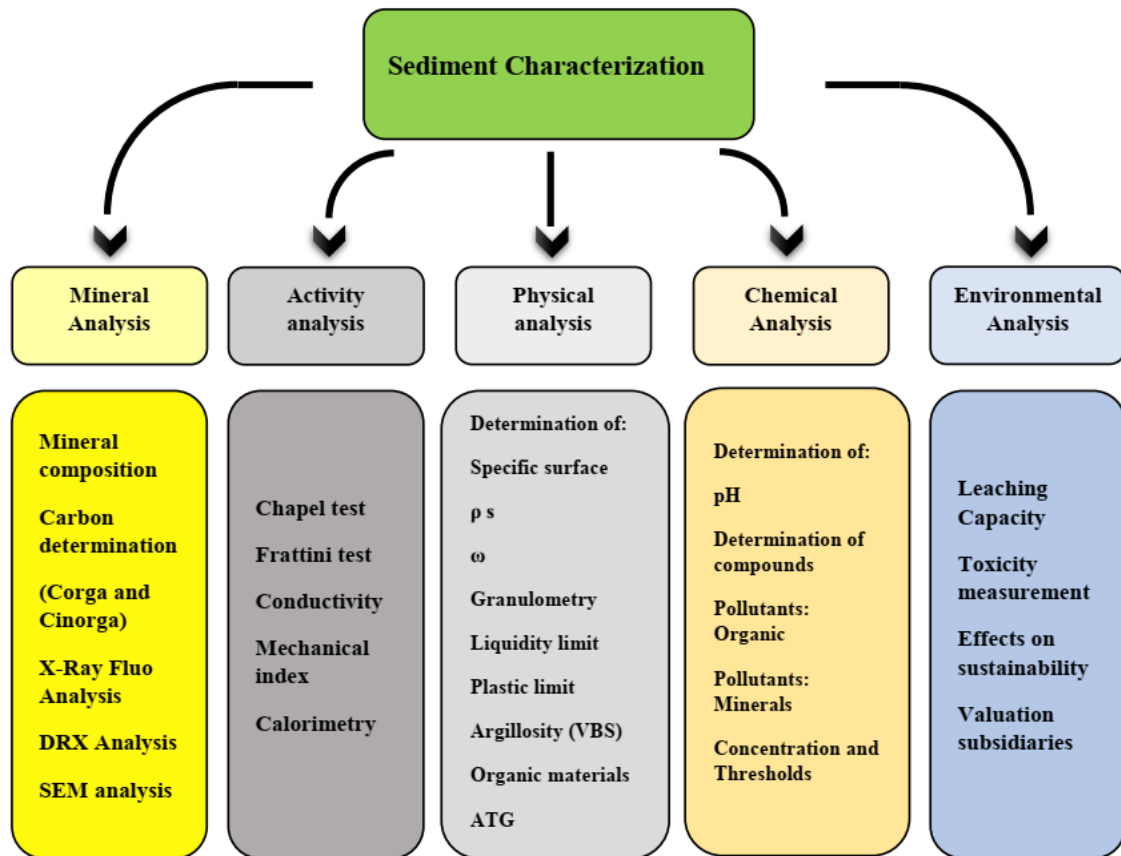


Figure 1. 4 : Methodological scheme (non-exhaustive) for sediment characterization.

## 1.6 MATERIALS

The valorisation of industrial by-products is at the heart of the research themes at the Civil and Environmental Engineering Department of the ITM Lille Douai (formerly the École des Mines de Douai). Our research studies have been exclusively oriented towards the valorisation of dredged sediments in the manufacture of mortars and/or concretes. The design of a concrete necessarily induces aggregates of various sizes and morphology. Regarding the granular composition is concerned, we will then have sediments, sand and incidentally mineral additions such as limestone fillers, silica fumes, metakaolin, crushed quartz, etc. The dredged sediments used are then subjected or not to an upstream treatment. In the present study, standard sand of siliceous nature, with rounded grains and a diameter of the largest aggregate of less than 2 mm ( $D_{max} = 2 \text{ mm}$ ) was used. Its silica content is at least 98%. For reasons of adequacy as well as its "standard" characteristics, we choose to work with a CEM I 52,5N cement (Eqiom usine d'Obourg) since it can be used for all types of mortars or concretes with high medium and short term strengths. This cement has a clinker content of 95% and a setting time of less than 4 hours. Also, its medium-high heat of hydration and low

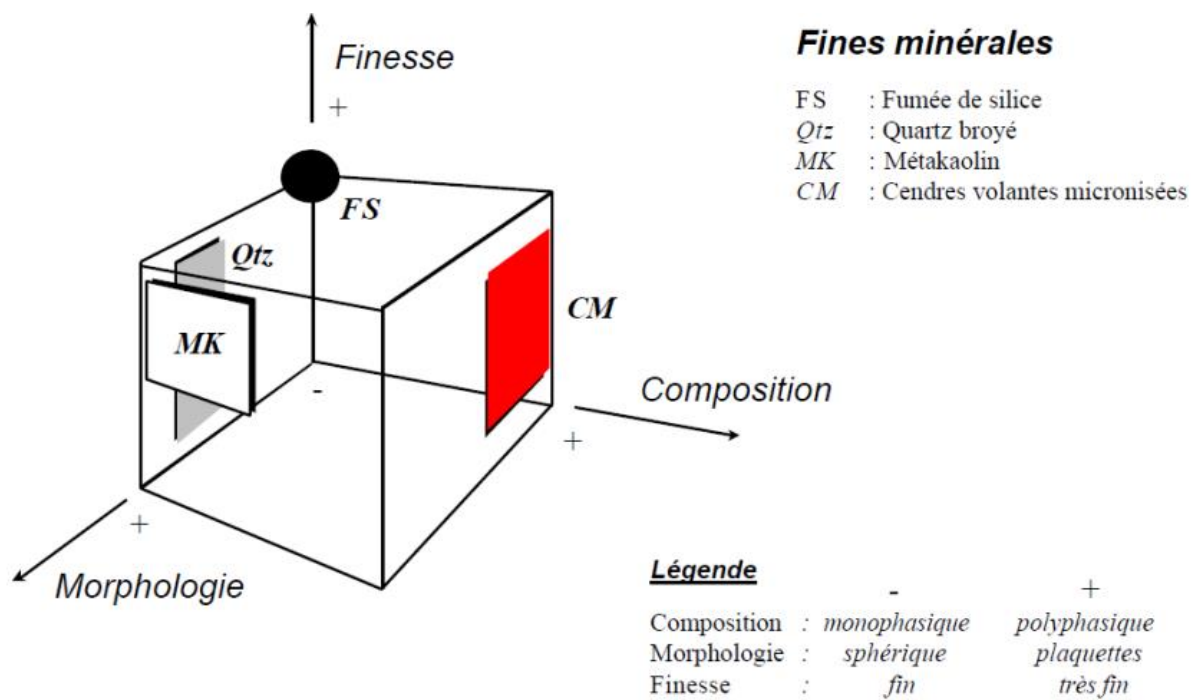
water demand (30%) is suitable since the presence of sediments may generate additional heat and water demand 4.2.4.

## 1.7 SEDIMENT TREATMENT

The sediments used in cementitious matrices are either raw or treated state. The treatments envisaged are the physical route by optimising the grinding and separation processes. But also thermal by exposing the product to high temperatures ( $> 600^{\circ}\text{C}$ ). These treatments aim to improve Physico-chemical characteristics such as the water demand, the ability to react in the presence of lime (pozzolanic character), the elimination of the organic fraction or the various pollutants present.

## 1.8 FORMULATION

The objective of this work is to formulate mortars based on recovered materials. As soon as the sediments are fine materials, high water demanders, the prior implementation of a test campaign to determine the water demand is necessary. These tests will be the homogeneous paste or smooth paste test introduced by Sedran [41] or the normal paste test [42], or by evapometry. These methods determine the characteristics in the fresh state as well as the optimum quantity of water for which the consistency of the mixture will be judged to be correct. Aiming to formulate composite and porous materials such as concrete, it seemed relevant to us to focus on the main theories of compactness of granular materials. These theories aim to determine the optimal proportions of the different constituents. It will be possible to form a granular skeleton as compact as possible by optimizing the particle size curve and thus optimize the important parameters (compactness, strength, durability, etc.). I would cite as an example the Feret method (1897), the Abrams method (1920), the Bolomey method (1925) [43] [44] [45], the Dreux-Gorisse method [46], etc. Depending on the case, certain important parameters such as the water/binder ratio (W/B), the substitution rate (p(%)), the maturation time, etc., will be varied. But also the nature of the sediment used and the type of cement will be taken into account. This will enable objective formulation laws to be derived, adapted to cementitious matrices based on sediment as a mineral addition. The influence of the addition on the matrix is taken into account by considering influential parameters such as morphology, fineness, composition, etc. (Fig 1.5).



**Figure 1. 5 :** Important criteria in the selection of a mineral addition [47].

## 1.9 CHARACTERIZATION - ANALYSIS AND OPERATION

Methods for quantifying the pozzolanic character of sediments will be used in this work. These methods will be based on physicochemical analyses. These include the method for measuring electrical conductivity (Luxan et al.) [48] [49] [50], the Chapelle test [51][52][53], the chemical method of the relative test to NF EN196-5:(2013) [54][55][56], or the method for determining the modified mechanical activity index [43]. As part of our studies, the prepared specimens undergo a battery of tests for consistent mechanical characterization. These tests concern strength measurements, determination of physical characteristics (modulus, porosity, etc).



# CHAPTER 2

## DREDGED SEDIMENTS AND CEMENTITIOUS MATRICES

2.1	DREDGED SEDIMENTS .....	14
2.1.1	Definition.....	14
2.1.2	Origin.....	15
2.1.3	General composition.....	16
2.1.4	Particle size composition .....	17
2.1.5	The fine fraction - Clay fraction .....	17
2.1.6	Water .....	19
2.1.7	Pollutants .....	20
2.1.8	Organic Matter.....	22
2.1.9	Pretreatment and Treatment.....	24
2.1.10	Chemical methods .....	32
2.1.11	Sediment Regulations .....	33
2.2	CEMENTITIOUS MATERIALS .....	40
2.2.1	Cement and its manufacture .....	40
2.2.2	Cement Hydration .....	41
2.2.3	Porosity in Cementitious Matrices .....	46
2.2.4	The matrix-aggregate interface.....	48
2.3	CONCLUSION.....	50

### **2.1 DREDGED SEDIMENTS**

#### **2.1.1 Definition**

Sediments are commonly referred to as mud related to fine materials. The sediments are often of a clay-limestone nature with high contents of organic elements and water, which is why they are sometimes referred to as sludge. According to Boutin [57], sediments can be defined as fine mineral particles with a few small rock elements to which plant or animal debris is mixed. It will be seen later on that neither this fine nature nor the possible natural cementation between the particles will be without consequences, once used in cementitious matrices.

For Beauchamp [58], sediments can be defined as fine materials resulting from continental wear. These actions of wear are either physical (fragmentation) or chemical (leaching) in nature, followed by transport and deposition by a carrier fluid. Finally, the universal

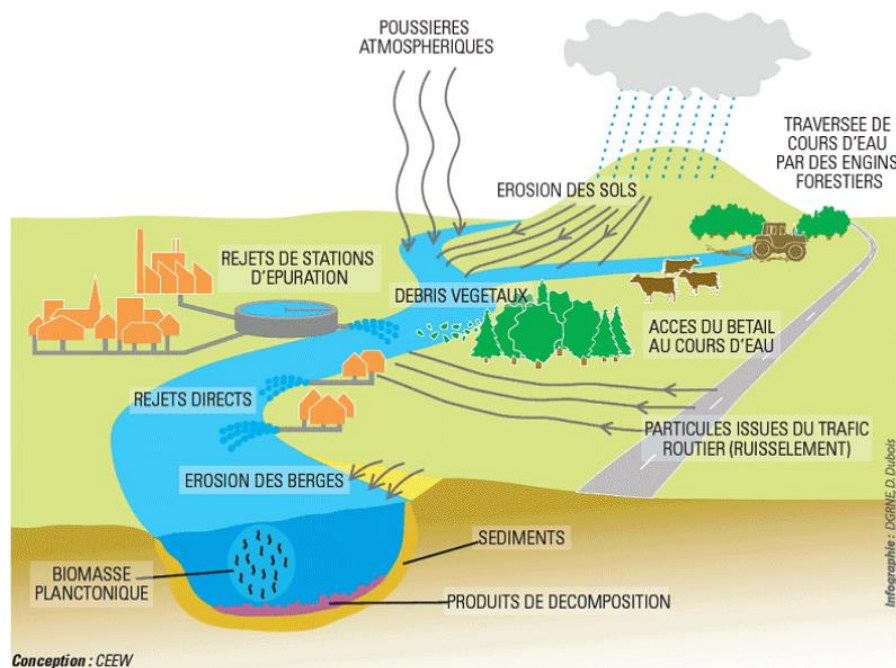
encyclopaedia describes sediments as the products of sedimentary phenomena relating to "current phenomena" on the surface of continents, on the sea bed.

### 2.1.2 Origin

Sediments can have different characteristics depending on their nature, morphology and their origin, but are in any case the result from deposit phenomena. In geological jargon, a distinction is made between sediments of endogenous or exogenous origin according to Schneider [59]. By endogenous, we must understand sediments whose origin is internal to the environment. These are generally animal or plant debris (macrophyte debris).

However, the exogenous origin is the product of an external contribution to the immediately neighbouring environment. For this, a flow of a fluid (water or air) (Fig. 1.6), ensures the transport of naturally occurring materials (soil erosion, decomposition of plant matter), or anthropogenic (input of materials, industrial discharges, etc.). Another proposed description by Beauchamp [58] defines according to the physical or chemical origin. He distinguishes as follows:

- detrital sedimentary rocks resulting from the destruction of rocks or organisms: gravel, sand, sandstone;
- Chemical sedimentary rocks resulting from the precipitation of bodies dissolved in water: rock salt, potash (saline rock based on  $K_2CO_3$ ), limestone tuffs, flint;
- Biochemical sedimentary rocks resulting from the synthetic activity of organisms: coals, continental limestone tuff (continental limestone rock).



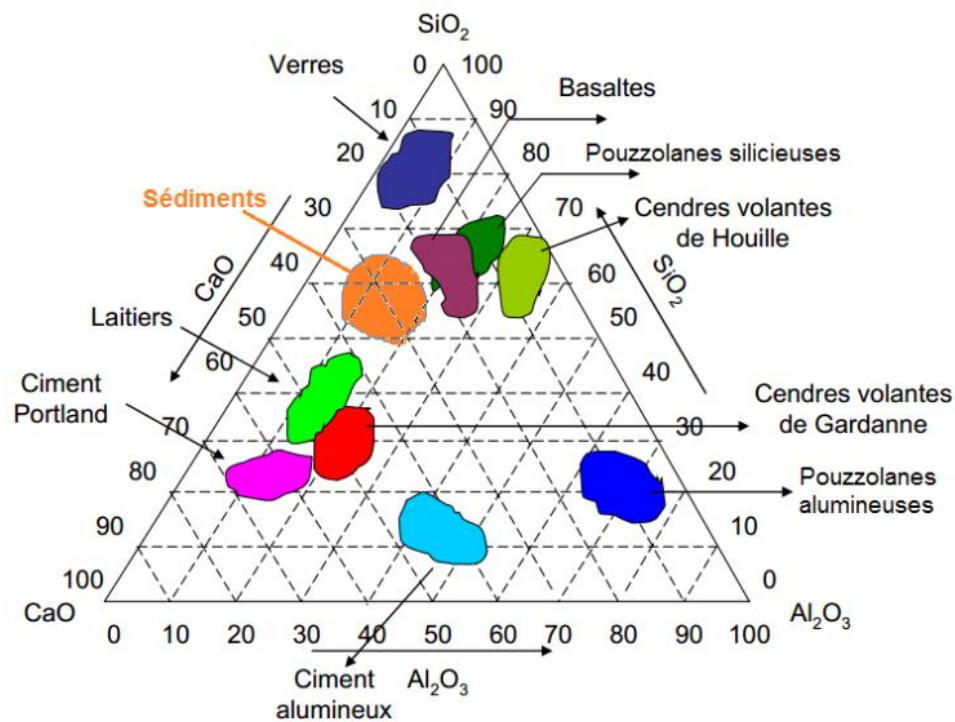
**Figure 1.6:** Origin of marine or river sediments [60].

### 2.1.3 General composition

For Schneider [59], sediment is essentially characterized by:

- its granulometry;
- it is mineral composition;
- it is content of water, organic matter and various elements (heavy metals, pollutants and organic micropollutants).

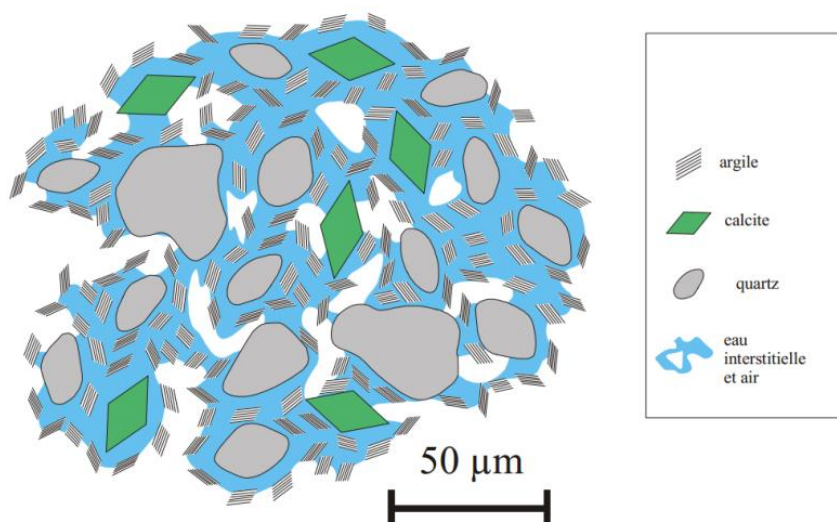
The smallest fractions in sediment are responsible for many properties. These fractions called "fine" are commonly accepted as corresponding to the phase below 63  $\mu\text{m}$ .



**Figure 1.7:** Sediment classification in the Keil-Rankine diagram.

It is interesting to use a so-called ternary diagram of fine soils (Fig 1.7) to appreciate certain characteristics. These relate the following characteristics [61] (Fig. 1.8).

- Mineral matrix (quartz, feldspars or carbonates);
- Clay, a fraction less than 2 $\mu\text{m}$  (kaolinite, montmorillonite, illite or smectite);
- Organic fraction (plant debris, microorganisms, humin, fulvic and humic acids);
- Relatively high water content, presence of organic and mineral pollutants.



**Figure 1.8:** Structure of silty-clay soils [62].

#### 2.1.4 Particle size composition

The raw sediments studied are composed of mineral particles with a diameter  $D_{max} < 300 \mu m$ . Dubois [6] and Trinh [37] have already established that sediments from GPMD are essentially clayey-silt or even sandy in places. Particle size plays a major role in the contaminant fixing capacity and treatability. Gosselin et al [63] have already conducted a particle size study of sediments in Hamburg and Montreal. It was shown that contamination of the coarse fraction was almost null, while the fine fraction ( $645 \mu m$ ) accumulated more than 70% of the contaminants.

This point will be discussed more fully below.

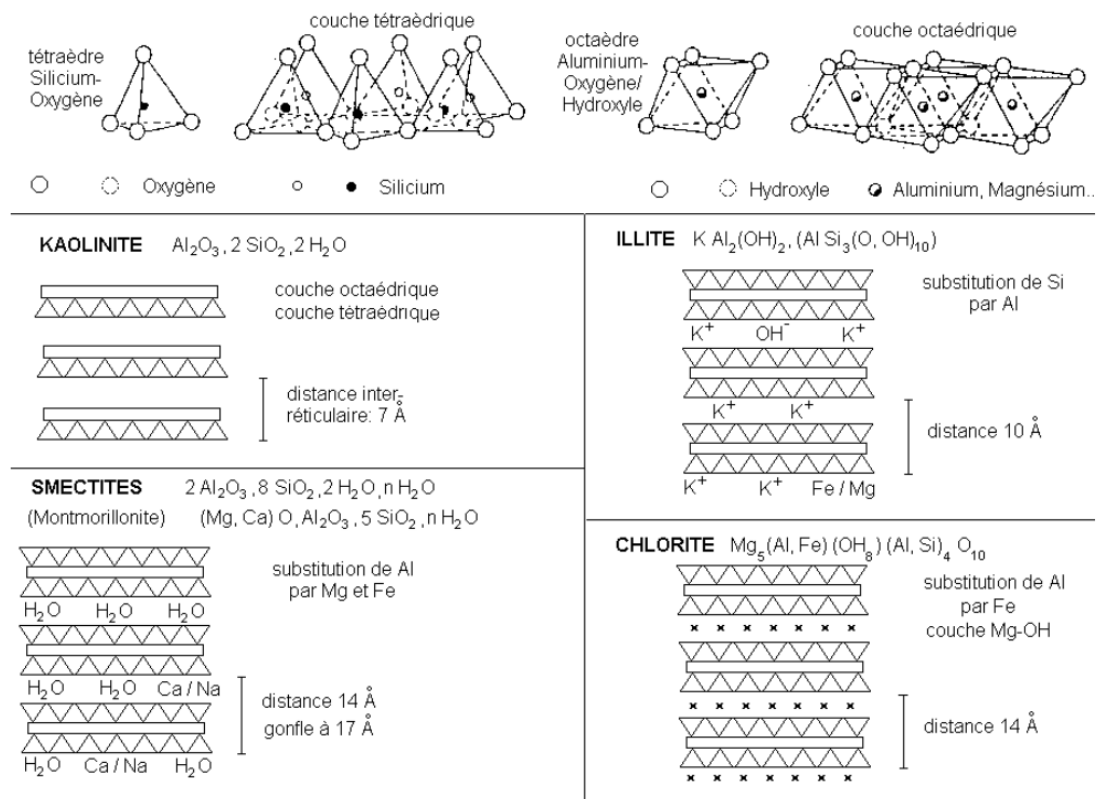
#### 2.1.5 The fine fraction - Clay fraction

As for the clay fraction, it is often the site of multiple Physico-chemical phenomena. Due to their layered structure, clays can fix water or microparticles. Also, clays are made up of hydrated calcium silicate molecules (Fig 2.4) with a phyllite morphology (in sheets: kaolinite, illite, smectite, chlorite, etc.) or fibrous (sepiolite, attapulgite, paligorskite, etc.).

For the first group, the structure is in the form of sheets (Fig. 1.9) composed of two basic units: the silica tetrahedron and the alumina octahedron [64] [65]. Each basic unit (particle) is the smallest typical stack of sheets that can be isolated in the laboratory. It consists of the superposition of a variable number of these sheets, their number being a function of the interaction forces. This property, called hygrophyllisis, is at the origin of the massive capture of water from the clays, with sometimes a relatively important swelling phenomenon. This is why, at the beginning of our studies, we conducted a series of tests evaluating the water

demand of sediments. Clays can also be characterized by thixotropic properties. That is to say, their capacity for destructuring or even liquefaction under mechanical stress.

Due to their fineness and electronegativity, charge exchanges can take place in particular in the presence of heavy metal ions. This results in an isomorphic substitution of the cations  $Al^{3+}$  and  $Si^{4+}$  take place, which is replaced by ions of lower valence [64] [65]. It is thus by a phenomenon of adsorption that sediments can capture, retain and accumulate contaminants which will serve to partially compensate for the default of charge. In addition to the Physico-chemical properties of the material, cationic exchange capacity is all the more important since cation is small [30].



**Figure 1.9:** The different structures of clay minerals [58].

Finally, one of the important properties of clays is its ability to develop pozzolanic properties. That is to say their capacity to react to form hydrates in the presence of lime  $Ca(OH)_2$  or  $CaO$ . For this, heat treatment may often be necessary [66]. San Nicolas [17] has already worked on Kaolins, which after adequate heat treatment developed pozzolanic properties similar to hydraulic cement, or even better. Some fine sediments with weakly crystallised clays may show relatively high pozzolanic activity [18]. Other experimental methods will be explained in section 4.1. In the context of their use in cementitious matrices, the work of Le Roux and Unikowski [64] [65] had earlier established the following four properties:

1. Water absorption: due to the sheet structure;
2. Screen effect: Clay grains at the matrix-aggregate interfaces can prevent bonding;
3. Pozzolanic effect: Development of hydrates in the presence of lime;
4. Action on compactness: Optimization of granular compactness.

### 2.1.6 Water

Sediments are materials strongly characterized by their relatively high water content. This exists in different forms inside the materials. The water content calculated based on dry mass is given by the formula below:

$$\omega = M_w/M_s \quad (2.1)$$

$M_w$ = Mass of water present.

$M_s$ = Mass of the solid fraction.

Depending on its degree of bonding with the material, water is available at different levels in the material. Four categories should generally be distinguished:

- 1) Free water is water filling the macroporosities of the soil. It is free to infiltrate and percolate under the action of gravity. It can be eliminated by a simple decanting.
- 2) Capillary water is present in the microporosities in the middle. The intercapillary forces of the order of  $\approx 12$  atm indispose this water to gravitation by the law of Jurin
4. However, it is accessible by evaporation or suction. The thickness of the capillary fringe varies in inverse ratio to the particle size.
- 3) Bound water is fixed to the surface of soil grains by intermolecular forces. It includes two categories:
  - "Hygroscopic" water or also "adsorbed water", which adheres directly to the grain and can only be extracted by the desiccation or a high vacuum.
  - The so-called "film water" adheres to the hygroscopic water (see Fig.1.10). Moreover, bound water cannot move under the effect of gravity and does not transmit hydrostatic pressures.
- 4) The constituent water or chemically bound water enters the chemical composition of the material. It is only accessible through advanced thermal processes.



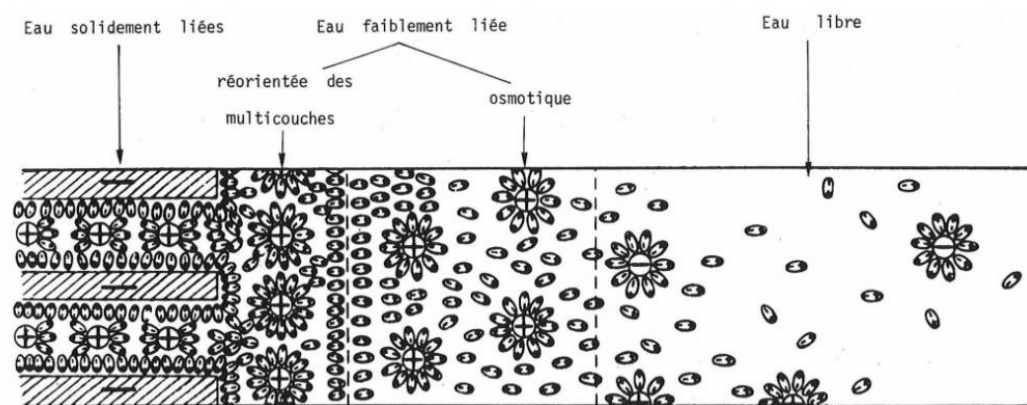


Figure 1.10: Soil water categories [65].

## 2.1.7 Pollutants

### 2.1.7.1 Mineral Pollutants

As soon as the emergence of methods for the valorization of materials such as sediments, the problem of contaminants has arisen. A fortiori, due to their fine nature, the presence of organic matter and microbiological activity, sediments tend to store substances, some of which are highly toxic: heavy metals, polyaromatic hydrocarbons (PAHs), organochlorines (OCs), organotins (OBT), pesticides and various biocides [35]. For Mac Farlane [67], the origin of this pollution is, among other things, the fallout from industrial activities, air pollution, household waste, etc.

The main Physico-chemical properties of sediments that control the interactions between dredged sediment and contaminants are according to Alzieu [35]:

- the quantity and type of fine particles (pelites);
- the pH of the medium;
- the redox potential;
- the quantity and nature of the ions present;
- the composition of organic matter (especially humic acids);
- salinity.

Schneider [59] suggests that some of these materials are carcinogenic and mutagenic. Among them, mercury (Hg effects on kidney teratogen), lead (Pb intelligence retardation), Arsenic (As skin cancer) and cadmium (Cd accumulation in the renal cortex) are the most toxic for human health [35]. The presence of many of these mineral pollutants is not without effect on

the proper formation of the cement matrix. The specific effects of Zinc (Zn), Copper (Cu) or Lead (Pb) will be particularly presented in section 4.2.6.

### 2.1.7.2 *Organic Pollutants*

#### 2.1.7.2.1 *Tributyltin (TBT)*

TBT or tributyltin (TBT) is used as an active ingredient in antifouling paints. These types of paint are used to protect ships against the attachment of living organisms to their hulls. These paints diffuse about  $5 \mu\text{g}/\text{cm}^2/\text{day}$  due to parking and maintenance operations [35]. In sediments, TBT is part of the family of organotin compounds and can exist in 02 different degraded organic forms: monobutyltin (MBT) and dibutyltin (DBT). However, TBT is a molecule degradable by photolytic or microbiological action and is stable because its half-life can be up to 19 years according to studies in mesocosms. Finally, (TBT) can have negative impacts on living marine organisms and humans. One example is imposex in molluscs, corresponding to a possible modification of their sexuality. We can also mention the influence on the calcification of certain oysters, growth problems as well as fish reproduction problems [35].

#### 2.1.7.2.2 *Polychlorinated biphenyls (PCBs)*

Polychlorinated biphenyls are a family of organochlorinated compounds with the chemical formula  $\text{C}_{10}\text{H}_{10-n}\text{Cl}_n$  and grouping not less than 209 congeners (based on the number of chlorine atoms). It is important to note that PCBs are used as additives in paints, inks and have the following properties: semi-volatile, hydrophobic and persistent compounds [35]. PCBs are derived from urban waste, landfills of used materials and its presence in dredged sediments and accentuated by the fineness and presence of organic matter [61]. Their toxicity has been proven to be the cause of many anomalies in living beings: hepatic hypertrophy, carcinogenic effects, chloro-acne, alteration of reproductive functions, etc [35]. Cases of gene mutations have been observed in the wrist strap by Alzieu [35].

#### 2.1.7.2.3 *Polycyclic aromatic hydrocarbons (PAHs)*

Polycyclic aromatic hydrocarbons (PAHs) are aromatic rings associated with carbon atoms [61] [35]. For Neff, they could originate from:

- secretion by living organisms (biosynthesis);
- the use of fossil fuels such as petroleum and its derivatives (petrol, diesel, etc.) or coal;



- pyrolysis of organic matter at high temperatures, forest fires, combustion of coals and oils.

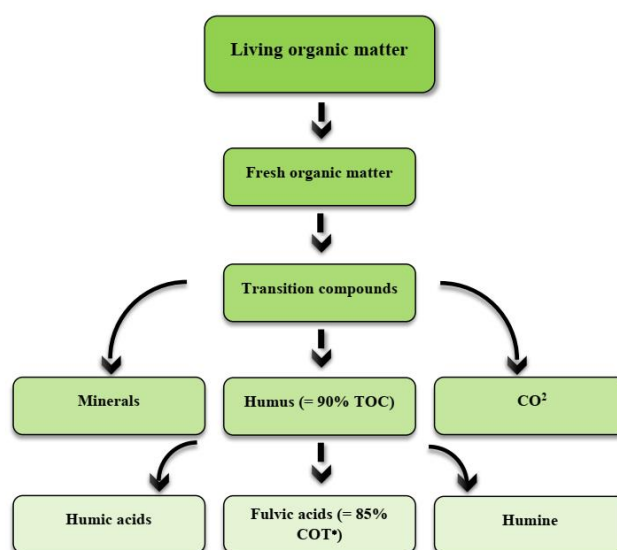
PAH can accumulate in the sediment due to their lipophilic properties depending on the levels encountered. Baumard [68] has already identified total PAH levels of up to 20 µg/g in Ajaccio harbour sediments. Finally, PAH can have an ecotoxicological effect and affect the cellular mechanisms of living organisms. In particular, they can cause carcinogenic or mutagenic anomalies, especially for mammals. We can cite these 16 molecules declared toxic by the Environment Protection Agency" in the United States (naphthalene, acenaphthylene, dufluorene, phenanthrene, etc).

## 2.1.8 Organic Matter

### 2.1.8.1 Composition

The organic matter present in the sediment has a mineral or vegetable origin. They are the result of the alteration of living organisms degraded and then transported and deposited by water or air. In sediments from flowing rivers, the organic fraction represents 2% to 10% [59]. Its presence confers specific properties to the sediment in terms of texture (organic matter can be sensitive to touch or visible) and colour (black or grey colour) or even scent. Mustin [69] has already proposed a categorisation of organic matter into 4 classes:

- active or living organic matter (active biomass);
- organic matter called fresh (plants, animal debris, excrement, etc.);
- evolutionary organic complexes called transient;
- stable organic compounds (mineral or organic).



**Figure 1.11:** Main evolutionary phases of organic matter [69].

In the case of sediments, it seems appropriate to recall the following definition proposed by Trinh [37], which divides organic matter in sediments into two categories:

- a) Non-humic substances: consisting of simple mineral compounds;
- b) Humic substances: consisting of organic macromolecules of natural origin and representing up to 90% of the total organic fraction according to Colin [36].

Humus is made up of 03 phases in continuous transformation:

- 1) Humic acids were insoluble in acids but soluble in bases. They are made up of very thin and flat layers linked together, forming a spongy reticular material.
- 2) Fulvic acids are soluble in acids and bases and constitute 85% of the total organic carbon [70].
- 3) Humin, which is insoluble in acids and humic substances and interacts with the solid or dissolved mineral fraction. This induces the formation of complexes or conglomerates. It is then formed by organo-mineral associations, namely:
  - a) by physisorption: inducing the agglomeration of particles;
  - b) by mixed complexation forming metal cations known as humates or fulvates more or less soluble in a liquid medium [70].

Humic substances are organic complexes consisting of phenolic or benzene carboxylic compounds (50% to 70%), and peptide and polysaccharide chains (30% to 50%) [30].

**Table 1. 2:** Proportions of chemical elements in organic matter [37].

Elements	Acide humique [%]	Fulvic acid [%]
Carbon	≈ 55	≈ 45
Oxygen	≈ 34	≈ 45
Hydrogen	≈ 4,5	≈ 5,4
Nitrogen	≈ 2,5	≈ 2,1
Sulfur	≈ 0,8	≈ 1,9

### 2.1.8.2 *Properties of humic substances*

**Colour:** The black colour of the sediment can be attributed to the organic fraction decomposed or in the transient decomposition phase.

**Water:** Organic matter can contain up to 20 times its weight [30] due in particular to humic acid, which can retain up to 16 times its weight in water. This phenomenon can also be amplified by the formation of argilohumic or limono-humic complexes. This delays drying and water penetration into the sediment and amplifies the presence of contaminants [6].

**Biological activity:** The presence of organic matter is at the origin of multiple processes of degradation, growth and mineralization. Organic matter also stimulates biological activity through aeration, supply and transfer phenomena. In marine sediments, in particular, there are certain micro-algae that produce toxins such as ichthyotoxins, deadly for certain phytoplankton organisms. Diarrhoeal DSP or paralytic PSP toxins can also be produced [35].

## 2.1.9 Pretreatment and Treatment

The management of dredged sediments is based on technical, socio-economic and environmental challenges and issues. Consequently, pre-treatment and treatment processes have been put in place. Furthermore, the treatment of dredged sediments can have various and multiple objectives for valorization purposes. These objectives may be to destroy, extract, immobilize or neutralize contaminants, the organic fraction, the complexing of pollutants, etc. [61].

### 2.1.9.1 *Pretreatment*

Pre-treatment is the initial procedure for valorisation. Pre-processing operations have several interests. Pre-treatment operations aim to reduce the volume of sediment to be treated by optimising recyclable volumes, to reduce the water content for ease of transport and storage, the pellet nature of the material, etc.

Existing pre-treatment techniques are [61]:

- Separation: Attrition technique, separation tank, coagulation / flocculation, screening, etc;
- Dehydration: basin lagooning (gpmd), evaporation, geopolymer fabrics, etc.

The active lagoon technique is used for the GPMD sediments. This technique mainly concerns dredged material extracted by hydraulic dredges. At the end of the process, dryness levels of up to 65% are reached, which facilitates transport and disposal [61].

In the GPMD, dredged sediments that cannot be submerged are stored in a managed area. This area consists of lagoons basins where the sediments are initially placed in settling basins to optimize drying [61].

### 2.1.9.2 *Treatment*

The implementation of environmental policies requires the development of efficient treatment processes. These processes aim to improve specific properties or neutralize pollutants. These treatment techniques are differentiated by their means of implementation, their efficiency, their interests, the limits and the costs.

Marot [70] proposes the following typology of treatment techniques:

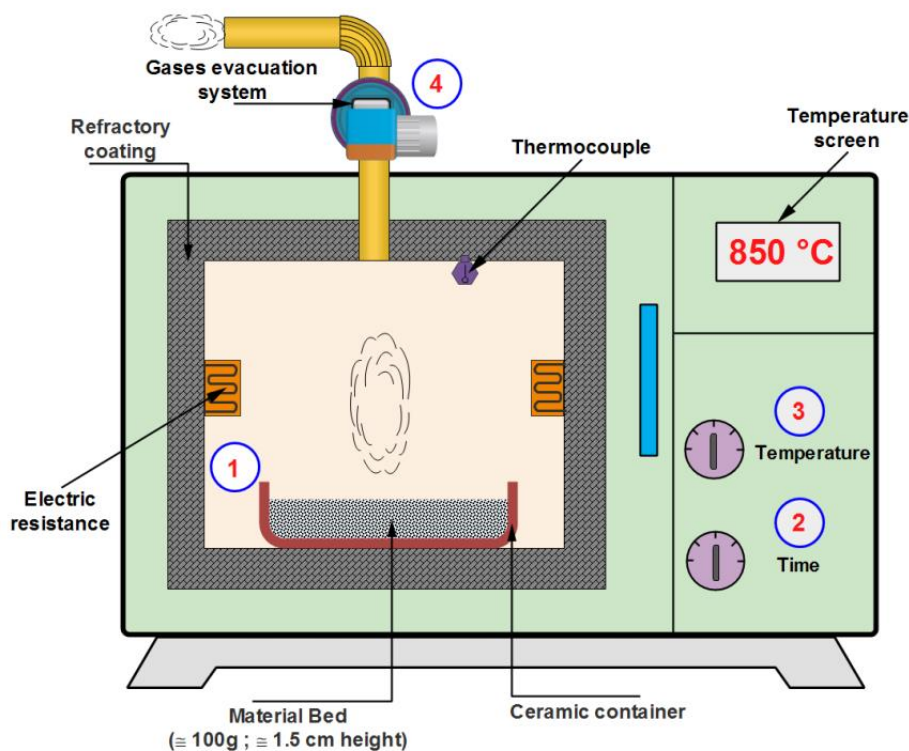
- **physical treatments** (flotation, vacuum extraction, ...), uses physical properties such as gravity or interparticle attraction;
- **mechanical treatments** (filter press, vacuum filter . . .);
- **Chemical treatments:** by adding a chemical oxidant to promote an elimination reaction (e.g. hydrogen peroxide  $H_2O_2$ );
- **Physico-chemical treatments** (phosphating, acidification, dechlorination, leaching, etc.), which, by mixing with chemical agents or sending an electric current, attract and separate polluted particles, etc. There is, for example, the process Novosol™ process using phosphating (stabilization) + calcination. This technique is also an industrialized technique. Treating sediments with a water content of 50% with this process costs about 70€/t [13].
- **Biological treatments** (bioremediation, phytoremediation, Sesatec™, bioreactor, composting, Rotamix™): use of living organisms such as bacteria, fungi, algae, enzymes, etc; to precipitate the biodegradation of organic pollutants such as hap or oils;
- **thermal treatments** (thermal desorption, incineration, vitrification, pyrolysis, oxidation), a process aimed at the total or partial disintegration of organic matter at high temperatures (600°C - 1200°C);
- **solidification stabilization** consists of adding a hydraulic binder such as cement, lime, pozzolans, or clay, or at low temperature (110°C - 150°C) using organic binders (bitumen), then stabilization after moulding [61].

In our studies, particular attention is paid to thermal treatments and physical methods of optimizing fineness by grinding.

### 2.1.9.3 Heat treatment by direct calcination

Incineration or calcination of dredged material is a thermal method used for sediment treatment. It consists of high-temperature calcination of  $600^{\circ}\text{C}$  –  $1200^{\circ}\text{C}$  to completely remove both organic contaminants and all water present, but also to render certain metallic pollutants inert. Its cost can be estimated at 40 to 120 €/T of MS [61].

A series of mortars based on raw sediments and another series of sediments treated by calcination will be used in our further studies. Those who have been undergone treated according to a protocol that can be described as shown in Figure 1.12:



**Figure 1.12:** Traditional calcination unit (AMAR Thesis, 2017).

#### 2.1.9.3.1 Steps in the process

The treatment is carried out using a static laboratory oven. This system, which remains immobile, nevertheless favours the formation of a bed of particles that often glued by sintering. It is then necessary to separate them by a secondary grinding. In the cement industry, for example, the kilns used are rotary kilns ovens 60 to 90m long and 4 to 5m in diameter. These ovens rotate around their axis of revolution allowing a more homogenous and

uniform firing of the material but still require consequent preheating and cooling times. These types of ovens are not used in our studies. The steps in the proposed process are as follows:

- 1) Steaming at 40 °C for 24 hours is done on the materials in advance to determine their initial organic matter content (NF P94-050:(1995)) and also to eliminate the water present. This choice also avoids the possible influence of steaming at 105 °C.
- 2) The products are ground (separation) using an automatic RETSCH type RS200 grinder initially set at 1000 r/min for 2 min or using a jaw crusher equipped with a sieve at its base. This then allows a fine product to be obtained (maximum aggregate diameter  $D_{max} \leq 100\mu m$  can be reached) and a granulometry controlled in this way.
- 3) Determining amounts of sediment are prepared, weighed and introduced into a preheated oven to an adequate temperature T (e.g. 750 °C). Firing is expected to vary between  $t = 1$  and 3 hours. The optimization of the choice of these two parameters will be discussed in section 4.2.5.
- 4) The baked product undergoes a secondary separation process by carrying out a secondary grinding aimed solely at dissociating the agglomerated grains during sintering.

The proposed methodology is described in Fig 1.12:

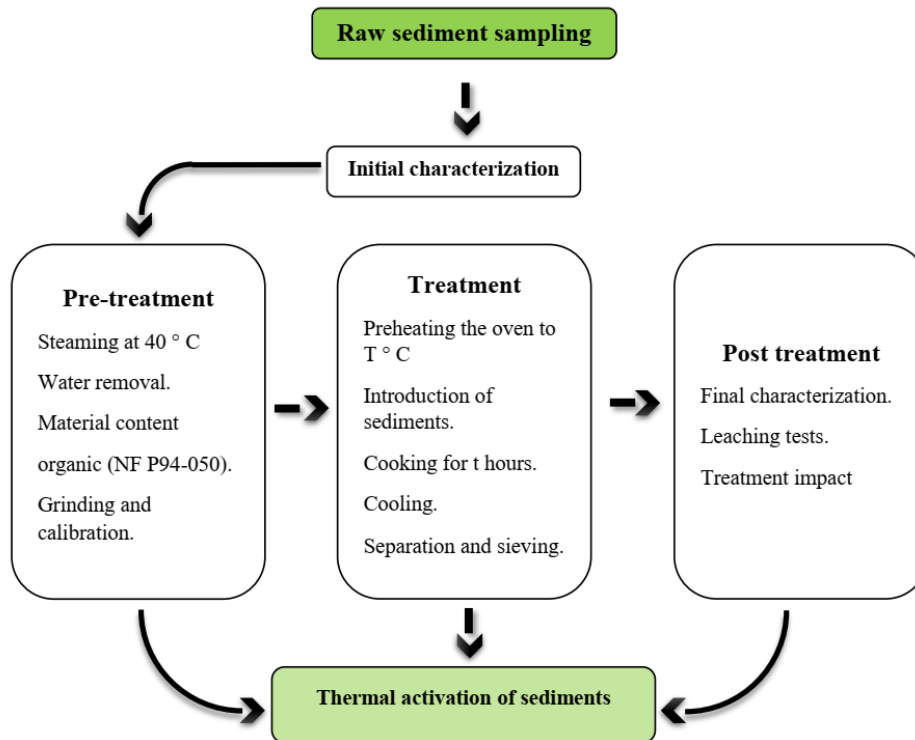


Figure 1.12: Direct calcination methodology.

### 2.1.9.3.2 Treatment Impacts

According to Benkaddour [66] and Anger [39], sieving, as well as grinding, can have beneficial effects because it increases the fineness of the product (an increase of the specific surface) and therefore its reactivity. These results are at that remain consistent with those of Gutteridge and Dalziel [71] who have already established the favouring of cement hydration reactions in the presence of reactive fillers, or inert. All the analyses carried out on the raw sediment are also carried out on the calcined sediment to assess the impact of the firing.

Inerting of metals occurs at temperatures between 200°C and 700°C [31]. The most volatile metals are transformed as gaseous emissions, very often as HCl, SO<sub>x</sub>, NO<sub>x</sub>, dioxins and furans [31]. However, it is useful noting that treatment of these fumes is required (especially concerning current legislation).

- HCl: combustion product of chlorinated compounds, organic residues, non-degraded plastics, etc ;
- SO<sub>x</sub> or (SO<sub>2</sub> or SO<sub>3</sub>) residues from the combustion of sulphurous products, industrial chemicals;
- NO<sub>x</sub> or (NO or NO<sub>2</sub> or N<sub>2</sub>O) nitrogen oxidation product;
- Dioxins and furans: form a group of halogenated polycyclic organic compounds (based on Chlorine and Benzene).

Previous studies based on the analysis of combustion residues and volatile emissions have established the combustion temperatures of carbonates frequently present in sediments [72] (Tab 1.3).

**Table 1. 3:** Decomposition temperature of the main carbonates [72].

Carbonates	Decomposition [°C]	Efficiency
Calcite	675	90% en 4h
Aragonite	645	-
Dolomite	450	20% en 16h
Magnesite	425	80% en 16h
Siderite	425	93% en 1/4 heure

It seems that there are also effects on pozzolanic activity or chemical activity in general. Limeira et al [16] suggest that this impact could be the result of heat treatment. By thermogravimetric analyses (TGA) combined with differential scanning calorimetry (DSC), the evolution of mass loss by combustion can be followed. They allow the constituents to follow, at a given temperature in a state of transformation.

#### **2.1.9.4 Flash calcination treatment**

Flash calcination is a heat treatment technique consisting of rapid exposure of finely divided materials in the presence of air at high temperatures [73]. This technique was initiated and developed by Professor Salvador [73]. The flash calcination technique was initially used to chemically activate certain clays such as kaolinite to give them pozzolanic properties [73].

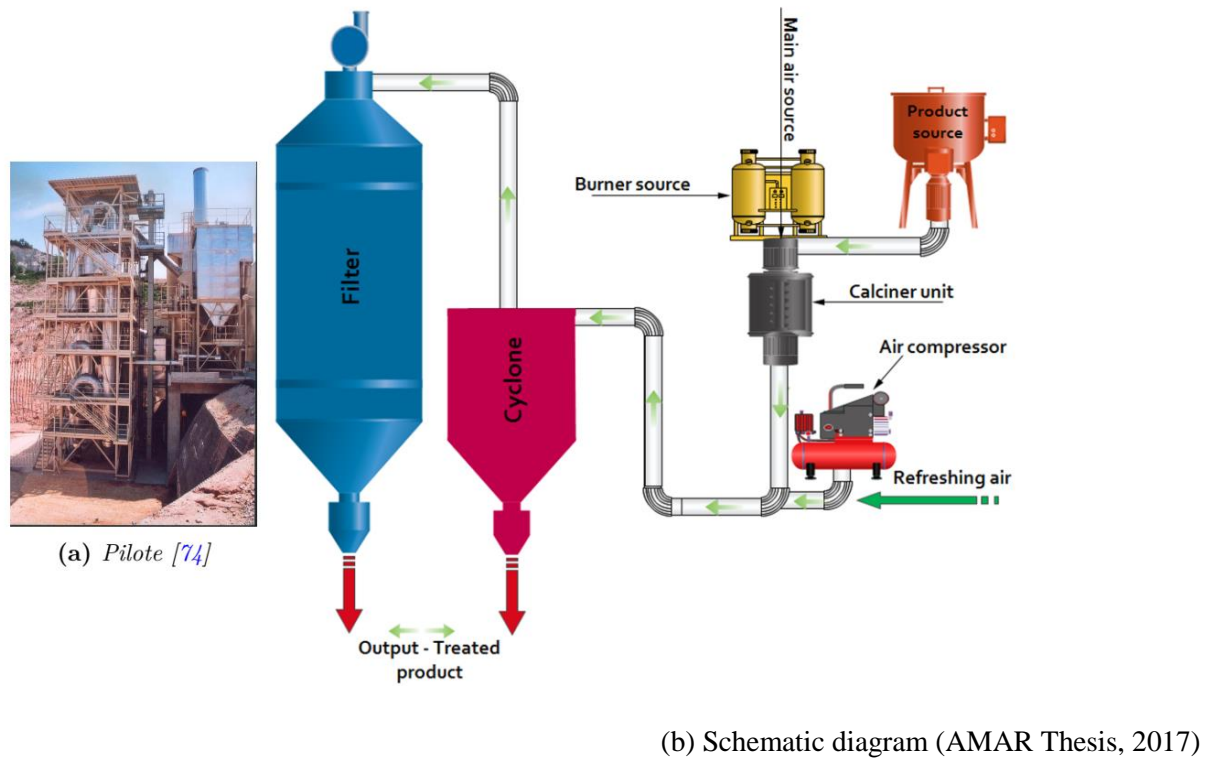
When applying this technique to certain categories of clays such as the Kaolins, a dehydroxylation process was identified. This corresponds to the elimination of a hydroxyl bond (OH) [74] [75]. Direct calcination can lead to such results. However, energy costs, in particular, are very often very high in this case or otherwise exorbitant to not encourage this choice. Also, due to the immediacy of the process, flash calcination allows a partial destructure of the material, a state of amorphization, and therefore a potential reactivity of the product [75]. However, two parameters are predominant: exposure time (about a few tenths (1/10) seconds), and cooking temperature; up to more than 1200°C at the core of the flame. The temperature is judiciously chosen based in particular on the thermal peaks of the ATG/ATD curve but also of the DSC, so that at the end, it has an amorphous character, relatively pronounced in the material.

In our studies, we propose to adapt this process to the treatment of dredged sediments. It will be an adaptation aiming to activate according to the same principle, certain phases of the sediment (in particular the clay phases).

##### **2.1.9.4.1 Flash calcination unit**

The flash calcination unit used is that of the company Argeco Developpement located on the Fumel site (France). In the following, we present the calcination tower. whose assembly scheme is shown in the following figure (Fig. 1.13). This is a semi-mobile unit. This unit is capable of producing 800 kg of material/hour. A burner produces hot gases in the combustion chamber (Cyclone) (See Fig 1.14). This can reach ' 800 to 1200 °C.





**Figure 1.13:** Image of a pilot unit and schematic diagram of the flash calcination unit.

#### 2.1.9.4.2 Steps in the flash calcination process

The following steps should be followed when flash calcining materials:

##### 1) Sampling

The steamed materials are finely ground and calibrated. Fineness is a major parameter of their future reactivity. According to studies, it is appropriate to have a passer-by at  $80\mu\text{m} > 80\%$  [73].

##### 2) Pre-heating

from  $100^{\circ}\text{C}$  to  $500^{\circ}\text{C}$  to raise the temperature of materials.

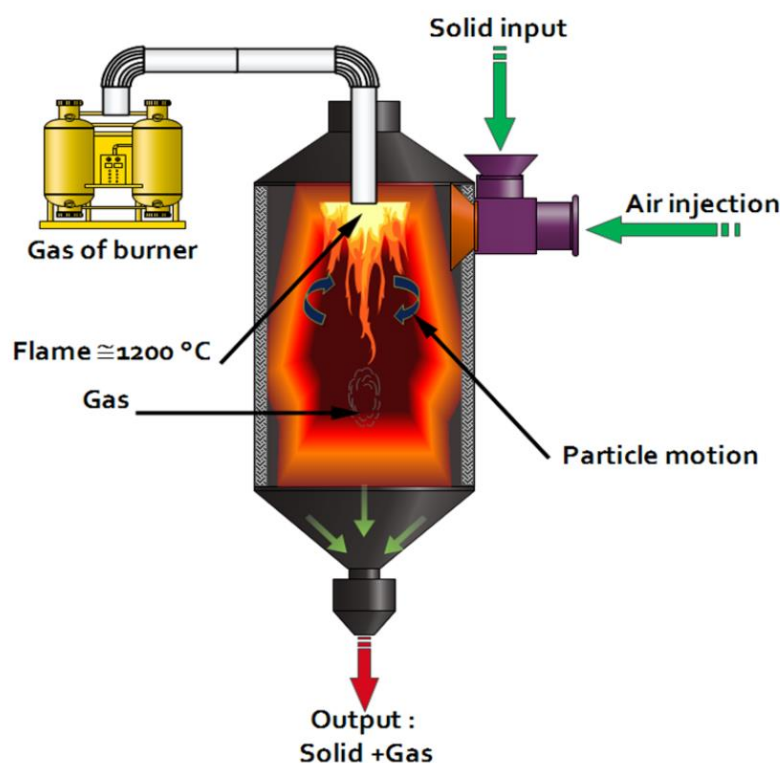
##### 3) Introduction of products

The materials are introduced into the combustion chamber using an air stream. The particles reside in the combustion chamber for about a tenth of a second. It is at this moment that the necessary physicochemical transformations occur, particularly due to the fineness and high temperatures (shape loading, gasification, advanced dehydration, etc.).

##### 4) Recovery-Cooling

It is carried out through two sub-units:

- Under cyclone by simple gravity, the material is recovered.
- Under filter by tempering with fresh air for cooling and separation of gases and materials.



**Figure 1.14:** Main unit for flash calcination (cyclone) (AMAR Thesis, 2017).

The prepared, dried, finely ground material is introduced into the cell described in Fig.1.14 using a stream of hot air. In place of the conventional extended calcination technique, flash calcination allows significant energy savings, efficient activation of the material, mobility of the processing process, etc. These gains can as much as 75% in energy (t 8000 MJ/t for pure clinker) compared to (t 2200 MJ/t for metakaolin) [17].

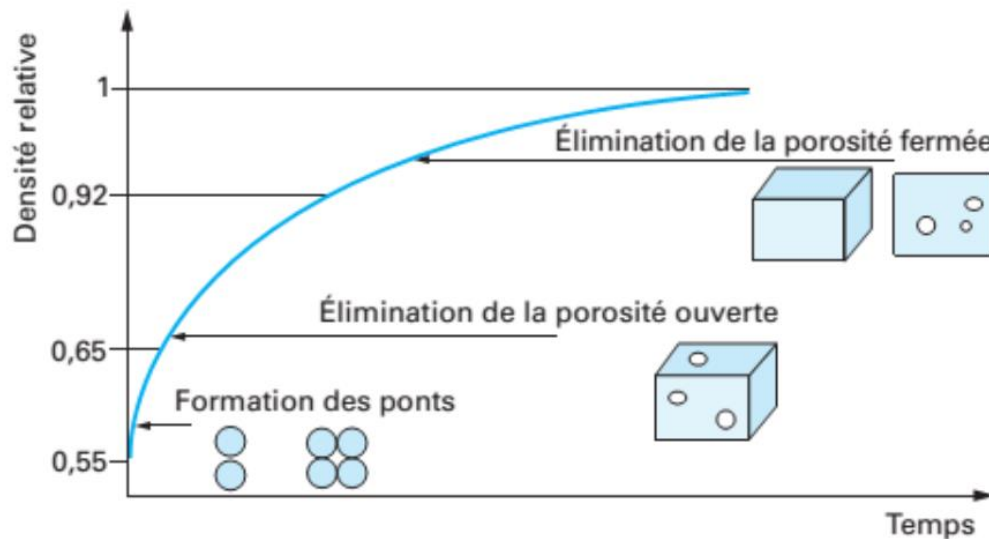
#### 2.1.9.5 The frittage

In addition to the multiple reactions mentioned above, one of the major conditions observed during calcination processes is sintering. Due to the high temperatures, the influence of heat, the particles undergo a sticking phenomenon corresponding to consolidation by total or partial consolidation of a powdery material [76].

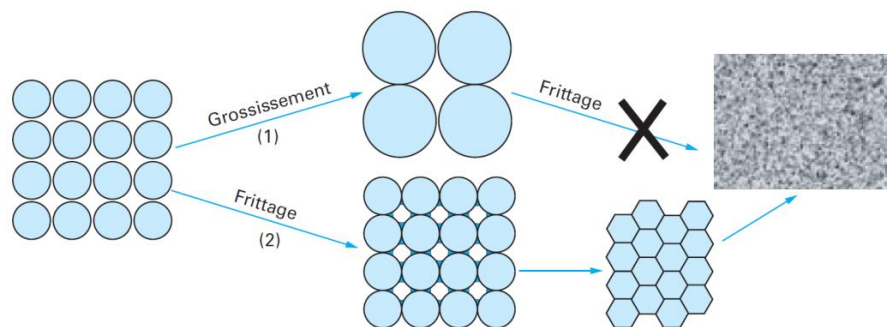
The term sintering could be defined as a heat treatment process, with or without the application of external pressures, by which an individual particle system or a porous body changes some of its properties in the direction of evolution towards a state of maximum compactness, i.e. zero porosity (Fig 2.11). Sintering is an interarticular link through molecular or atomic attraction under the impulse of heat (see Hausner Index). This leads to a densification of the material after recrystallisation. Sintering usually occurs at the so-called Tamann temperature =  $0.4 \approx 0.5 * T_{\text{fusion}}$ .

- Step 1: Granular reorganization and temperature rise;
- Step 2: Closing of the external pores and densification of the matrix;
- Step 3: Particle consolidation and removal of closed porosity.

Let's remember that sintering is not systematic. There may be magnification instead depending on the material source, as shown in Fig 1.15 and Fig 1.16.



**Figure 1.15:** Density evolution during sintering [76].



**Figure 1.16:** Sintering process [76].

### 2.1.10 Chemical methods

The chemical treatment aims to eliminate the organic fraction. The treatment process described below is derived from the Belgian standard: Standard NBN 589-207 §3 "Tests on construction sands - Organic matter content - §3 - Laboratory process with hydrogen peroxide" - 1969. This standard provides guidelines for determining soil characteristics by treating the oxidisable organic fraction (Eq. 2.2) with hydrogen peroxide.



It should be noted, that various chemicals can be used such as sodium hypochlorite (NaOCl) [77] and disodium proxidisulphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) [78], but the most widely used since its introduction in soil analysis by Robinson (in 1922), is hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) [79]. All these products are aimed at oxidizing the organic fraction but can have related consequences, notably by modifying the mineral structure [79]. Previous studies (Tab. 1.4) have already suggested certain protocols for the effective, but not total, removal of organic matter by chemical means [80] [81] [82] [83] [84].

**Table 1. 4:** Various Chemical Treatment Methods and their Impacts.

Mass	Protocol	Consequences	Ref.
30 g of soil and $d \leq 20\mu\text{m}$	Use 500 ml of a concentrated solution between 15 and 30% ( $\text{H}_2\text{O}_2$ ). Under Ambient temperature than to $70^\circ\text{C}$ . Duration = 24-72 hours	83 to 94 % elimination of the M.O. Impact on a granular skeleton	[80]
1 g of soil	Use 50 ml of a concentrated solution between 6% ( $\text{H}_2\text{O}_2$ ) repeated 5 times. Temperature: $80^\circ\text{C}$	66 to 97% elimination of the M.O. Impact on specific surface	[84]
4.5 g of soil	Use 250 ml of a concentrated solution at 6% of ( $\text{NaOCl}$ ) repeated 6*6 hours. Temperature= $25^\circ\text{C}$ ; pH=8	49 to 81% elimination of the M.O. Isolation of stable MO	[85]
0.5 g of soil	Use 20 g of ( $\text{Na}_4\text{P}_2\text{O}_7$ ) with Solution buffer with 22g ( $\text{NaHCO}_3$ )	16 to 99% elimination of the M.O. Isolation of stable MO	[78]

### 2.1.11 Sediment Regulations

As mentioned in the previous chapter, sediments, regardless of the degree of pollution, are considered to be waste to Decree No. 2002-540 of 18 April 2002. The rules put in place are generally aimed at preventing and protecting the marine environment from dredging and immersion operations.

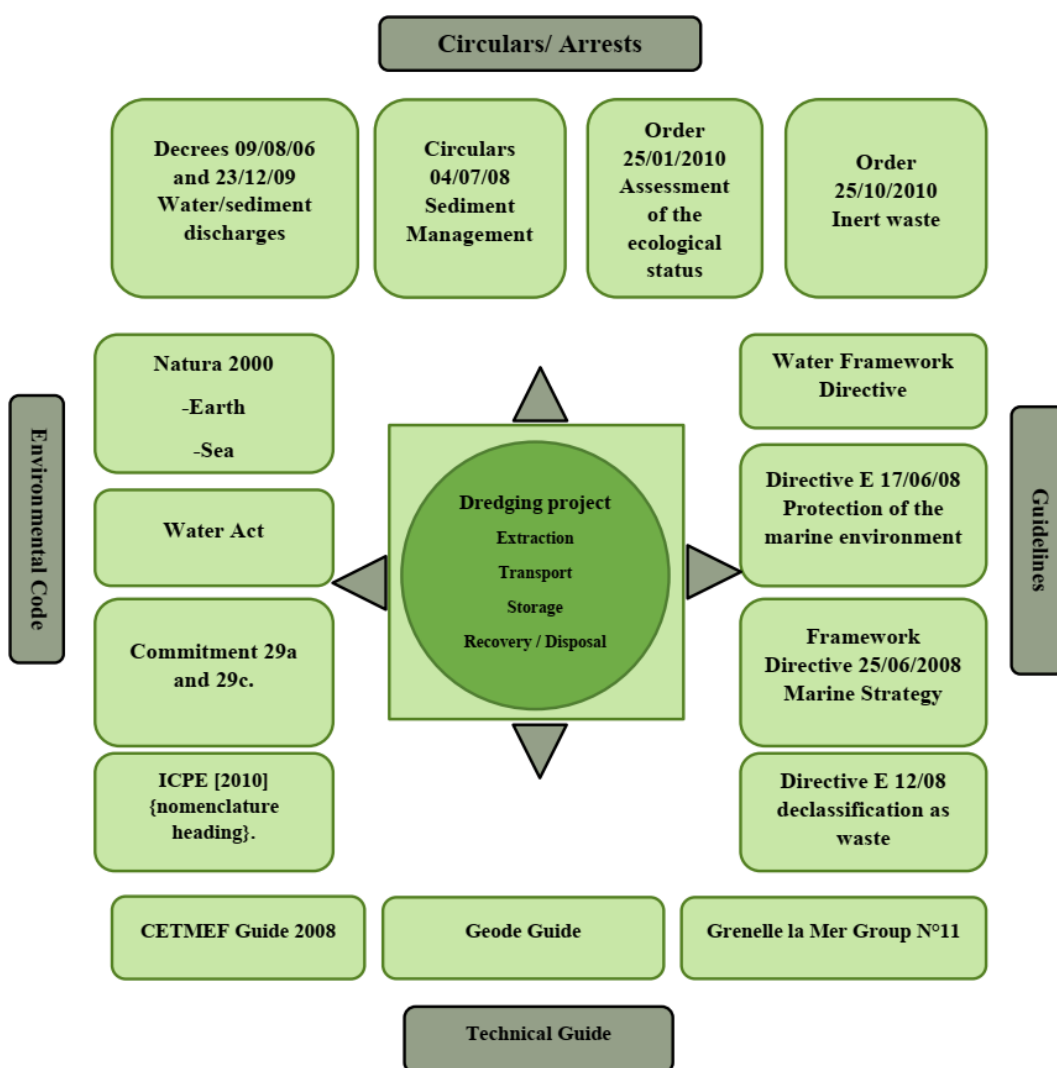


Figure 1.17: Sediment Management Regulatory Organization [32].

#### 2.1.11.1 Regulation at the international level

The following regulations are worth remembering:

- **The OsPar(1992) convention**, literally meaning Oslo-Paris, was definitively ratified by France in 2004. It is largely aimed to protect maritime areas by setting up rules for the prevention and minimisation of water pollution. In 2009, Ospar published a guide for the sustainable management of sediments as well as a study on the specification and speciation of pollutants generally present.
- **The London Protocol (1996)** is an updated version of the so-called London Convention and aims to prevent marine pollution possibly from immersion operations. This convention puts in place precautionary measures, taking into account the polluter-pays principle, setting up protection measures to protect according to economic and scientific capacity to effectively preserve the environment and resources.

- **The Barcelona Convention (1995)** adopted on 16 February 1976 and amended in 1995, it aims to protect the Mediterranean Sea. Composed of 22 signatory parties, its main objectives are pollution assessment, integration of the environment as an integral part of socio-economic development, protection of nature and improvement of the quality of life, etc... These guidelines aim to protect the Mediterranean's marine environment as well as sustainable development projects.

#### ***2.1.11.2 Regulation at the national level***

- Articles L. 214-1 to 6 of the Environment Code submitting dredging operations subject to declaration or authorisation by the Prefect.
- Circular 2000-62 of 14 June 2000 relating to the conditions of use of the marine sediment quality reference system and the applicable characterisation standards.
- The decree of 9 August 2006 sets the reference levels to be taken into account when analysing marine or estuarine sediments present in the natural or harbour environment. It defines the N1 and N2 reference thresholds for eight heavy metals and seven PCB congeners.

- Modification by the ministerial decree of 23 December 2009: setting the TBT thresholds.

- Modification by the ministerial decree of 17 July 2014: setting the thresholds for 16 types of HAP.

- The decree of October 28, 2010, consolidated by the decree of June 27, 2014: It relates to inert waste storage facilities; According to the same decree, inert waste is a waste that does not undergo any significant physical, chemical or biological modification. In addition to leaching tests, this decree defines threshold values for mineral and organic contaminants beyond which the waste cannot be considered inert. This decree defines the thresholds to be respected for physical parameters (pH, temperature, etc.), total content (TOC, BTEX, etc.) and leachate (metals, chlorides, phenol indices, etc.).

It should be recalled that there is also the Order of 9 September 1997 modified by the decree of 12 March 2012 fixing the thresholds for the storage of non-hazardous waste and the Order of 30 December 2002 modified by the decree of 10 October 2012 defining the storage thresholds of hazardous waste.

- The H14 protocol: This is a protocol for indexing the dangerousness of marine sediments as continental. It applies to materials exceeding the S1 threshold (Decree of 9 August 2006), for at least one dangerous contaminant [34]. It is based on the

implementation of a battery of ecotoxicological tests. It also makes it possible not to give a dangerous attribute to materials exceeding the N1(Geode) threshold, i.e. submerged.

**Table 1. 5:** Mineral Contaminants and Pollution Thresholds (in mg/kg DS).

Regulations			As	Ba	Cd	Cr	Cu	Mo	Ni	Pb	Sb	Se	Zn	Hg	
Arr.	28	October		0,5	20	0,04	0,5	2	0,5	0,4	0,5	0,06	0,1	4	0,01
2010															
14	June	2000	N1	25	-	1,2	90	45	-	37	100	-	-	276	0,4
(GEODE)			N2	50	-	2,4	180	90	-	74	200	-	-	552	0,8

**Table 1. 6:** Organic and Other Contaminants (mg/kg DS).

Arr. 28 October 2010	
Chloride( 5*)	800
Fluoride	10
Mercury	0,01
Sulfate ( 6*)	1000
Phenol Index	1
TOC (Elected)( 7)	500
FS ( 8* )	4000
TOC (solid)	30000
BTEX	6
PCB	1
Hydrocarbons	500
HAP	50

8. These limit values may be exceeded under specific provisions according to the Order.

### 2.1.11.3 German regulations

In both Germany and the Netherlands, sediment management policies generally concern national flood security, stopping and reducing erosion, but also the protection of the Germanic islands of Friesland and North Friesian as a natural barrier against flooding [86]. Around several actors (ministries, government agencies, etc.), the improvement of the living environment is thus organized by highlighting the notion of "common tasks". The management of sediments and dredging sludge is governed by soil quality decree of 18 April 2013. This decree enacts the 'Environmental Protection Act' and the 'Soil Protection Act' establishing permits in certain cases. It defines three limited thresholds in relation to the fate

of the volumes to be eliminated: disposal at sea or reuse at sea. Table 1.7 shows an extract of the threshold values for industrial-type recovery.

**Table 1. 7:** Mineral Contaminants and Pollution Thresholds (in mg/kg of DM).

	<b>Hg</b>	<b>Cd</b>	<b>Pb</b>	<b>Cr</b>	<b>Cu</b>	<b>Zn</b>	<b>Ni</b>	<b>Ti</b>	<b>Co</b>	<b>PCB</b>
<b>Thresholds</b>	4,8	4,3	530	180	190	40	100	900	190	40

It can be noted that these thresholds are very close to the N2 thresholds (GEODE, France). Except for certain elements such as Pb or Hg for example where we can have multiplying factors of the order of 10.

#### **2.1.11.4 Canadian Regulations**

In Canada, sediment management is governed around the definition of thresholds for the degree of harmfulness. Three levels are then defined: N1, N2, N3, corresponding respectively to thresholds without effect, minor effects and adverse effects (Tab 1.8). For thresholds lower than level N2, the sediments are potentially being used in structures, subject in certain cases to an additional study. For thresholds included in N2 and N3, they can then be intended for polluted sites. Thus, in Quebec, 5 concentration threshold criteria are defined [87]:

- Produced Effect (CES): Below this threshold, adverse effects are rarely observed;
- Probable effects (CEP): Above this threshold, adverse effects are frequently observed;
- Rare effects (CER): to prevent possible sediments contamination due to industrial activities.
- Occasional effects (CEO): this provides that rejection can only be authorised if the risk to marine species is removed.
- Frequent effects (CEF): open water discharge is then totally prohibited.

The threshold values for marine sediments are given in Table 1.9.

**Table 1. 8:** Pollution Thresholds for Mineral Contaminants (St. Lawrence River) (in mg/kg of DS) [88].

	<b>Hg</b>	<b>Cd</b>	<b>Pb</b>	<b>Cr</b>	<b>Cu</b>	<b>Zn</b>	<b>Ni</b>
<b>N1</b>	0,05	0,2	23	55	28	100	35
<b>N2</b>	0,2	0,9	42	55	28	150	35
<b>N3</b>	1	3	170	100	86	540	61



**Table 1. 9:** Mineral contaminants and pollution thresholds (in mg / kg DS) [87].

	<b>Hg</b>	<b>Cd</b>	<b>Pb</b>	<b>Cr</b>	<b>Cu</b>	<b>Zn</b>	<b>Ni</b>	<b>Fluorine</b>	<b>Pyrenees</b>
<b>CSE</b>	0,0051	0,32	18	30	11	70	-	0,01	0,041
<b>CEP</b>	0,13	0,67	30	52	19	120	-	0,021	0,15
<b>CER</b>	0,29	2,1	54	96	42	180	-	0,061	0,42
<b>CEO</b>	0,7	4,2	110	160	110	270	-	0,14	1,4
<b>CEF</b>	1,4	7,2	230	290	230	430	-	1,2	3,8

It can, therefore, note that for Canada, the N2 threshold is less severe than the N1 threshold (GEODE, France) and that their N3 threshold is substantially equivalent to the N2 threshold (GEODE, France).

#### **2.1.11.5 Regulations in the USA**

Sediments, and more generally materials from dredging can be recovered. However, the policy in place provides for proving that the use that will be made of sediments does not present a risk to the environment, fauna and flora, that it is safe for the health and safety of humans. It must also be shown that the proposed reclamation is not contrary to state laws [89]. The regulations are very specific to each State. For example, in the State of Maryland, it is the Maryland Department of the Environment (MDE) decides. In the State of New Jersey, it is the New Jersey Department of Environmental Protection (NJDEP) which decides according to different laws such as Waterfront Development Law, Rules on Coastal Zone Management, Water Pollution Control Act [90] [91]. Usually, sediment testing is done before the sediment is dredged and sampling is regulated. The disposal of dredged sediments at sea is regulated by the US Army Corp of Engineers (USACE) and the US Environmental Protection Agency (USEPA). Section 404 of the Clean Water Act (CWA) allows dredged material in US waters to be used for sand supply to beaches or placement in submerged lands. The National Environmental Policy Act (NEPA) and the Endangered Species Act (ESA) require the consideration of specific impacts in the context of enhancement projects. The Resource Conservation and Recovery Act (RCRA) and the Toxic Substances Control Act (TSCA) are also to be considered in development projects. Although dredged material is regulated in the solid waste category in some states, there are exceptions to this classification based on the results of characterisation tests and end-uses. Several ways of valorization are then recommended [89].

- Beach filling when  $D_{\max}$  (63 m) - 75%;
- habitats and marine protection tools, Artificial Islands;
- Structural or non-structural filling materials;

- Use on agricultural land, etc.

Below (Tab 1.9) is an extract of the thresholds for certain elements for the State of Wisconsin; thresholds beyond which a declaration-authorization is required.

**Table 1. 9:** Mineral Contaminants and Pollution Thresholds (in mg/kg of DS) [89].

	Hg	Cd	Pb	Cr	Cu	Zn	Ni	Toluene	Fluorine	Cyanides
<b>Thresholds</b>	14	1	400	-	600	1500	250	1000	2300	1100

These thresholds are therefore 5 to 10 times higher than the N2 thresholds (GEODE, France), which corresponds to greater flexibility and valorization possibilities.

#### **2.1.11.6 Sediment recovery projects: A global ambition**

In 2013, the GPMD ordered the construction of 110 concrete blocks based on sediments. This project aimed to recover  $\approx 600 \text{ m}^3$  of dredged sediment through the construction of 4 to 6  $\text{m}^3$  wave breaking blocks. The sediments are then initially treated at 4% with a sulpho-aluminous AliPré ® cement. The blocks produced incorporate 12% and 20% sediment and strengths of 39 MPa were reached at 28 days. Environmental monitoring was carried out and the durability was studied as part of Achour's thesis [32] and has qualified the blocks at 12% as durable [32]. There is also the Freyssinet road 12 within the GPMD enclosure on which 450  $\text{m}^3$  of dry sediment from the harbour was used in its foundation layer.

Also in the USA, sediments are used in various valorization projects (up to 230,000  $\text{m}^3$ ), for example in Cleveland as earthmoving material in an industrial zone development project. Or in Wisconsin in the formation of flood barrier islands ( $\approx 2,350,000 \text{ m}^3$ ; \$20 million) [92].

In Belgium, for example, sediments are used for the formation of dykes, as in Vlassenbroek, where 105,000  $\text{m}^3$  of sediments are treated and developed by the company Envisan to protect from flood phenomena.

There are also works around the world based on sediments (Port of Rotterdam, the Palm Island in Dubai, the National Theatre in London, or the artificial island of Chek Lap Kok, etc [16] as mentioned earlier.

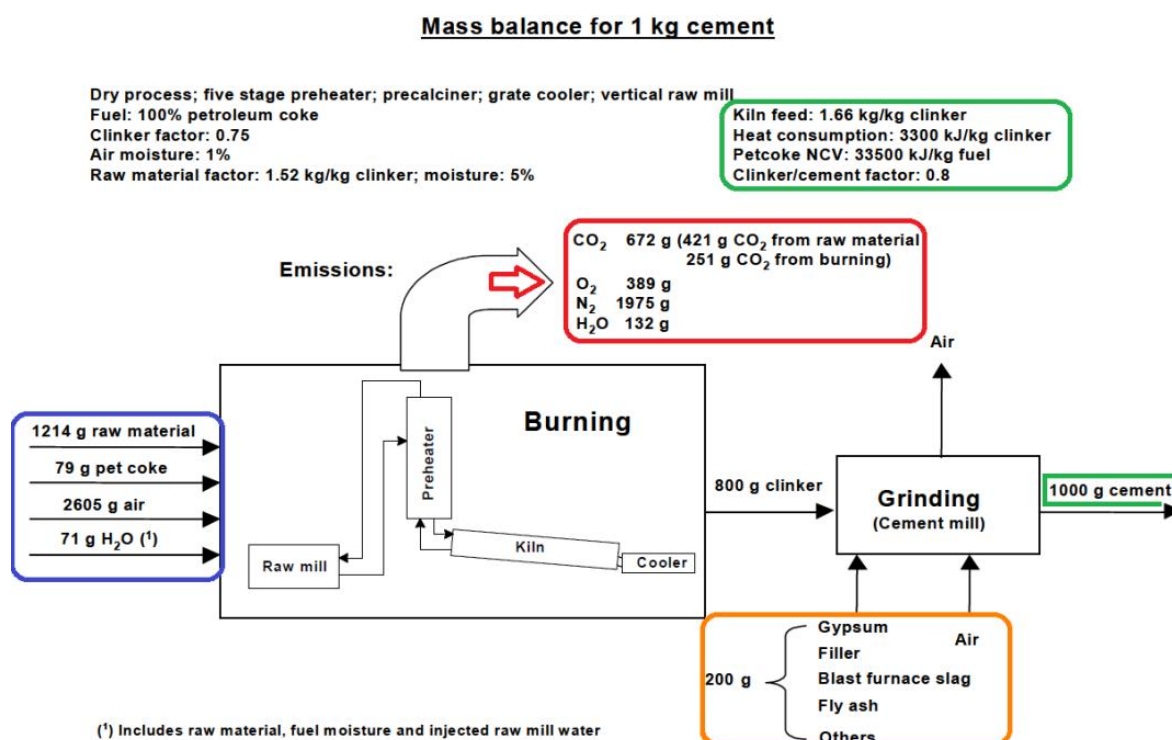
## 2.2 CEMENTITIOUS MATERIALS

Concrete is an old and widely used material because of its mechanical properties that have been appreciated for a very long time. The Egyptians were already using it around 2600 BC in the pyramid of Abu Rawash. Concrete is the most widely used manufactured material in the world after water. This material did not stop evolving until the invention of reinforced concrete in 1867 by Joseph Monier (1823 - 1906) or prestressed in 1928 by Eugène Freyssinet [93].

Concrete is a multiphase material consisting of a granular skeleton and a cementitious matrix. Due to chemical hydration reactions followed by hardening, the whole becomes rigid. This gives the material-specific physicochemical properties: elastic properties, high compressive and low tensile strength, permeability, etc. These properties cannot exist without a string of chemical chain reactions, triggered upon contact between anhydrous cement and water. These reactions give rise initially to portlandite ( $\text{Ca(OH)}_2$ ) which acts as a trigger on the setting, then to various hydrates (C-S-H, C-A-H, C-A-S-H, etc.) representing the "glue" of the matrix.

### 2.2.1 Cement and its manufacture

Cement is an artificial material produced from firing for 1 hour at  $1450^\circ\text{C}$  a mixture of 75% to 80% limestone and 15% to 20% clay and possibly correctors (fillers, slag, bauxite, etc.), thus giving birth to the clinker. This phase is preceded by a decarbonisation process (to  $700^\circ\text{C}$  –  $950^\circ\text{C}$ ) which is very polluting and endothermic (1776kJ/kg of pure limestone is required) [94]. The energy required for clinker firing can be estimated as  $3 \text{ MJ/kg} \leq E \leq 8 \text{ MJ/kg}$  [95] [74], depending on the type of firing and the kiln. Electricity consumption is 12 - 19 KWh/t clinker and 115 - 130 KWh/t cement [94] at a rate of 55 - 60 e/MWh (EDF tariff). Also, consideration must be taken into account the energy required to extract and transport raw materials, grinding, storage, etc. For these few reasons, it remains clear that promoting materials with a lower economic and ecological footprint is necessary. Below is a descriptive diagram of the principle of dry cement manufacture, which is the least energy-consuming (Fig. 1.18).



**Figure 1.18:** Dry Cement Manufacturing Balance [95].

## 2.2.2 Cement Hydration

It should also be remembered that cement is a hydraulic binder (reacts with water). In reality, during its manufacture, limestone provides calcium oxide (CaO), clays, silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) and iron oxide (Fe<sub>2</sub>O<sub>3</sub>) [96]. It is also necessary to fine grinding ( $\leq 100\mu\text{m}$ ) at the end of the cycle, as well as mixing of the constituents. However, it will be necessary to incorporate gypsum ((CaSO<sub>4</sub>, 2H<sub>2</sub>O)) for retarding the setting as well as possible additions to obtain specific rheological and mechanical properties. The proportions of the main constituents are given in Tab 1.10.

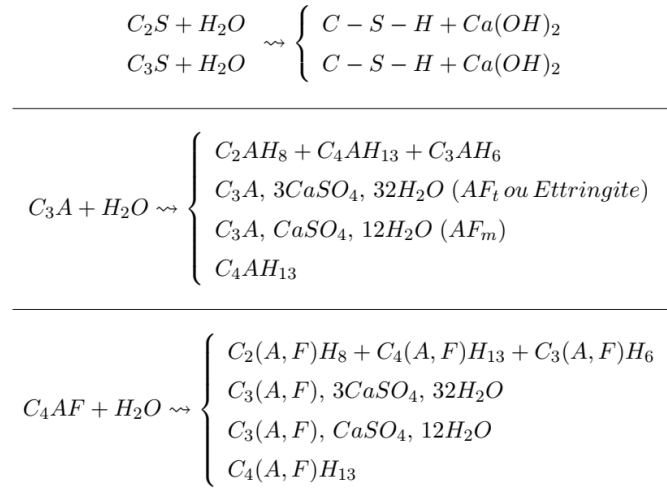
**Table 1. 10:** Main chemical fractions in hydraulic cement and their respective proportions [93].

Name	Chemical formula	Proportion
Tricalcium silicate or alite	$C_3S = 3CaOSiO_2$	55 à 70%
Dicalcium silicate or belite	$C_2S = 2CaO, SiO_2$	18 à 20%
Tricalcium aluminate or celite	$C_3A = 3CaO, Al_2O_3$	8 à 10%
Tetracalcic aluminoferrite or brownmillerite	$C_4AF = 4CaO, Al_2O_3Fe_2O_3$	6 à 10%

Cement does not have their pozzolanic properties, but rather binding properties. The definition proposed by Lea [93] is one that is often presented and is similar to that used in standards ACTM C 125-07: "Pozzolans are commonly defined as materials that do not have

binding properties in themselves but which, when combined with lime at ordinary temperature and in the presence of water, form stable insoluble compounds with binding properties".

The hydration of cement requires the holding of multiple chemical reactions. It is these reactions that give rise to hydrates (hydrated calcium silicates or C-S-H) and compounds essential to the durability of the matrices such as portlandite or various hydrates. The reaction schemes during hydration are as follows [93] [96]:



According to Mazars [93], a portion of cement with a weight ratio of E / C = 0.5 has the following proportions after the hydration reactions (at 28 days):

\*  $\Rightarrow$  86% hydrates including :

- $\approx$  56% C-S-H
- $\approx$  20% portlandite (Ca(OH)<sub>2</sub>)
- $\approx$  10% sulfoaluminates

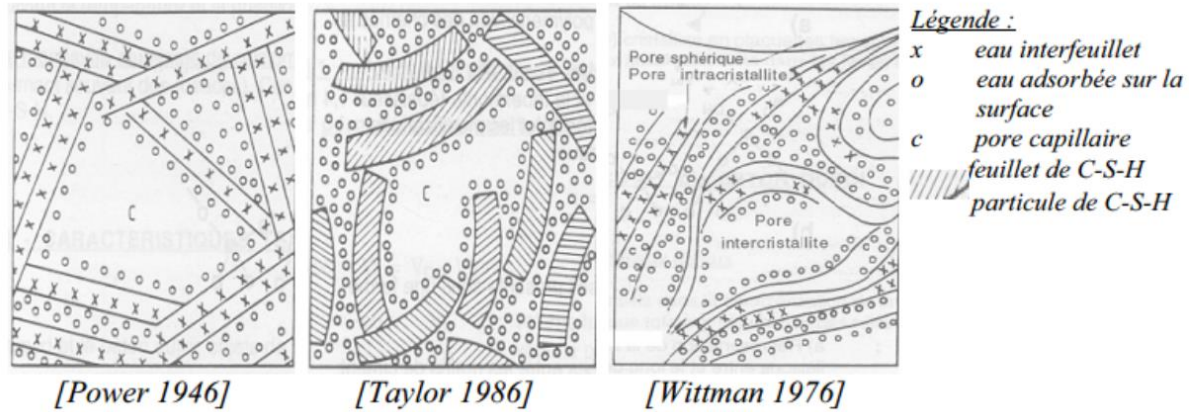
\*  $\Rightarrow$  7% water

\*  $\Rightarrow$  7% voids

### 2.2.2.1 Calcium silicate hydrates C-S-H

This is the main hydrated phase produced. The C-S-H family includes a large number of ternary base compounds (mCaO, nSiO<sub>2</sub>, pH<sub>2</sub>O). C-S-H is often called C-S-H gel because of its low crystallisation and high water content. Under the microscope, C-S-H seems to be very thin sheets which, by entanglement, roll up on themselves giving rise to hollow tubes [93]. They generally have a density between 2,00 and 2,65 g/cm<sup>3</sup> with a high specific surface area (of the order of 10 m<sup>2</sup>/g) [96]. Authors have already proposed structuring models for the

elementary particles of C-S-H (Fig.1.19). Its structure is generally described as a microcrystal to tangled interlamellar [93]. It is deposited around the grains and connects it to the matrix [97]. Hence its importance because it plays a major role in certain mechanisms of setting, resistance, durability, etc. [97].

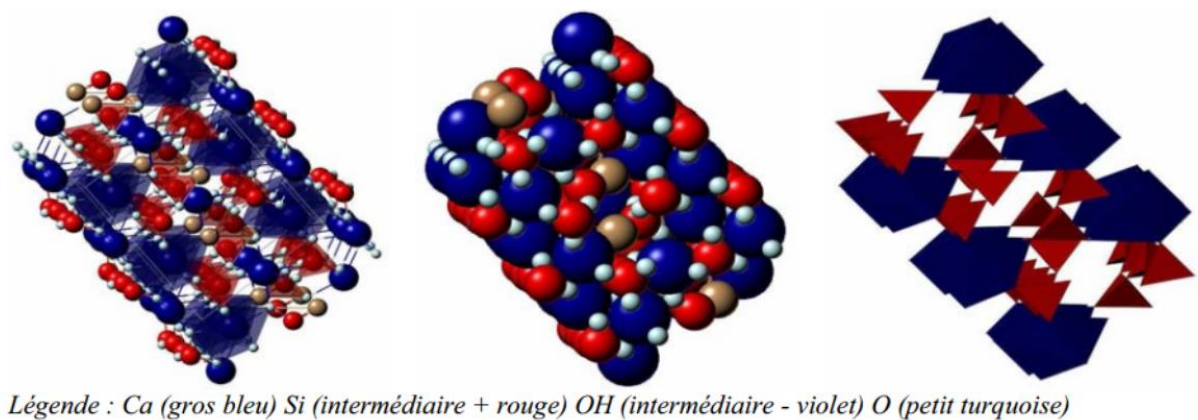


**Figure 1.19:** C-S-H Gel Schematic [96].

Sierra based on the work of Feldman (cited by [93]), considers that the cohesion and therefore the resistance of matter originates:

- Cohesion and interlamelious welding;
- The structuring of interleaf and interlaminar water fixed by surface forces such as Van Der Waals-type through hydrogen bridges.

Research using X-ray diffraction or nanotechnology or various identification techniques [98] [99] [100] [101] [102] have concluded that the structure of C-S-H would rather resemble that of tobermorite (See Fig 1.20)  $[\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_{22}\text{H}_2\text{O}]$  known as 11 Å ([103]) or jennite  $[\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_{68}\text{H}_2\text{O}]$  [104] or their association [105][106].



**Figure 1.20:** Molecular representation of Tobermorite [103].



As noted earlier, C-S-H is derived from the hydration of Alite ( $C_3S$ ) and Belite ( $C_2S$ ). Their germination and maturation correspond to the existence of a structure whose authors diverge on its physicochemical nature (Fig 1.21; Fig 1.22):

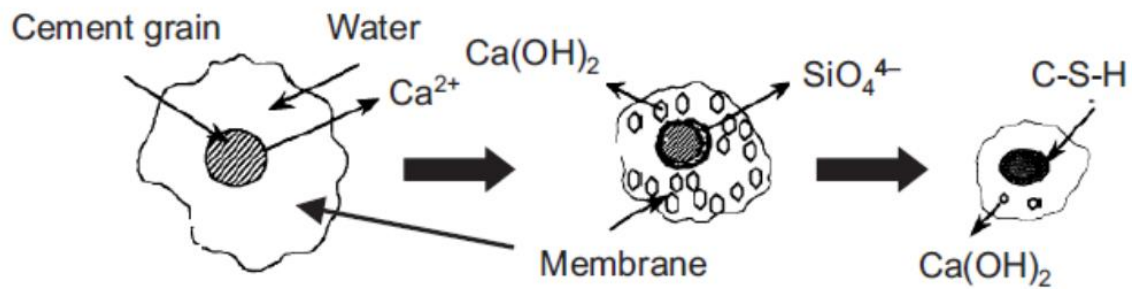


Figure 1.21: Colloid model of the C-S-H gel [107].

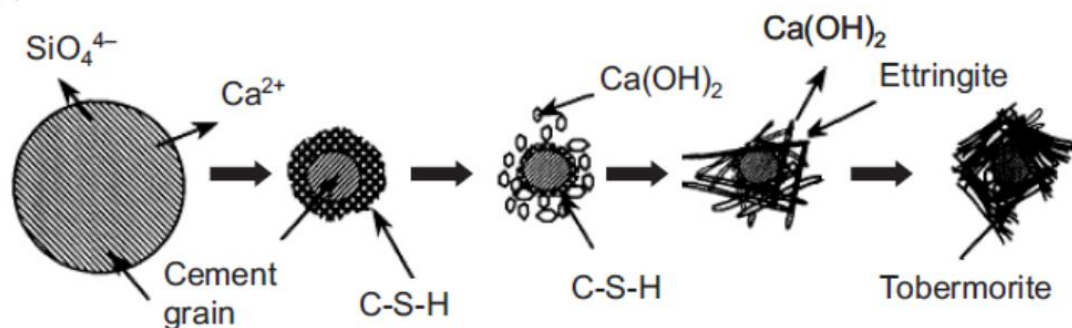


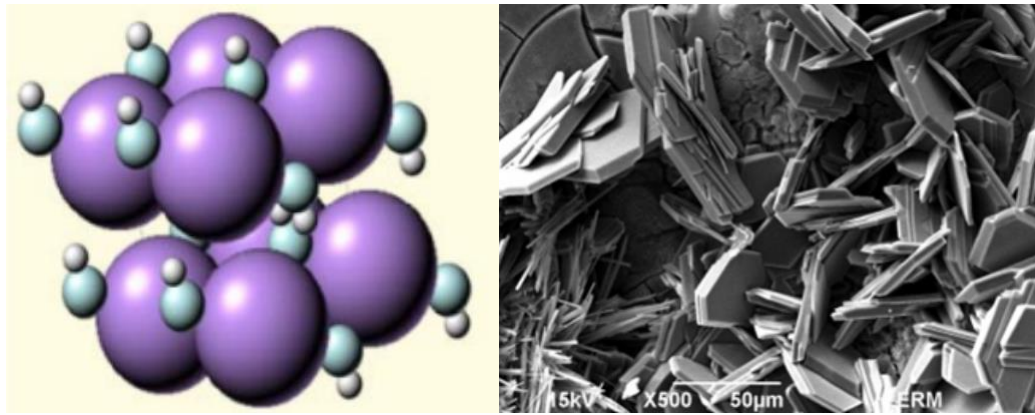
Figure 1.22: Crystal model of the C-S-H [107].

C-S-H undoubtedly plays a major role in cement matrices. They are the main elements responsible for the cohesion and hardening of the cement. Manzano [97] considers them to be the main factors determining the physical and chemical characteristics of cementitious matrices.

#### 2.2.2.2 Portlandite $Ca(OH)_2$

Derived from the hydration of Alite ( $C_2S$ ) and Belite ( $C_3S$ ), its chemical formula is  $Ca(OH)_2$ . During hydration, its germination gives rise by crystallisation to stacked hexagonal platelets (2.19b). Henderson (cited in [96]) proposes the atomic representation shown in Fig. 1.23 and gives the following characteristics:

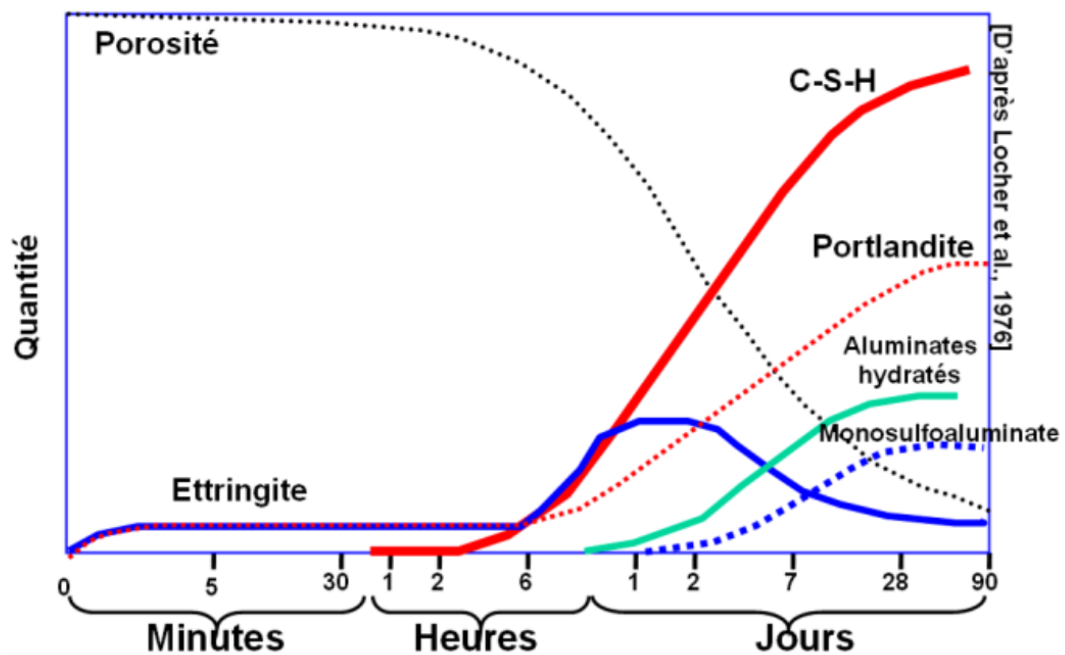
Density  $\rho = 2,25 \text{ g/cm}^3$ ; pH = 12,5; Solubility ( $20^\circ\text{C}$ ) = 1,2 g/l [96].



(a) Molecular structure of portlandite (b) SEM analysis of portlandite (LERM)

**Figure 1.23:** Molecular model and structure of portlandite [96].

Portlandite crystals show a particular cleavage [93] [108]. Its early precipitation also serves as a trigger for the setting. This makes it plays no less important, especially in the mechanical strength of concrete, at the paste-aggregate interfaces (transition halo or ITZ). Indeed, for common concretes, at rupture, laminations due to the main stresses are observed in these places. The hydration of  $C_3A$  and  $C_4AF$  goes through the formation of other types of compounds. In particular, there is the early formation of ettringite  $C_6AS_3H_{32}$  in the form of prisms entangled around the cementitious aggregate. Its formation is required to avoid so-called "flash setting" phenomena. Its transformation into monosulfoaluminate  $C_4AS_3H_{12}$  structured in hexagonal platelets is observed subsequently. There are also other types of hydrates (aluminates) that can be formed ( $C_nAH_m$ ). The overall cement hydration kinetics described by various authors could be represented as follows (Fig 1.24).



**Figure 1.24:** Cement hydration kinetics.



These different stages of formation are typical of the hydration of a common cement. Their knowledge allows appreciating the different processes taking place during hydration. This makes it possible to favour or block target mechanisms, to have specific effects such as rapid or delayed setting, control of the hydration heat, etc.

### 2.2.3 Porosity in Cementitious Matrices

Previous work has shown that porosity is an important factor in the determination of elastic modulus [93] and compressive strength (Powers, Balshin, Hasselman and Ryshkewitch) [109]. The porosity of concrete is a function that evolves inversely to the degree of hydration (Eq.2.3a;2.3b) [109] and remains increasing in proportion to the water/cement ratio [93].

$$q \approx 1 - 0.5 \left( \frac{t_R}{t} \right)^{0.2} \quad (2.3a)$$

$$\sigma = \sigma_0 (1 - P)^A \text{ (d'après BALSHIN)} \quad (2.3b)$$

In these equations:

$q$  = degree of hydration;  $t_R$  = reference time (= 3 days);  $t$  = age of matrix.

$\sigma$  = Compressive strength of the matrix;  $\sigma_0$  = Compressive strength for an zero porosity;

$P$  = matrix porosity;  $A$  = experimental constant.

- For an increasing W/C ratio, the pore volume and their diameter increase in the same way (Fig. 1.25).
- The 1% variation in porosity results to a drop in the strength of  $\approx 2$  MPa and a loss of elasticity of  $\approx 2000$  MPa (Fig 1.26) [93].
- There is a critical porosity value below which the loading of the cement matrix leads to its collapse [109].

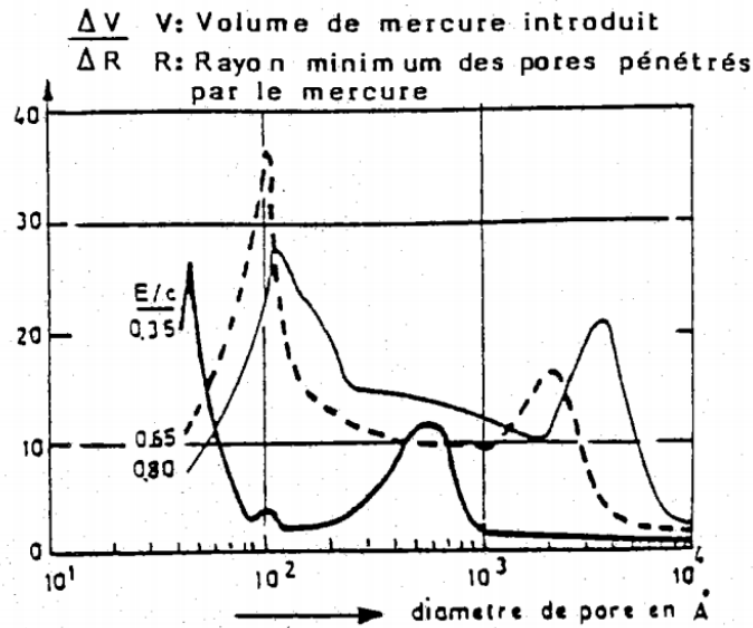


Figure 1.25: Distribution of porosity relative to W/C (Verbeck and Helmuth [93]).

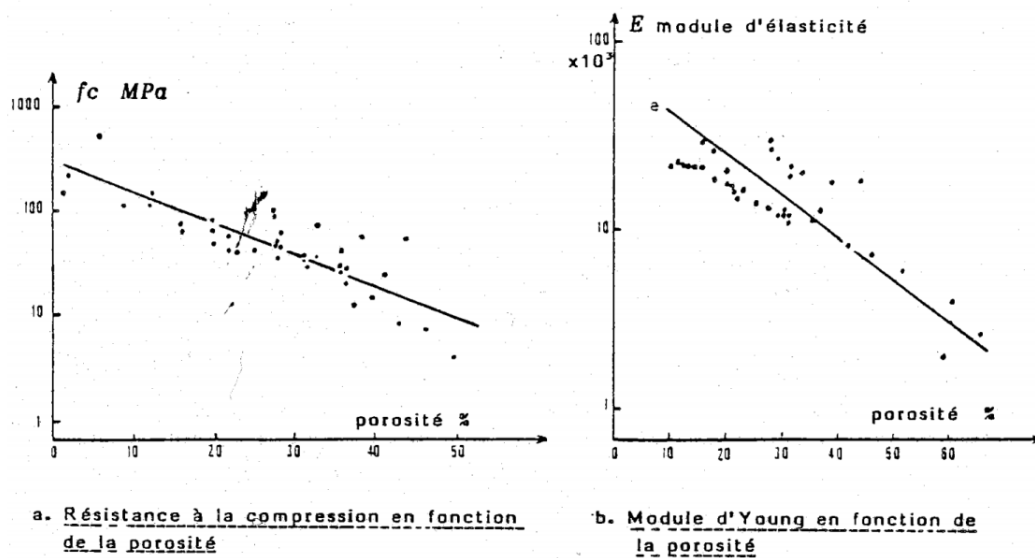
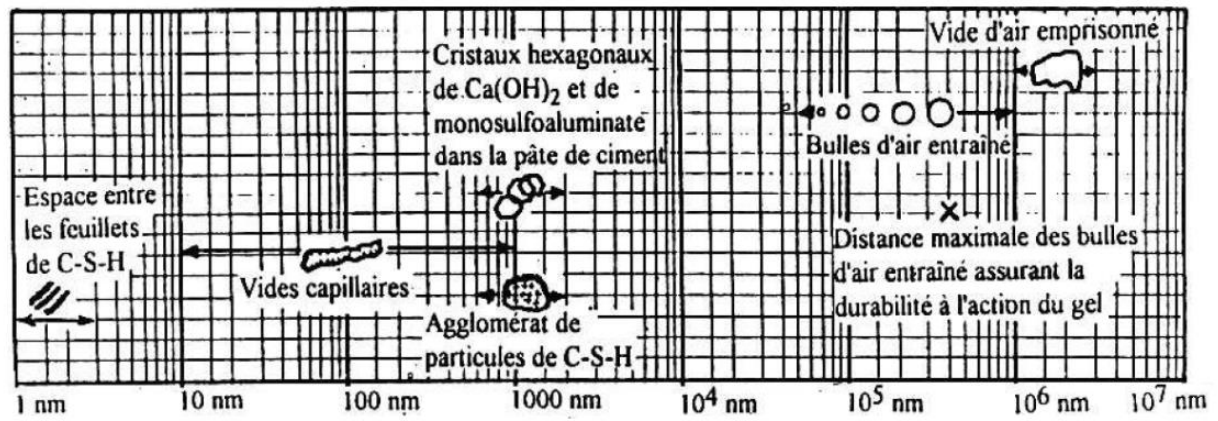


Figure 1.26: Variation of resistance and elastic module based on porosity (Feldman and Baudoin [93]).

According to Mazars [93] and Nielsen [109], there are two types of pores to consider (Fig 1.27) :

- The fine pores of C-S-H with a size in the order of 50 to 100 Å.
- Capillary pores resulting from the voids left by the effective water having reacted, and of dimensions up to 1000 Å.



**Figure 1.27:** Porosimetry and phases of a cementitious matrix (MEHTA (1986)).

Even if Balshin considers that it was total porosity that determined the resistance (Eq.2.3a), work carried out by Granju and Maso [108] [110] seemed to prove that only the capillary pores significantly impacted the resistance.

#### 2.2.4 The matrix-aggregate interface

Concrete can be considered as triphasic with a particular structure in the vicinity of aggregates [111]. This zone known as the Interfacial Transitional Zone refers to a physical environment governing the quality of adhesion between the matrix and the aggregate. This zone has some specific properties. In ordinary concrete, the damage would occur at this location. Also, it plays a decisive role, through its permeability, on the durability of the matrix (diffusion, leaching of the aggregates, etc). It has the following properties according to Scrivner and Pratt [110]:

- The porosity increases as the Itz approaches. This is mainly due to the water film of about 10  $\mu\text{m}$  thick surrounding the grain during mixing [108]. This porosity is, in fact, the result of a wall effect;
- Portlandite crystals are in increasing proportion and present a particular cleavage highlighted by the work of Farran and Barnes [93] in particular;
- The rate of ettringite increases considerably, in particular, because of its role in the mixing process.

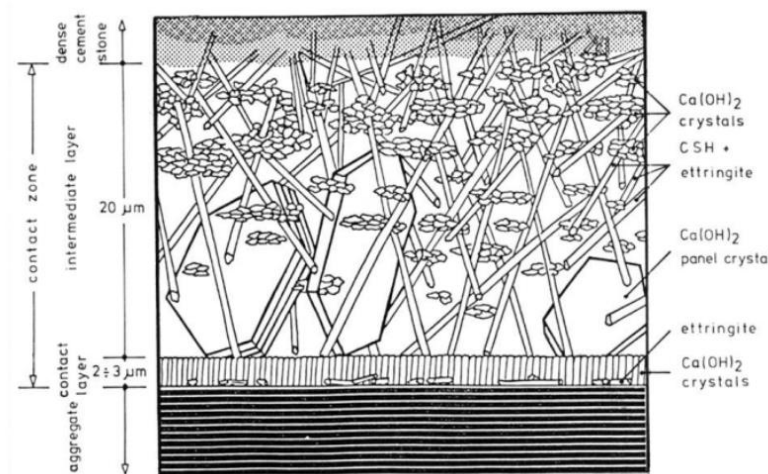
These properties, of course, have an impact on the characteristics of the matrix [112]. For Mazo [108], we can cite the following parameters: elastic modulus, elasticity threshold, crack generation, etc. However, other studies have limited the possible impact, qualifying it as low, especially on limestone aggregates [113] [114].

The structure of the Itz has been studied previously and 4 main models emerge, describing two main areas:

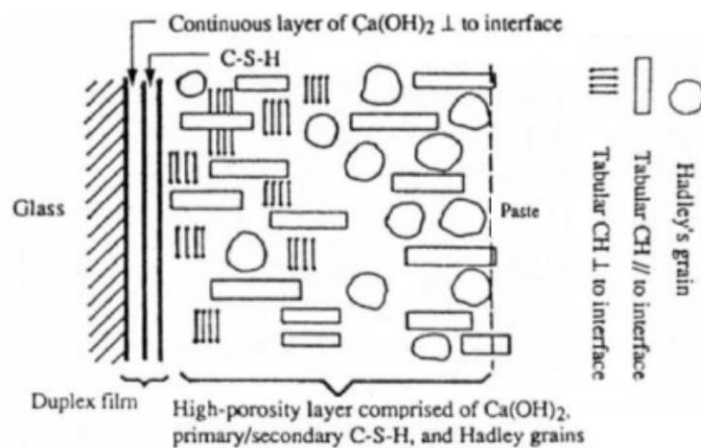
- 1) A duplex film consisting of a thick film of  $0.5\ \mu\text{m}$  of preferentially oriented portlandite crystals, superimposed on a C-S-H film of the same thickness according to Barnes [115]. On the other hand, for Zimbelmann [116], Monteiro [115] and Bentur [115], the duplex film is  $2\ \mu\text{m}$  to  $3\ \mu\text{m}$  thick (Fig. 1.28) and consists of large cleaved portlandite crystals and ettringite.
- 2) This zone is  $20\ \mu\text{m}$  thick according to Barnes [117] but is  $50\ \mu\text{m}$  thick for Zimbelmann [116] (Fig 1.28).

The authors also differ in its composition:

- a) It would consist of large portlandite crystals and C-S-H [117];
- b) Entangled ettringite crystals (according to Zimbelmann [116]);
- c) Hadley grains (Fig 1.29) (for Monteiro (1986)).



**Figure 1.28:** ITZ model according to Zimbelmann [116].



**Figure 1.29:** ITZ model according to Barnes [115].

## 2.3 CONCLUSION

Sediments are silico-clay-limestone materials, resulting from erosion/deposit phenomena and possessing specific properties. They are essentially consisting of:

- A mineral matrix (quartz, feldspars or carbonates, etc). Clay fractions (kaolinite, montmorillonite, illite or smectites);
- The organic fraction (plant debris, microorganisms, humin, fulvic and humic acids);
- A relatively high water content, and the presence of various organic and mineral pollutants.

Due of their fineness, the clay fraction and the organic matter present in different successive or concomitant transient forms, are favourable to the capture of certain mineral contaminants (Pb, Cr, Zn etc.) or organic (HAP, PCB, etc); they are fixed in clay-humic complexes.

Like thermal, physical or chemical methods, treatment techniques aim to eliminate a specific fraction, or to improve certain target properties, or to modify other physicochemical characteristics of the material. In our studies, physical (grinding) and thermal (calcination) techniques are preferred because of their ability to activate the material and thus allow the efficient use of sediments as mineral addition in cementitious matrices.

Current regulations allow us to set threshold values, defining the dangerousness and the possibility of use in the recovery industries. The GEODE (N1 and N2) and ISDI thresholds will be referred to in our study cases.

Cementitious material is always a conglomerate of several compounds: hydration results. The effects of the presence of sediment need to be properly assessed. There are two categories of pores in cementitious matrices. The fine pores ( $\leq 100 \text{ \AA}$ ) of CSH and capillary pores in the order of  $\leq 1000 \text{ \AA}$  which can be modified at various levels by the presence of mineral additions in general and fine sediments in particular.

Subsequently, the second part of this work will be devoted to the presentation of the main experimental methods that will be used both in the formulation methods and in the study of the physicochemical impact of the presence of sediments on the cementitious matrix.

# CHAPTER 3

## MATERIALS AND METHODS

---

3.1	CEMENT .....	52
3.2	MINERAL ADDITIONS .....	53
3.2.1	Dredged sediments .....	53
3.3	PHYSICAL AND CHEMICAL CHARACTERISTICS OF MATERIALS USED .....	54
3.4	PREPARATION OF MORTARS .....	54
3.5	SETTING TIME .....	55
3.6	MECHANIC PERFORMANCES .....	55
3.7	MERCURY POROSITY .....	55

---

### **3.1 INTRODUCTION**

The SURICATES project aims to increase the reuse of sediments from ports and canals in North-Western Europe for the flood and erosion control. It also aims to put in place new solutions and methods, to increase the application of sediments with a large volume in projects operated by the territories. Managers will have the role of protecting and optimising costs and benefits; to find a sustainable solution to the authorities and managers of the port and waterways.

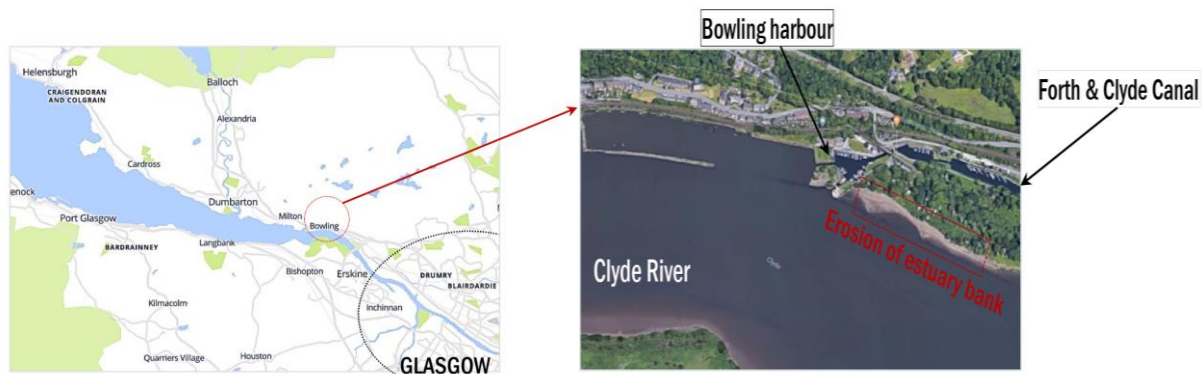
Dredged sediments are one of the largest potential waste streams according to regulations; with a quantity of 200Mt/year. They are part of our potential mineral resources for recovery in civil engineering and environmental protection. Sediments are eligible for a circular economy thinking, with an application in the circular's context economy to take part in a global approach for climate change mitigation, reducing major risks and consuming natural resources (SedNet, 2019). The amount of dredged sediments for access to European ports and waterways represents 200 Mt/year, of which it will manage 80 million tonnes. More than 99% of the dredged marine sediments are returned to the sea, managed as waste with only 1% (0.8Mt/year) being reused.

The SURICATES project aims to use 220,000 tonnes of sediment as a raw material in 4 new solutions to build protection systems. It aims to valorize 1.3Mt/year of fine sediments in 5 years, and 2.3Mt/year within 10 years in the European Union. We will reuse these fine sediments for eco-innovative solutions, with a 25% increase in reuse compared to the current quantity (200,000 tonnes). This project will have a large scale potential on other tested and operated sites (European Circular Economy Policy). It aims at an EU strategy on waste and sustainable transport by waterway.

The aim of this scientific work is the valorization of Scottish sediments in civil engineering, 12 samples from the SURICATES project have been analysed:

- 5 samples from the Laggan of Scotland (Caledonian Canal) (C1, C2, C3, C4, C5).
- 4 samples from Glasgow Bowling (Forth & Clyde) (B1, B2, B3, B4).
- 3 samples from Glasgow (Forth&Clyde) (G1, G2, G3).

Figure 1.30 shows the sampling sites in Scotland. We continued the experimental work with a full characterisation of the study samples.



**Figure 1.30:** Sampling sites in Scotland.

### 3.2 CEMENT

The kind of cement used in the different mortar formulation is Portland cement CEM I 52,5N that has been used with European standard EN197-1 (2012). The Bogue composition for this cement is presented in Table 1.11 It has an absolute density of  $3.15\text{g/cm}^3$  according to the NFP 18-555 standard. This cement consists of clinker between 95 to 100% and between 0 to 5% secondary constituents (gypsum).



**Table 1. 11:** Mineralogical composition and characteristics of cement.

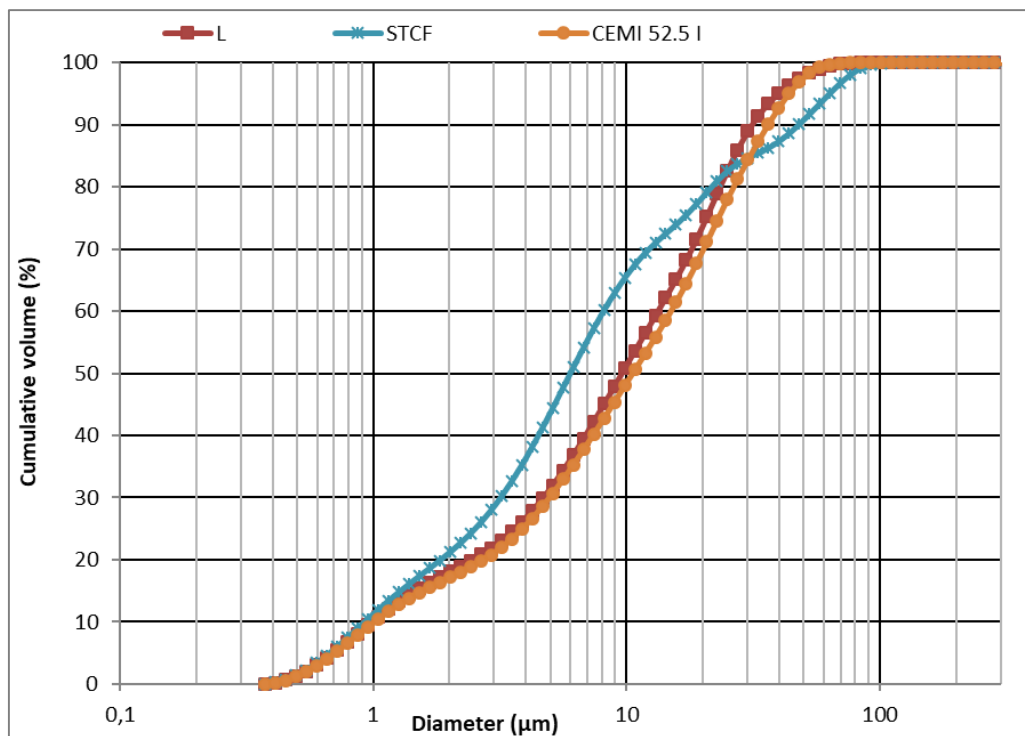
	Density (g/cm <sup>3</sup> )	BET surface area (cm <sup>2</sup> /g)	LOI (%)	C <sub>2</sub> S <sup>a</sup> (%)	C <sub>3</sub> S <sup>a</sup> (%)	C <sub>3</sub> A <sup>a</sup> (%)	C <sub>4</sub> AF <sup>a</sup> (%)
<b>Cement</b>	3.15	9194	1.9	6.55	67.33	7.76	10.35

<sup>a</sup> Cement chemistry abbreviations: *C* CaO, *S* SiO<sub>2</sub>, *A* Al<sub>2</sub>O<sub>3</sub>, *F* Fe<sub>2</sub>O<sub>3</sub>.

### 3.3 MINERAL ADDITIONS

We used in our study two types of additions: the calcined dredged sediment (STCF) and blast furnace slag (L). The results obtained by the granulometry test are performed using a BEKMAN-COULTER LS13320 of these additions are presented in figure 1.31.

The laser granulometry analysis allows us to determine the granular particle distribution under 1 µm. The samples were also set to wet analysis. The particle size distribution of calcined sediment indicated a greater percentage of the fine particles compared to the blast furnace slag (L). It can be justified by the proportion of 90% of the calcined sediment particles which are less than 50µm compared to 70% for blast furnace slag.



**Figure 1.31:** Laser granulometry of calcined sediment (STCF), blast furnace slag (L) and cement (CEMI 52.5).

#### 3.3.1 Dredged sediments

The calcined dredged sediment (STCF) used in the formulation of mortar was brought from the Laggan Caledonian Canal site, which is located in the UK. The selected sample of the sediment was homogenized, and all organic residues of grass removed. It was next dried,



sterilized at 60°C then crushed and sieved 80µm. After that, sediment calcined using the direct calcination method at 750°C in the laboratory [118].

### 3.4 PHYSICAL AND CHEMICAL CHARACTERISTICS OF MATERIALS USED

Table 1.12 illustrates the physical characteristics of the materials used, the cement density is 3,21, the blast furnace slag is 2,91 and the calcined sediment is 2,64. Calcined sediments have the highest specific surface area with the lowest heat treatment and with a higher water demand of 53% [119].

**Table 1. 12:** Physical characterization of materials used.

	<b>Cement</b>	<b>BFS</b>	<b>Calcined sediment</b>
<b>Density (g/cm<sup>3</sup>)</b>	3.21	2.91	2.64
<b>BET (cm<sup>2</sup>/g)</b>	9194	-	59930
<b>Water demand (%)</b>	32	33	53

Table 1.13 summarizes the chemical elements results of the materials used. The analysis concerned determination of the proportion of every substance by X-ray Fluorescence (XRF). It has shown the presence of the principal chemical elements generally present in sediment material: Oxygen (45.7%), Silicon (2.56%) and Calcium (16,48).

These results are near those found in previous studies [120], [121] conducted on the valorisation of marine sediments. It is also noted that the chemical composition values of the materials used were lower the threshold values. The sediments studied are classified as non-hazardous waste, according to French law.

**Table 1. 13:** Chemical composition of materials used.

<b>Element</b>	<b>Al</b>	<b>Ca</b>	<b>Cl</b>	<b>Cr</b>	<b>Fe</b>	<b>K</b>	<b>Mg</b>	<b>Mn</b>	<b>Na</b>	<b>O</b>	<b>P</b>	<b>S</b>	<b>Si</b>	<b>Sr</b>	<b>Ti</b>	<b>Zn</b>
<b>Cement</b>	2.7	43.5	0.1	-	2.8	0.6	0.7	-	0.5	38.9	0.2	1.8	7.6	0.1	0.2	0.2
<b>Sediment</b>	5.11	16.48	1,47	Traces	6.22	1.56	1.49	0.12	1.55	45.7	0.18	2.56	16.92	Traces	0.27	0.09
<b>Blast furnace slag</b>	5.71	29.14	Traces	-	0.37	0.38	3.76	0.15	0.25	43.7	-	0.68	15.29	Traces	0,4	-

### 3.5 PREPARATION OF MORTARS

Several mortar formulations were prepared using a CEM I, slag and calcined sediments as illustrated in Table 1.14. The main variables considered in this formulation were slag and

calcined sediment. According to the standard (EN 196-1), a reference mortar was made up of one-part cement ( $450\text{kg/m}^3$ ), three parts sand and half apart water, with a  $W/B=0.5$  ratios. A second mortar with addition was obtained by the mass replacement of a cement fraction of around 50% by blast furnace slag. Three other mortars were made by replacing a 50% fraction of cement with slag and calcined sediments, and slag was also substituted with a rate of 10%, 15% and 20% by calcined sediments.

**Table 1. 14:** Composition of the different mortar formulations.

<b>Composition of mixtures</b>			
<b>Naming</b>	<b>Cement (%)</b>	<b>Blast furnace slag (%)</b>	<b>Sediment (%)</b>
<b>C</b>	100	0	0
<b>L</b>	50	50	0
<b>STCF10</b>	50	40	10
<b>STCF15</b>	50	35	15
<b>STCF20</b>	50	30	20

### 3.6 SETTING TIME

The test consists of measuring the setting time on an all binders paste, of normal consistency, using the Vicatronic 106 091 device. According to the standard NF EN 196-3.

### 3.7 MECHANIC PERFORMANCES

For compressive strength, determination several prismatic sample  $4*4*16$  cm (NF EN 196-1) were tested at each following ages 14, 28, 60 and 90 days' maturation. To evaluate the compression strength and flexural strength of the mortar, all mortars were conserved at a temperature of  $20\text{ }^{\circ}\text{C}\pm 2\text{ }^{\circ}\text{C}$ . The compressive strength tests were realized with a load rise of  $2400\text{N/s} \pm 200\text{N/s}$ . The flexural strength tests were carried out with the speed loading of  $50\text{N/s} \pm \text{N/s}$ .

### 3.8 MERCURY POROSITY

Porosity measurement was performed utilizing a mercury porosity technique on mortar fragments (NF p 94-410-3). This method gives quick access to pore dispersion, with great precision in the scope of  $3\text{nm}$  to  $360\mu\text{m}$  and the mercury pressure extends stress of  $30,000\text{ psi}$  ( $206\text{ MPa}$ ) [122], [123].

# CHAPTER

# 4

## RESULTS AND ANALYSES

---

4.1	THERMO GRAVIMETRIC ANALYSIS (TGA) .....	56
4.2	PHYSICAL CHARACTERISATION .....	57
4.3	DIFFRACTION ANALYSIS (XRD) .....	59
4.4	THERMOGRAVIMETRIC ANALYSIS (TGA) .....	59
4.5	SITTING TIMES .....	61
4.6	MECHANICAL PERFORMANCE .....	62
4.6.1	Compressive strength of mortars .....	62
4.6.2	Flexural strength of mortars .....	63
4.7	MERCURY POROSITY .....	63
4.8	CONCLUSIONS .....	64

---

### **4.1 THERMO GRAVIMETRIC ANALYSIS (TGA)**

The ATG (Thermo Gravimetric Analysis) analysis technique allows to follow over time, the mass fluctuations of a material sample exposed to a thermal and physicochemical controlled environment. It is also ideal for monitoring emissions such as gases (CO<sub>2</sub>, CO, etc.) or water losses (H<sub>2</sub>O). This can be very useful for sediment, which is relatively heterogeneous and initially muddy (figure 1.33).

Significant transformations occur between 100°C and 750°C. Indeed, between 100°C and 450°C, the elimination of absorbed water and bound water is mainly observed. As well as the elimination of the organic fraction and the reactions related to the various pollutants present (HAP, PCB, TBT, etc.). Also, the observed modifications can be mineralogical, in particular, the beginning of clay transformation (Kaolin MetaKaolin) at 550°C and the decomposition of carbonates at 730°C [12]. The CO<sub>2</sub> peak appearing between 600°C and 750°C is induced by the probable decarbonisation of calcite [12].

The analysis of the TGA curve also allows several interpretations to be made as to the Physico-chemical composition of the material. Carbon monoxide (CO) release is related to the incomplete oxidation reaction of organic matter and other organic compounds.

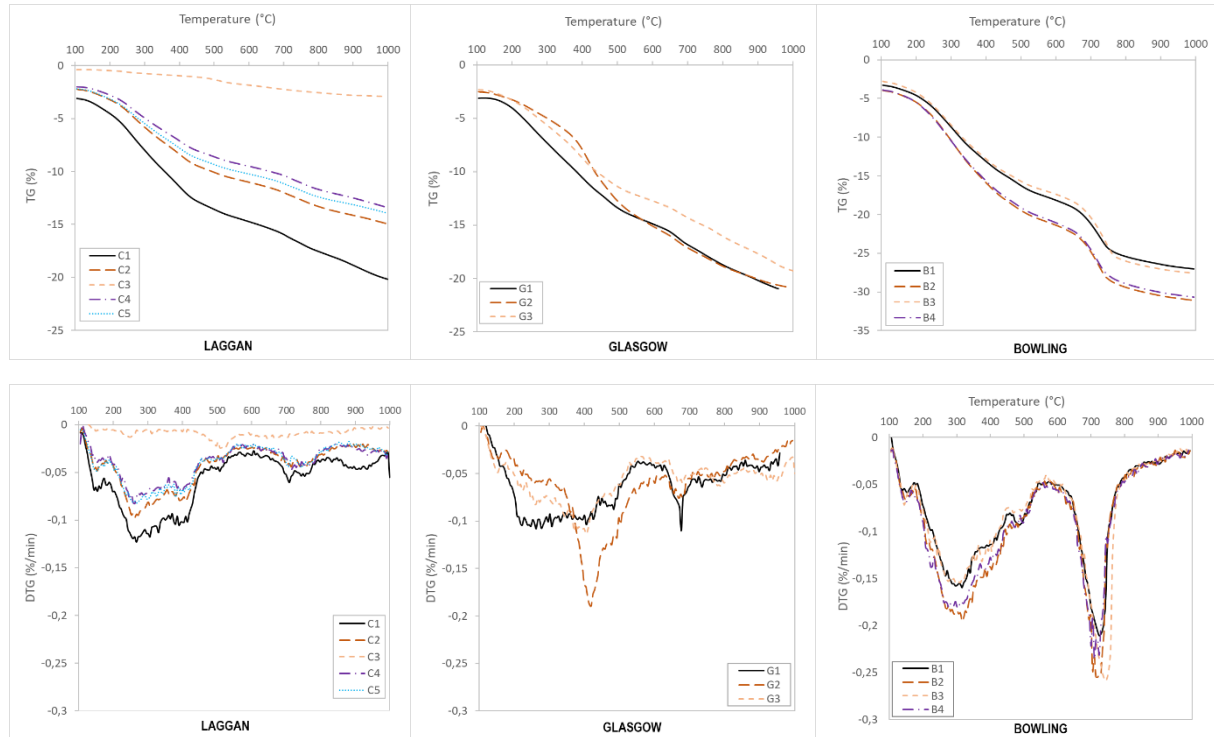


Figure 1.33: TGA/TDS analysis of raw sediment (SB).

## 4.2 PHYSICAL CHARACTERISATION

The physical characterisation showed that the samples from the Caledonian Canal (C1, C2, C3, C4, C5), have a very high potential for valorization as a pozzolanic addition. The Glasgow Bowling (Forth & Clyde) samples (B1, B2, B3, B4) have a potential for valorization as aggregates, on the other hand, the Glasgow (Forth & Clyde) samples (G1, G2, G3) are not recommended for valorization in concrete, due to their high organic matter and zinc content (Table 1.15).

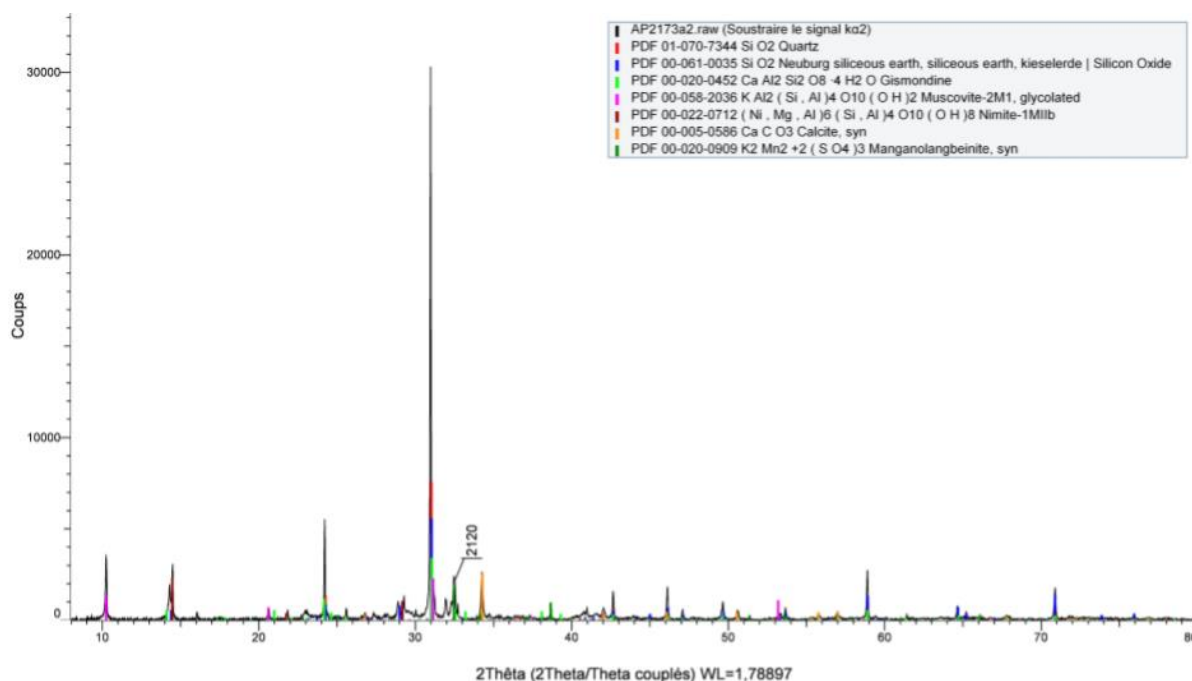
Based on TGA analyses and physical characterization of all sediment samples from Scotland, the Caledonian Canal C2 sample shows the best potential for pozzolanic addition. These results show very high potential for partial substitution of the C2 sample to the cement. In the continuation of this experimental work, the choice focused on the sample C2 of Caledonian channel.

15: Porosity of the cementitious matrix studied.

Sediment		Substitute for sand/pozzolanic addition: hypotheses at this stage	Specific density (g.cm <sup>-3</sup> )	LOI - 450°C (%)	LOI - 550°C (%)
C1	LAGGAN/Caledonian Canal	Substitute for sand/pozzolanic addition	2.29	18.17	18.83
C2		Good candidate for the pozzolanic addition	2.47	13.60	14.17
C3		Definetly substitute for sand	2.74	0.94	1.47
C4		Substitute for sand/pozzolanic addition	2.51	11.37	11.96
C5		Substitute for sand	2.48	12.51	13.05
B1	Forth&Clyde - BOWLING	Substitute for sand (concrete block with sediment) while taking care of the setting time due to heavy metals and organic matter.  Poor reliability of calcination (use as pozzolanic material) due to the low content of clay-loam and high levels of organic matter.	2.29	22.87	23.86
B2			2.23	27.27	28.16
B3			2.23	24.78	25.88
B4			2.23	26.26	27.37
G1	Forth&Clyde - GLASGOW	The high content of organic matter and	2.37	19.19	21.54
G2		Zinc : not recommended for both	2.08	33.19	35.43
G3		applications	2.47	15.36	17.95

### 4.3 DIFFRACTION ANALYSIS (XRD)

Figure 1.34 shows XRD diffractograms of dredged sediment (C2), it used to find the qualitative mineral composition of the tested samples, it is essentially made out of some crystalline minerals and amorphous phases; which indicates that the samples are rich in muscovite, illite and quartz, as properly as albite [124]–[127].



**Figure 1.34:** XRD mineralogical analysis of dredged sediment (C2).

### 4.4 THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermogram achieved by the thermogravimetric and differential thermal analysis (TG/DTA) of raw sediment C2 (fig 1.35), and at a heating rate of 5° C/min in temperatures that varied from 100 to 1000 °C; this thermal method can determine a relationship between mass loss of raw sediment and temperature treatment. The results are presented in fig. For raw sediments.

Dehydration phase [100 – 150 °C]: at low temperature the free water and some of the interlayer water escape from the raw material. Followed by little loss of mass of raw sediment that shows that a more loss of mass maybe because of the bloating capacities of this raw sediment (rich in Muscovite and low-crystalline illite) [128]–[131].

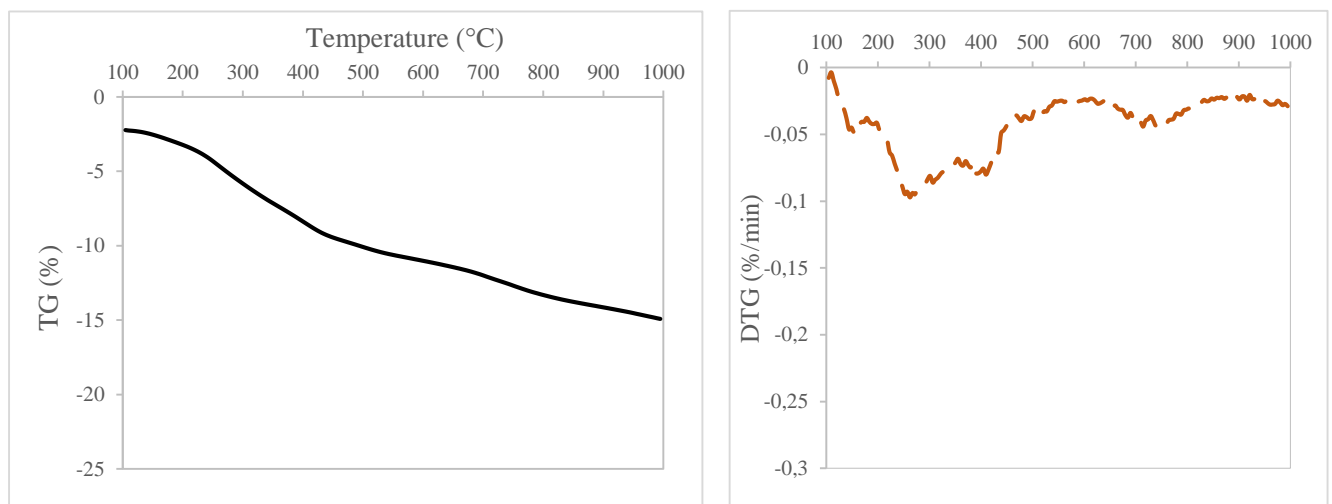
Dihydroxylation phase [450 – 709 °C]: the mass loss was seen from 450 °C to 709 °C. The loss of H<sub>2</sub>O likely relates to the water content of clay minerals from the OH groups contained in the clay Dihydroxylation results an endothermic peak and loss of mass [129], [132]. The decomposition of the organic matter was seen between 450°C and 550°C, and at this range

numerous chemical reactions may happen: As kaolinite is changed to metakaolin there is also a structural transformation from octahedral aluminium coordination to tetrahedral which prompts to a loss of crystalline [133], and the transition of a -quartz, which is the most steady  $\text{SiO}_2$  polymorph at ambient temperature, to b-quartz [134]. The change of illite into dehydrated illite, prevails to the layered structure of the original illite [125], [135].

Decarbonisation phase [758 - 930 °C] at this level, the limestone ( $\text{CaCO}_3$ ) is decomposed into calcium oxide, CaO with emissions of Carbone dioxide ( $\text{CO}_2$ ), however, note that the heating rate importantly affects the temperature of calcite decomposition [130], [136]. The decarbonisation of calcite is related to loss of mass [129]. The residual CaO created as the calcite, may impact the reactivity of this calcined sediment [124], [125].

Recrystallisation phase: it's associate to an exothermic change without a loss of mass that restructures the material. The recrystallisation of these structurally disordered substances (amorphous phases) into greater stable high-temperature crystalline stages at temperatures over tan 900 C, can also result in a loss of pozzolanic reactivity [128], [130]. The best effective temperature for calcination acquires pozzolanic material should be between the end of dehydroxylation and also the starting of recrystallisation [137], which means in the range of 700 and 900 C when utilizing sediment.

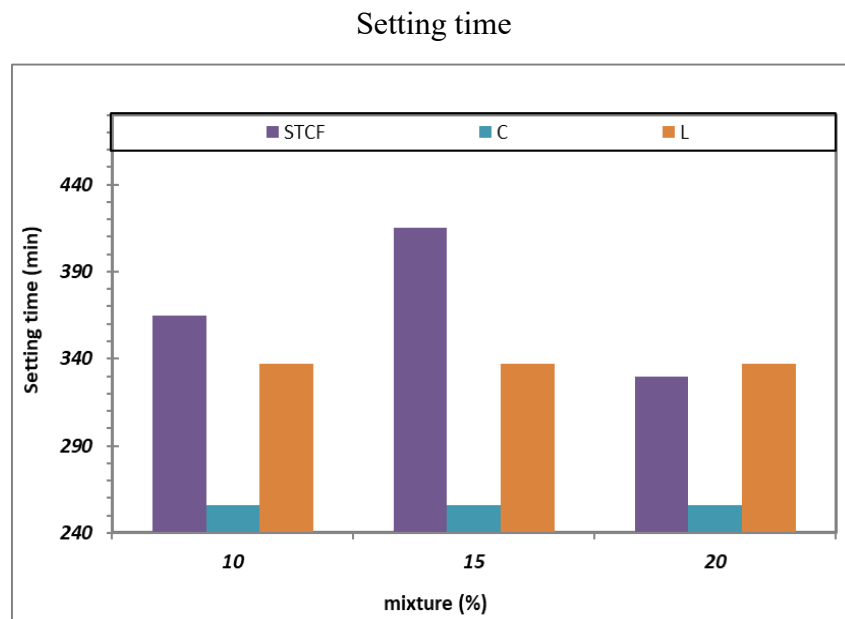
The evaluation affirms the preference of the calcination temperatures, which is over the optimum of 750 °C.



**Figure 1.35:** DTA/TG analysis of dredged sediment (C2).

## 4.5 SITTING TIMES

The results relative to setting times of the different components of mortars are shown in figure 1.36.



**Figure 1.36:** Influence of calcined sediment content on the setting time.

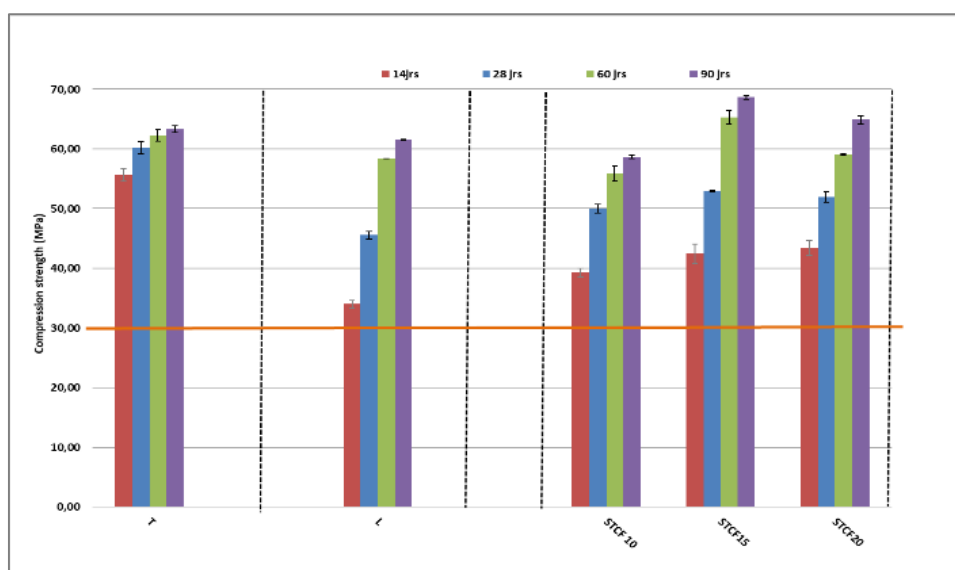
The substitution of cement by slags and calcined sediments changes the demand for water and the normalized consistency and consequently the setting time of the different binders (Fig. (1.32)). Hydration allows the formation of calcium silicate hydrate gel (C-S-H), the formation of portlandite (CH) and ettringite ( $C_3A \cdot 3CS \cdot H_{32}$ ). Hydrates precipitation is due to the dissolution of the anhydrous compounds, which starts to produce ionic constituents ( $Ca^{+2}$ ,  $OH^-$ ,  $Na^+$ , ...) then the formation of hydrates in the solution. Hydration in the solid-state takes place directly on the surface of the anhydrous cement compounds [130], [138]. Figure 1.32 shows that the setting time is directly influenced by the rate of substitution by calcined sediments, a slight decrease in setting time was observed compared to the increase in the rate of substitution. An increase in the fineness of the new binders is strongly due to the substitution rate of calcined sediments [129], [139]. Generally, the setting time of the different pastes is not greatly affected by the presence of calcined sediments; up to a 20% substitution rate.



## 4.6 MECHANICAL PERFORMANCE

### 4.6.1 Compressive strength of mortars

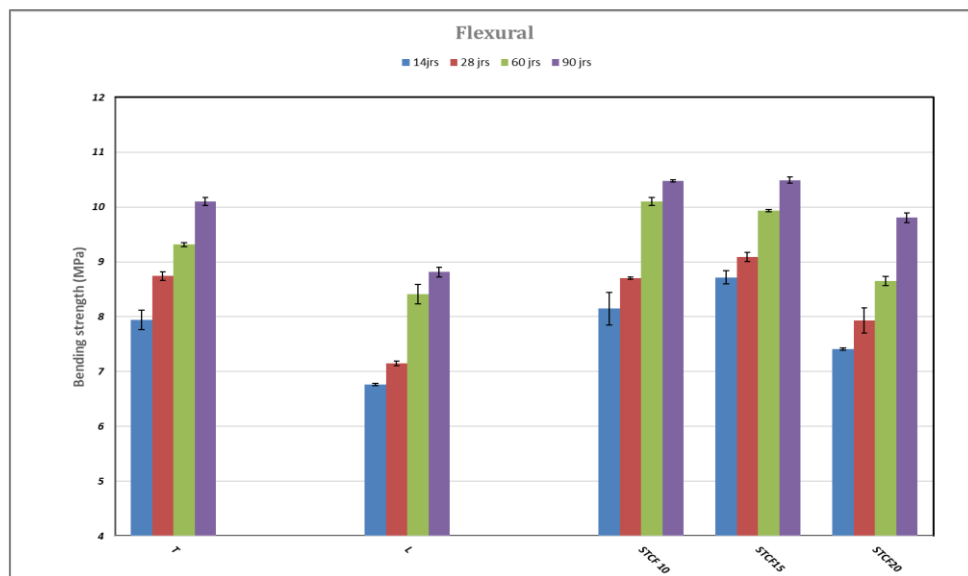
The results of the evolution of the compressive strength of mortar, formulated with slag and calcined sediment, are shown in figure 1.37. From these figures, the results of the compressive strengths of mortars based on 50% cement and 50% of blast furnace slags show a decrease in compressive strengths of 34 Mpa and 45 Mpa; after 14 days and 28 days. This is in comparison with the control mortar, which presents resistances of the order of 56 Mpa and 60 Mpa; respectively after 14 and 28 days. The impact of the slag contribution of strength during the early age isn't visible, however, at a later age, it looks to be more significant [140], [141]. Mortars based on 50% cement and a substitution dosage of slag by calcined sediments of the order of 10, 15 or 20%, show a slight improvement in compressive strength of the order of 39Mpa, 43Mpa or 44Mpa. A linear increase in compressive strengths was maintained for 60 days and 90 days, for the different types of mortars based on partial substitution of cement by slag and calcined sediments. Improvements in the compressive strengths of mortars composed of 50% cement, 35% slag and 15% calcined sediment were observed after 60 days and 90 days. This affirms previous results announced by Bougara [142]–[144], which exhibit that the early strength is essentially dictated by the fineness of the OPC fraction and later by the slag fraction. These improvements in compressive strength were from 106.45% at 60 days and 107.93% at 90 days. These same results are consistent with what has been described in the literature regarding the substitution of cement by slag [142], [143], [145] and calcined sediments [119], [127], [129], [146], [147].



**Figure 1.37:** Compressive strength of mortars with slag and calcined sediment.

### 4.6.2 Flexural strength of mortars

The effects of the flexural strength development of mortar specimens formulated with slag and calcined sediment are clearly shown in Figure 1.38 where it is easily observed that the flexural strength of all mortars increment consistently with age, and shows no decrease in strength. From our investigation, it tends to be expressed that generally, the incorporation of slag and calcined sediment allows in enhancing the flexural strengths, at all substitution rates.



**Figure 1.34:** Flexural strength of mortars with slag and calcined sediment.

### 4.7 MERCURY POROSITY

Table 1.15 shows the total volume of porosity (P) values.

**Table 1. 15:** Porosity of the cementitious matrix studied.

Porosity of the cementitious matrix (%)	14 days	28 days	60 days	90 days
<b>T</b>	12,46	11,87	11,33	11,1
<b>L</b>	16,44	12,55	11,33	8,25
<b>STCF10</b>	12,37	8,81	8,39	7,89
<b>STCF15</b>	11,84	10,58	8,85	7,12
<b>STCF20</b>	12,1	10,45	9,52	8,81

Table 1.15 shows a linear decrease in porosity with age for all mortars studied. However, a higher porosity can be observed at 14 days and 28 days, for mortars based on 50% cement and 50% slag. This variation is typical. It is the consequence of the latent hydration of the slag in Portland cement. This is widely confirmed in the literature [148]. The mortar based on 50%

cement and 50% slag (L) is coarser than the control mortar (T) (Table 1.15). For 60 days, and especially after 90 days of curing; the pore size distribution of cement-based mortars substituted by slag and calcined sediments of the order of 10%, 15% and 20%; has evolved considerably into small pores. These results can be explained by the hydration of the slag and calcined sediments; after the consumption of lime (CH); leading to the formation of additional "CSH" gels which contribute to the densification of the porous structure of the matrix [149], [150].

#### 4.8 CONCLUSIONS

The fight against sedimentation, therefore, represents a considerable challenge, ports and canals creating a reservoir that constitutes a large sediment pit and which, over the years of sedimentation deposits will reduce the expected storage capacity. Sedimentation control is always possible by hydraulic or mechanical dredging operations. Disposal areas are planned to receive the excavated material and create storage areas in the vicinity. It is imperative to think about eliminating them. The best way would be to recycle them. This study aims to use slag and calcined sediment from Scotland (of pozzolanic character) as a partial replacement in Portland cement. This would permit acquiring binders with comparable characteristics or greater than Portland cement without additions.

From the results of our experimental investigation, it is clear that this study has shown:

- On the one hand, these results reduce the environmental impact of re-using dredging sediment from ports and canals in North-West Europe to combat flooding. Sediments are eligible in the circular economy thinking through the application of a global approach, to mitigate impacts of climate change, the reduction of major risks and natural resource consumption; by partial substitution of cement for slags and calcined sediments.
- On the other hand, these same results reduce the financial costs of dredging, through the valorisation of calcined sediments and slag; as co-products in the manufacture of cement.
- The physical and chemical characterization of the calcined sediments revealed a good pozzolanic character that can be valorised as a co-product in the cement industry.
- Mineralogical analysis (DRX) of dredged sediments has shown that Scottish sediments are rich in Muscovite, illite, quartz and albite.
- The thermogravimetric analysis (TGA/DTG) confirmed the metastable and crystalline state of the sediments, as well as the pozzolanic effect of the calcined sediments by the appearance of a non-crystalline phase detected by the DTG curves. This allowed the determination of the

optimum calcination temperature giving an artificial pozzolanic material; which can be used as a partial substitute for cement: the temperature range for the amorphisation of Scottish sediments is between 600°C and 900°C.

- These results show that setting time is directly influenced by the rate of substitution of calcined sediments. A slight decrease in setting time was observed when the substitution rate increased. The increase in the fineness of the new binders is strongly due to the rate of substitution by calcined sediments.
- The evolution of the compressive strength of mortars has shown a linear increase in compressive strength for 90 days, for the different types of mortars based on partial substitution of cement by slag and calcined sediments. The best compressive strengths were observed in mortars composed of 50% cement, 35% slag and 15% calcined sediment; and this after 60 days and 90 days.
- The porosity of mortars based on partial substitution by slag and calcined sediments is greater than that of a mortar without addition at an early age. However, in the long-term these mortars develop a more refined pore size distribution; particularly for mortars composed of 50% cement, 35% slag and 15% calcined sediment; and this after 60 days and 90 days.
- Finally, it can be said that the addition of calcined sediments from Scotland can give an artificial pozzolan character. This saves significant amounts of energy.

# BIBLIOGRAPHICAL REFERENCES

- [1] Gary Laustsen : Reduce–recycle–reuse : guidelines for promoting perioperative waste management. *AORN journal*, 85(4):717–728, 2007. [https://doi.org/10.1016/S0001-2092\(07\)60146-X](https://doi.org/10.1016/S0001-2092(07)60146-X).
- [2] KE Noll, CN Haas et JW Patterson : Recovery, recycle and reuse : of hazardous waste. *Journal of the Air Pollution Control Association*, 36(10):1163–1168, 1986. <http://dx.doi.org/10.1080/00022470.1986.10466165>.
- [3] Ciaran J Lynn, Ravindra K Dhir, Gurmeh S Ghataora et Roger P West : Sewage sludge ash characteristics and potential for use in concrete. *Construction and Building Materials*, 98:767–779, 2015. <http://dx.doi.org/10.1016/j.conbuildmat.2015.08.122>.
- [4] Dongxing Wang : *Solidification et valorisation de sédiments du port de Dunkerque en travaux routiers*. Thèse de doctorat, Université de Lille 1- Ecole des Mines de Douai, 2011. [5] Ministère de l’environnement et du développement durable : Groupe de travail numéro 11 – sédiments de dragag. Rapport technique, 2011. <http://www.developpement-durable.gouv.fr/IMG/pdf/G11-2.pdf>.
- [6] Vincent Dubois, Nor Edine Abriak, Rachid Zentar et Gérard Ballivy : The use of marine sediments as a pavement base material. *Waste Management*, 29(2):p774 – 782, 2009. <http://dx.doi.org/10.1016/j.wasman.2008.05.004>.
- [7] Abdelhafid Kasmi, Nor-Edine Abriak, Mahfoud Benzerzour et Hassane Azrar : Effect of dewatering by the addition of flocculation aid on treated river sediments for valorization in road construction. *Waste and Biomass Valorization*, 3(8):585–597, 2016.
- [8] Valérie Cappuyns, Valentine Deweirt et Sandra Rousseau : Dredged sediments as a resource for brick production : Possibilities and barriers from a consumers’ perspective. *Waste Management*, 38:p372 – 380, 2015. <http://dx.doi.org/10.1016/j.wasman.2014.12.025>.
- [9] Issameddine Khezami : *Approche expérimentale de valorisation des sédiments de dragage dans des applications de Génie Civil*. Thèse de doctorat, Lille 1, 2014.
- [10] Hongseob Oh, Juwon Lee, N Banthia, S Talukdar *et al.* : An experimental study of the physicochemical properties of a cement matrix containing dredged materials. *Materials Sciences and Applications*, 2(07):p847, 2011. <http://dx.doi.org/10.4236/msa.2011.27115>.
- [11] Nadia BELAS, Salima AGGOUN, Abdelatif BENAÏSSA, Ali KHEIRBEK *et al.* : Valorisation des déchets naturels dans l’élaboration des nouveaux bétons et matériaux de construction. *20ème Congrès Français de Mécanique*, 28 août/2 sept. 2011-25044 Besançon, France (FR), 2011. <http://documents.irevues.inist.fr/handle/2042/46183>.
- [12] Tuan Anh Dang, Siham Kamali-Bernard et William Agbodjan Prince : Design of new blended cement based on marine dredged sediment. *Construction and Building Materials*, 41:602–611, 2013. <http://dx.doi.org/doi:10.1016/j.conbuildmat.2012.11.088>.
- [13] E Rozière, M Samara, A Loukili et D Damidot : Valorisation of sediments in selfconsolidating concrete : mix-design and microstructure. *Construction and Building Materials*, 81:1–10, 2015. <http://dx.doi.org/10.1016/j.conbuildmat.2015.01.080>.
- [14] Mahfoud Benzerzour, Mouhamadou Amar et Nor-edine Abriak : New experimental approach of the reuse of dredged sediments in a cement matrix by physical and heat treatment. *Construction and Building Materials*, 140:432–444, 2017. <https://doi.org/10.1016/j.conbuildmat.2017.02.142>.
- [15] Mahfoud Benzerzour, Walid Maherzi, Mouhamadou Amar, Nor-Edine Abriak et Denis Damidot : Formulation of mortars based on thermally treated sediments. *Journal of Material Cycles and Waste Management*, pages 1–12, 2017. <https://doi.org/10.1007/s10163-017-0626-0>.
- [16] J Limeira, M Etxeberria, L Agulló et Daniel Molina : Mechanical and durability properties of concrete made with dredged marine sand. *Construction and Building Materials*, 25(11):p4165–4174, 2011. <http://dx.doi.org/10.1016/j.conbuildmat.2011.04.053>.
- [17] R. San Nicolas, M. Cyr et G. Escadeillas : Characteristics and applications of flash metakaolins. *Applied Clay Science*, 83–84:p253 – 262, 2013. <http://dx.doi.org/10.1016/j.clay.2013.08.036>.
- [18] O. Rodríguez, L. Kacimi, A. López-Delgado, M. Frías et A. Guerrero : Characterization of algerian reservoir sludges for use as active additions in cement : New pozzolans for eco-cement manufacture. *Construction and Building Materials*, 40:p275 – 279, 2013. <http://dx.doi.org/10.1016/j.conbuildmat.2012.10.016>.
- [19] Christian Meyer : The greening of the concrete industry. *Cement and concrete composites*, 31(8):601–605, 2009. <https://doi.org/10.1016/j.cemconcomp.2008.12.010>.

- [20] Raili Kajaste et Markku Hurme : Cement industry greenhouse gas emissions–management options and abatement cost. *Journal of Cleaner Production*, 112:4041–4052, 2016. <https://doi.org/10.1016/j.jclepro.2015.07.055>.
- [21] Union nationale des industries de carrières et matériaux de construction : Rapport et statistiques sur les granulats. Rapport technique, UNICEM, 2015. <http://www.unicem.fr/wp-content/uploads/rapport-d-activite-2015-unicem.pdf>.
- [22] Richard Maillot : *Mémento technique des granulats*. Presses des MINES, 2001.
- [23] Infociments : Rapport d'activité 2016. Rapport technique, Infociments, 2016. <http://www.infociments.fr/telecharger/ST-G08-2015.pdf>.
- [24] A. Bouamrane, D. Chahidi ELOuazzani, L. Tiruta Barna et K. Mansouri : Valorisation des boues de papeterie comme matières premières secondaires dans les mortiers de ciment portland. 2013. [http://www.jmaterenvironsci.com/Document/vol5/vol5\\_N2/74-JMES-513-2013-Bouamrane.pdf](http://www.jmaterenvironsci.com/Document/vol5/vol5_N2/74-JMES-513-2013-Bouamrane.pdf).
- [25] A Zacco, A Gianoncelli, R Ardesi, S Sacrato, L Guerini, E Bontempi, G Tomasoni, M Alberti et LE Depero : Use of colloidal silica to obtain a new inert from municipal solid waste incinerator (mswi) fly ash : first results about reuse. *Clean technologies and environmental policy*, 14(2):291–297, 2012. <http://dx.doi.org/10.1007/s10098-011-0401-1>.
- [26] R Sinem Atgin, Omar El-Agha, Abdullah Zararsız, Ahmet Kocataş, Hatice Parlak et Gürdal Tuncel : Investigation of the sediment pollution in izmir bay : trace elements. *Spectrochimica Acta Part B : Atomic Spectroscopy*, 55(7):1151–1164, 2000. [http://dx.doi.org/10.1016/S0584-8547\(00\)00231-7](http://dx.doi.org/10.1016/S0584-8547(00)00231-7).
- [27] Pascal Grégoire : *Modèle conceptuel d'aide à la décision multicritère pour le choix négocié d'un scénario de dragage maritime*. Thèse de doctorat, Université d'Artois, 2004.
- [28] Jérôme Foucher : Valorisation des déblais sableux de dragage portuaire en france. Rapport technique, Ifremer, 2005.
- [29] Rapport d'activité du port autonome de dunkerque. Rapport technique, GPMD, 2015. <http://www.dunkerque-port.fr/index.php?cmpref=47247&lang=fr&module=media&action=Display>.
- [30] Souhila Kribi : *Décomposition des matières organiques et stabilisation des métaux lourds dans les sédiments de dragage*. Thèse de doctorat, INSA, Lyon, 2005.
- [31] Jocelyn Ramaroson : *Calcination des sédiments de dragage contaminés. Études des propriétés physico-chimiques*. Thèse de doctorat, INSA, Lyon, 2008.
- [32] Raouf Achour : *Valorisation et caractérisation de la durabilité d'un matériau routier et d'un béton à base de sédiments de dragage*. Thèse de doctorat, Douai, MINES, 2013.
- [33] Mouhamadou Amar, Mahfoud Benzerzour, Nor-Edine Abriak et Yannick MamindyPajany : Study of the pozzolanic activity of a dredged sediment from dunkirk harbour. *Powder Technology*, 320:748–764, 2017. <https://doi.org/10.1016/j.powtec.2017.07.055>.
- [34] Emmanuel Garbolino, Jean-Luc Aqua et Nor-Edine Abriak : Applicability of h14 protocol for sediments in order to consider their valorization : Limits and benefits. *Chemical Engineering Transactions*, 36:p631, 2014. <http://dx.doi.org/10.3303/CET1436106>.
- [35] Claude Alzieu *et al.* : Dragages et environnement marin : état des connaissances=dredging and marine environment : state of the art. Rapport technique, 1999. <http://archimer.ifremer.fr/doc/1999/rapport-1040.pdf>.
- [36] David Colin : *Valorisation de sédiments fins de dragage en technique routière*. Thèse de doctorat, Caen, 2003.
- [37] Tran Ngoc Thanh : *Valorisation de sédiments marins et fluviaux en technique routière*. Thèse de doctorat, Université d'Artois - Mines Douai, 2009.
- [38] Kay Hamer et Volker Karius : Brick production with dredged harbour sediments. An industrial-scale experiment. *Waste Management*, 22(5):p521–530, 2002. [http://dx.doi.org/10.1016/S0956-053X\(01\)00048-4](http://dx.doi.org/10.1016/S0956-053X(01)00048-4).
- [39] Baptiste Aanger, Isabelle Moulin, Emmanuel Perin, François Thery et Daniel Levacher : Utilisation de sédiments fins de barrage dans la fabrication de mortiers. *XIIIèmes Journées Nationales Génie Côtier-Génie*, 155:2–4, 2014. <http://dx.doi.org/10.5150/jngcgc.2014.105>.
- [40] M. Benzerzour, R. Mansi, N-E. Abriak et F. Becquart : Mathematical model for beneficial use of dredged sediments in road construction. *Journal of Catalytic Materials and Environment*, pages 1–6, 2014. [http://www.ijeit.com/Vol%203/Issue%205/IJEIT1412201311\\_34.pdf](http://www.ijeit.com/Vol%203/Issue%205/IJEIT1412201311_34.pdf).
- [41] Thierry Sedran : *Rhéologie et rhéométrie des bétons. Application aux bétons autonivelants*. Thèse de doctorat, 1999.
- [42] A. Lecomte, J.M. Mechling et C. Diliberto : Indice de serrage des pâtes de consistance normale. pages p1–12, 2006. <http://www-lmdc.insa-toulouse.fr/RF2B/Actes-RF2B-2006/%25pdf-Lecomte.pdf>.
- [43] Jean Bolomey : Granulation et prévision de la résistance probable des bétons. *Travaux*, 19(30):p228–232, 1935. <http://dx.doi.org/10.5169/seals-47570>.

- [44] Jean Bolomey : Durcissement des mortiers et bétons. 1928. <http://dx.doi.org/10.5169/seals-41091>.
- [45] Jean Bolomey : Détermination de la résistance à la compression des mortiers et bétons. pages p126–134, 1925. <http://dx.doi.org/10.5169/seals-39509>.
- [46] Jacques Baron et René Lesage : La composition du béton hydraulique du laboratoire au chantier. LCPC, 1976.
- [47] Martin Cyr : *Contribution à la caractérisation des fines minérales et à la compréhension de leur rôle joué dans le comportement rhéologique des matrices cimentaires*. Thèse de doctorat, INSA de Toulouse ; Université de Sherbrooke, 1999.
- [48] M.P. de Luxán, F. Madruga et J. Saavedra : Rapid evaluation of pozzolanic activity of natural products by conductivity measurement. *Cement and concrete research*, 19(1):p63–68, 1989. [http://dx.doi.org/10.1016/0008-8846\(89\)90066-5](http://dx.doi.org/10.1016/0008-8846(89)90066-5).
- [49] J Payá, M.V Borrachero, J Monzó, E Peris-Mora et F Amahjour : Enhanced conductivity measurement techniques for evaluation of fly ash pozzolanic activity. *Cement and Concrete Research*, 31(1):41 – 49, 2001. [http://dx.doi.org/10.1016/S0008-8846\(00\)00434-8](http://dx.doi.org/10.1016/S0008-8846(00)00434-8).
- [50] B. Uzal, L. Turanlı, H. Yücel, M.C. Göncüoğlu et A. Çulfaz : Pozzolanic activity of clinoptilolite : A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan. *Cement and Concrete Research*, 40(3):398 – 404, 2010. <http://dx.doi.org/10.1016/j.cemconres.2009.10.016>.
- [51] Jean-Michel Mechling : *Formulation de bétons courants avec les grès du Luxembourg et les kieselguhrs usagés des brasseries*. Thèse de doctorat, Université Henri Poincaré, Nancy 1, 2000.
- [52] A.L.G. Gastaldini, M.F. Hengen, M.C.C. Gastaldini, F.D. do Amaral, M.B. Antolini et T. Coletto : The use of water treatment plant sludge ash as a mineral addition. *Construction and Building Materials*, 94:513 – 520, 2015. <http://dx.doi.org/10.1016/j.conbuildmat.2015.07.038>.
- [53] Valdecir Angelo Quarcioni, Fabiano Ferreira Chotoli, Antonio Carlos Vieira Coelho et Maria Alba Cincotto : Indirect and direct chapelpe's methods for the determination of lime consumption in pozzolanic materials. *Revista IBRACON de Estruturas e Materiais*, 8(1):1–7, 2015. <http://dx.doi.org/10.1590/S1983-41952015000100002>.
- [54] S. Donatello, M. Tyrer et C.R. Cheeseman : Comparison of test methods to assess pozzolanic activity. *Cement and Concrete Composites*, 32(2):121 – 127, 2010. <http://dx.doi.org/10.1016/j.cemconcomp.2009.10.008>.
- [55] Alejandra Tironi, Monica A. Trezza, Alberto N. Scian et Edgardo F. Irassar : Assessment of pozzolanic activity of different calcined clays. *Cement and Concrete Composites*, 37:319 – 327, 2013. <http://dx.doi.org/10.1016/j.cemconcomp.2013.01.002>.
- [56] Ciarán J. Lynn, Ravindra K. Dhir, Gurmeh S. Ghataora et Roger P. West : Sewage sludge ash characteristics and potential for use in concrete. *Construction and Building Materials*, 98:767 – 779, 2015. <http://dx.doi.org/10.1016/j.conbuildmat.2015.08.122>.
- [57] Roland Boutin : *Dragage et rejets en mer : les produits de type vase*. Presses de l'école nationale des ponts et chaussées, 2000.
- [58] Jacques Beauchamp : "sediments et roches sédimentaires". <https://www.u-picardie.fr/beauchamp/>, 2013.
- [59] G. Schneider : Boues de curage des cours d'eau. *Le courrier de l'environnement de l'INRA*, 43:p146–147, 2001. <http://www7.inra.fr/dpenv/curage.htm#1A>.
- [60] Administration Wallonne : Rapport analytique. Rapport technique, 2006-2007. <http://etat.environnement.wallonie.be/index.php?page=le-rapport-analytique-2006-2007>.
- [61] Agence de l'eau. : Méthode de gestion et de réutilisation des sédiments pollués – inventaire détaillé des techniques de curage, transport, traitement et usage des sédiments. Rapport technique, 2002. <http://www.eauartois-picardie.fr/>.
- [62] Nicolas Cabane : *Sols traités à la chaux et aux liants hydrauliques : Contribution à l'identification et à l'analyse des éléments perturbateurs de la stabilisation*. Thèse de doctorat, Université Jean Monnet-Saint-Etienne, 2004.
- [63] Anne Gosselin, Denis Blackburn et Mario Bergeron : *Protocole d'évaluation de la traitabilité des sédiments, des sols et des boues à l'aide des technologies minéralurgique*. Environnement Canada, 1999.
- [64] André Le Roux et Zilmar Unikowski : Mise en évidence de l'influence des fines argileuses dans les granulats à béton. *Bull. Liaison des LCPC*, (110), 1980. <http://www.geotech-fr.org/sites/default/files/revues/blpc/BLPC%20110%20pp%20101-108%20Le%20Roux.pdf>.
- [65] Zilmar Unikowski : Influence des argiles sur les propriétés des mortiers de ciment. *Rapport de recherche LCPC*, (110):p1–87, 1982. [http://www.ifsttar.fr/fileadmin/user\\_upload/editions/lcpc/RapportsDeRecherche/RapportDeRecherche-LCPC-RR110.pdf](http://www.ifsttar.fr/fileadmin/user_upload/editions/lcpc/RapportsDeRecherche/RapportDeRecherche-LCPC-RR110.pdf).
- [66] Mokhtaria Benkaddour, Fatiha Kazi Aoual et Abdelaziz Semcha : Durabilité des mortiers à base de

- pouzzolane naturelle et de pouzzolane artificielle. *Revue Nature et Technologie*. n, 1:p-1, 2009. [http://www.univ-chlef.dz/RevueNatec/art\\_01\\_07.pdf](http://www.univ-chlef.dz/RevueNatec/art_01_07.pdf).
- [67] F. Mac Farlane : *Méthodologie de gestion des matériaux de dragage maritime-Application au Port Autonome de Dunkerque*. Thèse de doctorat, Université d'Artois, 2004.
- [68] Pascale Baumard : *Biogéochimie des composés aromatiques dans l'environnement marin*. Thèse de doctorat, 1997.
- [69] M. Mustin : *Le compost*, volume ISBN 2 864 72008 6. Editions Francois Dubosc, 1987.
- [70] Franck Marot : *Caractérisation et traitement de sédiments de dragage contenant des polluants métalliques*. Thèse de doctorat, 1998.
- [71] Walter A. Gutteridge et John A. Dalziel : Filler cement : The effect of the secondary component on the hydration of portland cement : Part 2 : Fine hydraulic binders. *Cement and Concrete Research*, 20(6):p853-861, 1990. [https://doi.org/10.1016/0008-8846\(90\)90046-Z](https://doi.org/10.1016/0008-8846(90)90046-Z).
- [72] Isabella Bisutti, Ines Hilke, Jens Schumacher et Michael Raessler : A novel single-run dual temperature combustion (srdtc) method for the determination of organic, in-organic and total carbon in soil samples. *Talanta*, 71(2):p521 - 528, 2007. <http://dx.doi.org/10.1016/j.talanta.2006.04.022>.
- [73] S. Salvador et O. Pons : A semi-mobile flash dryer/calciner unit to manufacture pozzolana from raw clay soils—application to soil stabilisation. *Construction and Building Materials*, 14(2):p109-117, 2000. [http://dx.doi.org/10.1016/S0950-0618\(00\)00005-2](http://dx.doi.org/10.1016/S0950-0618(00)00005-2).
- [74] Rackel San Nicolas : *Approche performantielle des bétons avec métakaolins obtenus par calcination flash*. Thèse de doctorat, Université Paul Sabatier-Toulouse III, 2011.
- [75] Christelle Bich : *Contribution à l'étude de l'activation thermique du kaolin : évolution de la structure cristallographique et activité pouzzolanique*. Thèse de doctorat, Villeurbanne, INSA, 2005.
- [76] Didier Bernache-Assollant et Jean-Pierre Bonnet : *Frittage : aspects physicochimiques*. Ed. Techniques Ingénieur, 2005. <http://www.techniques-ingenieur.fr/res/pdf/encyclopedia/42106210-af6620.pdf>.
- [77] JU Anderson : An improved pretreatment for mineralogical analysis of samples containing organic matter. *Clays and Clay Minerals*, 10(3):380-388, 1963.
- [78] Karin Eusterhues, Cornelia Rumpel, Markus Kleber et Ingrid Kögel-Knabner : Stabilisation of soil organic matter by interactions with minerals as revealed by mineral dissolution and oxidative degradation. *Organic Geochemistry*, 34(12):1591-1600, 2003. <http://dx.doi.org/10.1016/j.orggeochem.2003.08.007>.
- [79] R Mikutta, M Kleber, K Kaiser et R Jahn : Review : Organic matter removal from soils using hydrogen peroxide , sodium hypochlorite, and disodium peroxodisulfate. *Soil science society of America journal*, 69(1):120-135, 2005. <http://dx.doi.org/doi:10.2136/sssaj2005.0120>.
- [80] Jens Leifeld et Ingrid Kögel-Knabner : Organic carbon and nitrogen in fine soil fractions after treatment with hydrogen peroxide. *Soil Biology and Biochemistry*, 33(15):2155-2158, 2001. [http://dx.doi.org/10.1016/S0038-0717\(01\)00127-4](http://dx.doi.org/10.1016/S0038-0717(01)00127-4).
- [81] MichaeláK Schultz, StevenáR Biegalski, KennetháG W Inn, WilliamáC Burnett, JoyleneáL W Thomas, GregoryáE Smith *et al.* : Optimizing the removal of carbon phases in soils and sediments for sequential chemical extractions by coulometry. *Journal of Environmental Monitoring*, 1(2):183-190, 1999. <http://dx.doi.org/10.1039/A900534J>.
- [82] BH Shieldrick et C Wang : Particle size distribution. soil sampling and methods of analysis. martin r. carter (ed.). canadian society of soil science, 1993.
- [83] Michael WI Schmidt et Angela G Noack : Black carbon in soils and sediments : analysis, distribution, implications, and current challenges. *Global biogeochemical cycles*, 14(3):777-793, 2000. <http://dx.doi.org/10.1029/1999GB001208>.
- [84] BKG Theng, GG Ristori, CA Santi et HJ Percival : An improved method for determining the specific surface areas of topsoils with varied organic matter content, texture and clay mineral composition. *European Journal of Soil Science*, 50(2):309-316, 1999. <http://dx.doi.org/10.1046/j.1365-2389.1999.00230.x>.
- [85] R Mikutta, M Kleber et R Jahn : Poorly crystalline minerals protect organic carbon in clay subfractions from acid subsoil horizons. *Geoderma*, 128(1):106-115, 2005. <http://dx.doi.org/10.1016/j.geoderma.2004.12.018>.
- [86] H Kunz : Artificial beach nourishment on norderney, a case study. *In Coastal Engineering 1990*, pages 3254-3267. 1991. <http://dx.doi.org/10.1061/9780872627765.249>.
- [87] Direction de L'Environnement du Canada : L ' évaluation du risque écotoxicologique du rejet en eau libre des sédiments , en soutien à la gestion des projets de dragage en eau douce. Rapport technique, 2013.
- [88] Mohamed Miraoui : *Mise en œuvre d ' une démarche de prétraitement et de traitement des sédiments de dragage en vue d ' une valorisation dans le génie civil*. Thèse de doctorat, 2010.



- [89] Department of Environmental Protection : Dredging Technical Manual « The Management and Regulation of Dredging Activities and Dredges Material Disposal in New Jersey's Tidal Waters. Rapport technique, 1997.
- [90] Maryland Port Administration : Innovative Reuse of Dredged Material. Rapport technique April, 2010. <http://www.mpsafepassage.org/projectFiles/innovative{ }reuse.pdf>.
- [91] Bob Martinez Center, Rick Scott Governor, Carlos Lopez-Cantera, Lt Governor et Jonathan P Steverson : Guidance Document SWM-21.42 Regulation of contaminated dredge material technical considerations. pages 1–60, 2016.
- [92] Gene Clark et David L Knight : Beneficial use of dredged material in the great lakes, 2013.
- [93] Jacky Mazars : *Application de la mécanique de l'endommagement au comportement non linéaire et à la rupture du béton de structure*. Thèse de doctorat, 1984.
- [94] Alain REGNAULT Robert BASTIER, Alexandre BOCAN, Bernard GILBERT : Fours de cimenterie Ateliers de cuisson du clinker. *Techniques de l'Ingénieur*, 33(0):1–24, 2017. <http://www.techniques-ingenieur.fr/res/pdf/encyclopedia/42209210-be8845.pdf>.
- [95] Institute for Prospective Technological Studies Sustainable Production et Consumption Unit European IPPC Bureau : Production of Cement, Lime and Magnesium Oxide, 2013. [http://ied.ineris.fr/sites/default/files/files/CLM\\_BREF\\_042013.pdf](http://ied.ineris.fr/sites/default/files/files/CLM_BREF_042013.pdf).
- [96] Franck Cassagnabere : *Produits préfabriqués en béton filé : Vers l'amélioration des performances du matériau pour mieux gérer le procédé de production*. Thèse de doctorat, Université de Toulouse, Toulouse, 2007.
- [97] H. Manzano, A. Ayuela et J.S. Dolado : On the formation of cementitious c-s-h nanoparticles. *Journal of computer-aided materials design*, 14(1):p45–51, 2007. <http://dx.doi.org/10.1007/s10820-006-9030-0>.
- [98] R. James Kirkpatrick, J.L. Yarger, Paul F. McMillan, Yu Ping et Xiandong Cong : Raman spectroscopy of c-s-h, tobermorite, and jennite. *Advanced Cement Based Materials*, 5(3–4):p93 – 99, 1997. [http://dx.doi.org/10.1016/S1065-7355\(97\)00001-1](http://dx.doi.org/10.1016/S1065-7355(97)00001-1).
- [99] R.J. Kirkpatrick, G.E. Brown, Ning Xu et Xiandong Cong : Ca x-ray absorption spectroscopy of c—s—h and some model compounds. *Advances in Cement Research*, 9(33):p31–36, 1997. <https://doi.org/10.1680/adcr.1997.9.33.31>.
- [100] Nicolas Lequeux, Alain Morau, Samuel Philippot et Philippe Boch : Extended x-ray absorption fine structure investigation of calcium silicate hydrates. *Journal of the American Ceramic Society*, 82(5):p1299–1306, 1999. <http://dx.doi.org/10.1111/j.1151-2916.1999.tb01911.x>.
- [101] Pawel Rejmak, Jorge S Dolado, Malcolm J Stott et Andrés Ayuela : <sup>29</sup>Si nmr in cement : a theoretical study on calcium silicate hydrates. *The Journal of Physical Chemistry C*, 116(17):p9755–9761, 2012.
- [102] Ping Yu, R. James Kirkpatrick, Brent Poe, Paul F. McMillan et Xiandong Cong : Structure of calcium silicate hydrate (c-s-h) : Near-, mid-, and far-infrared spectroscopy. *Journal of the American Ceramic Society*, 82(3):p742–748, 1999.
- [103] Stefano Merlino, Elena Bonaccorsi et Thomas Armbruster : Tobermorites : Their real structure and order-disorder (od) character. *American Mineralogist*, 84:p1613–1621, 1999. <https://doi.org/10.2138/am-1999-1015>.
- [104] E. Bonaccorsi, S. Merlino et H.F.W. Taylor : The crystal structure of jennite, Ca<sub>9</sub>Si<sub>6</sub>O<sub>18</sub>(OH)<sub>6</sub>·8H<sub>2</sub>O. *Cement and Concrete Research*, 34(9):p1481–1488, 2004.
- [105] Ivan Klur : *Etude par RMN de la structure des silicates de calcium hydratés*. Thèse de doctorat, 1996.
- [106] I.G. Richardson : Tobermorite/jennite-and tobermorite/calcium hydroxide-based models for the structure of csh : applicability to hardened pastes of tricalcium silicate, β-dicalcium silicate, portland cement, and blends of portland cement with blast-furnace slag, metakaolin, or silica fume. *Cement and Concrete Research*, 34(9):p1733–1777, 2004. <http://dx.doi.org/10.1016/j.cemconres.2004.05.034>.
- [107] Metal Yousuf, A. Mollah, Rajan K. Vempati, T-C. Lin et David L. Cocke : The interfacial chemistry of solidification/stabilization of metals in cement and pozzolanic material systems. *Waste Management*, 15(2):p137–148, 1995. [http://dx.doi.org/10.1016/0956-053X\(95\)00013-P](http://dx.doi.org/10.1016/0956-053X(95)00013-P).
- [108] J.C. Maso : *Influence of the interfacial transition zone on composite mechanical properties*. 1996.
- [109] L. Fuglsang Nielsen : Strength development in hardened cement paste : examination of some empirical equations. *Materials and Structures*, 26(5):p255–260, 1993. <http://dx.doi.org/10.1007/BF02472946>.
- [110] KL Scrivener et PL Pratt : The characterization and quantification of cement and concrete microstructures. *Pore Structure and Construction Materials Properties*, pages 61–68, 1987.
- [111] JP Ollivier, JC Maso et B Bourdette : Interfacial transition zone in concrete. *Advanced Cement Based Materials*, 2(1):p30–38, 1995. [http://dx.doi.org/10.1016/1065-7355\(95\)90037-3](http://dx.doi.org/10.1016/1065-7355(95)90037-3).
- [112] J.J. Zheng, C.Q. Li et X.Z. Zhou : Thickness of interfacial transition zone and cement content profiles around aggregates. *Magazine of Concrete Research*, 57(7):p397–406, 2005.

- [113] François De Larrard : *Structures granulaires et formulation des bétons*. Laboratoire Central des Ponts et Chaussées, 2000.
- [114] Prasada Rao Rangaraju, Jan Olek et Sidney Diamond : An investigation into the influence of inter-aggregate spacing and the extent of the itz on properties of portland cement concretes. *Cement and Concrete Research*, 40(11):p1601–1608, 2010. <http://dx.doi.org/10.1016/j.cemconres.2010.07.002>.
- [115] Mouhamadou Bassir DIOP, Maryline CORNEN, Ahmed LOUKILI, Eric GARCIADIAZ, Ibrahima Khalil CISSE, Siham KAMALI BERNARD et Fabrice BERNARD : *Etude du béton à l'échelle mesoscopique : simulation numérique et tests de micro-indentation*. Thèse de doctorat.
- [116] R. Zimbelmann : A contribution to the problem of cement-aggregate bond. *Cement and Concrete Research*, 15(5):p801–808, 1985. [http://dx.doi.org/10.1016/0008-8846\(85\)90146-2](http://dx.doi.org/10.1016/0008-8846(85)90146-2).
- [117] B.D. Barnes, Sidney Diamond et W.L. Dolch : The contact zone between portland cement paste and glass “aggregate” surfaces. *Cement and Concrete Research*, 8(2):p233–243, 1978. [http://dx.doi.org/10.1016/0008-8846\(78\)90012-1](http://dx.doi.org/10.1016/0008-8846(78)90012-1).
- [118] A. Semcha, « Valorisation des sédiments de dragage : Applications dans le BTP, cas du barrage de Fergoug », thèse, Université de Reims Champagne-Ardenne, 2006.
- [119] F. Taieb, N. Belas, et H. A. Mesbah, « Influence of treated mud on free shrinkage and cracking tendency of self-compacting concrete equivalent mortars », *Materiales de Construcción*, vol. 69, no 334, p. 186, avr. 2019, doi: 10.3989/mc.2019.02318.
- [120] V. Dubois, « Etude du comportement physico-mécanique et caractérisation environnementale des sédiments marins : valorisation en technique routière », Université d'Artois, 2006.
- [121] T. N. Thanh, « Valorisation de sédiments marins et fluviaux en technique routière », Université d'Artois, 2009.
- [122] W. Maherzi, I. Ennahal, M. Benzerzour, Y. Mamindy-Pajany, et N.-E. Abriak, « Study of the polymer mortar based on dredged sediments and epoxy resin: Effect of the sediments on the behavior of the polymer mortar », *Powder Technology*, vol. 361, p. 968-982, févr. 2020, doi: 10.1016/j.powtec.2019.10.104.
- [123] L. F. Nielsen, « Strength development in hardened cement paste: examination of some empirical equations », *Materials and Structures*, vol. 26, no 5, p. 255-260, juin 1993, doi: 10.1007/BF02472946.
- [124] Z. E.-A. Laidani, B. Benabed, R. Abousnina, M. K. Gueddouda, et E.-H. Kadri, « Experimental investigation on effects of calcined bentonite on fresh, strength and durability properties of sustainable self-compacting concrete », *Construction and Building Materials*, vol. 230, p. 117062, janv. 2020, doi: 10.1016/j.conbuildmat.2019.117062.
- [125] Z. E.-A. Laidani, B. Benabed, R. Abousnina, M. K. Gueddouda, et M. J. Khatib, « Potential pozzolanicity of Algerian calcined bentonite used as cement replacement: optimisation of calcination temperature and effect on strength of self-compacting mortars », *European Journal of Environmental and Civil Engineering*, vol. 0, no 0, p. 1-23, janv. 2020, doi: 10.1080/19648189.2020.1713898.
- [126] I. Ennahal, W. Maherzi, Y. Mamindy-Pajany, M. Benzerzour, et N.-E. Abriak, « Eco-friendly polymers mortar for floor covering based on dredged sediments of the north of France », *J Mater Cycles Waste Manag*, vol. 21, no 4, p. 861-871, juill. 2019, doi: 10.1007/s10163-019-00843-3.
- [127] A. el Mahdi Safhi, M. Benzerzour, P. Rivard, et N.-E. Abriak, « Feasibility of using marine sediments in SCC pastes as supplementary cementitious materials », *Powder Technology*, vol. 344, p. 730-740, févr. 2019, doi: 10.1016/j.powtec.2018.12.060.
- [128] A. Alujas, R. Fernández, R. Quintana, K. L. Scrivener, et F. Martirena, « Pozzolanic reactivity of low grade kaolinitic clays: Influence of calcination temperature and impact of calcination products on OPC hydration », *Applied Clay Science*, vol. 108, p. 94-101, mai 2015, doi: 10.1016/j.clay.2015.01.028.
- [129] M. A. Chikouche, E. Ghorbel, et M. Bibi, « The possibility of using dredging sludge in manufacturing cements: Optimization of heat treatment cycle and ratio replacement », *Construction and Building Materials*, vol. 106, p. 330-341, mars 2016, doi: 10.1016/j.conbuildmat.2015.12.128.

- [130] S. Mohammed, « Processing, effect and reactivity assessment of artificial pozzolans obtained from clays and clay wastes: A review », *Construction and Building Materials*, vol. 140, p. 10-19, juin 2017, doi: 10.1016/j.conbuildmat.2017.02.078.
- [131] S. C. Taylor-Lange, E. L. Lamon, K. A. Riding, et M. C. G. Juenger, « Calcined kaolinite–bentonite clay blends as supplementary cementitious materials », *Applied Clay Science*, vol. 108, p. 84-93, mai 2015, doi: 10.1016/j.clay.2015.01.025.
- [132] F. Gridi-Bennadji, B. Beneu, J. P. Laval, et P. Blanchart, « Structural transformations of Muscovite at high temperature by X-ray and neutron diffraction », *Applied Clay Science*, vol. 38, no 3, p. 259-267, févr. 2008, doi: 10.1016/j.clay.2007.03.003.
- [133] I. Janotka, F. Puertas, M. Palacios, M. Kuliffayová, et C. Varga, « Metakaolin sand–blended-cement pastes: Rheology, hydration process and mechanical properties », *Construction and Building Materials*, vol. 24, no 5, p. 791-802, mai 2010, doi: 10.1016/j.conbuildmat.2009.10.028.
- [134] K. Aasly, T. Malvik, et E. H. Myrhaug, « Advanced methods to characterize thermal properties of quartz », présenté à *Proceeding of the XI International Conference on Innovations in Ferro Alloy Industry*, New Delhi, India, 2007, p. 381–392.
- [135] T. Jiang, G. Li, G. Qiu, X. Fan, et Z. Huang, « Thermal activation and alkali dissolution of silicon from illite », *Applied Clay Science*, vol. 40, no 1-4, p. 81-89, juin 2008, doi: 10.1016/j.clay.2007.08.002.
- [136] J. P. Sanders et P. K. Gallagher, « Kinetic analyses using simultaneous TG/DSC measurements », *Journal of Thermal Analysis and Calorimetry*, vol. 82, no 3, p. 659-664, nov. 2005, doi: 10.1007/s10973-005-0946-5.
- [137] A. A. Al-Rawas, A. Wahid Hago, T. C. Corcoran, et K. M. Al-Ghafri, « Properties of Omani artificial pozzolana (sarooj) », *Applied Clay Science*, vol. 13, no 4, p. 275-292, oct. 1998, doi: 10.1016/S0169-1317(98)00029-5.
- [138] A. Bresson, « Influence de la minéralogie sur le comportement des mortiers de ciment au jeune âge », Université Laval Québec, 2006.
- [139] S.-C. Pan, D.-H. Tseng, C.-C. Lee, et C. Lee, « Influence of the fineness of sewage sludge ash on the mortar properties », *Cement and Concrete Research*, vol. 33, no 11, p. 1749-1754, nov. 2003, doi: 10.1016/S0008-8846(03)00165-0.
- [140] D. M. Roy et G. M. Ldorn, « Hydration, Structure, and Properties of Blast Furnace Slag Cements, Mortars, and Concrete », *JP*, vol. 79, no 6, p. 444-457, nov. 1982, doi: 10.14359/10919.
- [141] F. J. Hogan et J. W. Meusel, « Evaluation for Durability and Strength Development of a Ground Granulated Blast Furnace Slag », *CCA*, vol. 3, no 1, p. 40-52, juill. 1981, doi: 10.1520/CCA10201J.
- [142] A. Bougara, C. Lynsdale, et K. Ezziiane, « Activation of Algerian slag in mortars », *Construction and Building Materials*, vol. 23, no 1, p. 542-547, janv. 2009, doi: 10.1016/j.conbuildmat.2007.10.012.
- [143] A. Bougara, C. Lynsdale, et N. B. Milestone, « The influence of slag properties, mix parameters and curing temperature on hydration and strength development of slag/cement blends », *Construction and Building Materials*, vol. 187, p. 339-347, oct. 2018, doi: 10.1016/j.conbuildmat.2018.07.166.
- [144] A. Bougara, C. Lynsdale, et N. B. Milestone, « Reactivity and performance of blastfurnace slags of differing origin », *Cement and Concrete Composites*, vol. 32, no 4, p. 319-324, avr. 2010, doi: 10.1016/j.cemconcomp.2009.12.002.
- [145] A. Hadjsadok, S. Kenai, L. Courard, F. Michel, et J. Khatib, « Durability of mortar and concretes containing slag with low hydraulic activity », *Cement and Concrete Composites*, vol. 34, no 5, p. 671-677, mai 2012, doi: 10.1016/j.cemconcomp.2012.02.011.
- [146] K. Belguesmia, N. B. Belaribi, O. Amiri, N. Leklou, et O. Belaribi, « Influence of treated sediment substitution percentage on workability, strength and porosity of SCC », *Journal of Materials and Engineering Structures « JMES »*, vol. 5, no 1, p. 47-55, mars 2018.

- [147] A. el Mahdi Safhi, M. Benzerzour, P. Rivard, N.-E. Abriak, et I. Ennahal, « Development of Self-Compacting Mortars Based on Treated Marine Sediments », *Journal of Building Engineering*, déc. 2018, doi: 10.1016/j.jobbe.2018.12.024.
- [148] A. Cheng, R. Huang, J.-K. Wu, et C.-H. Chen, « Influence of GGBS on durability and corrosion behavior of reinforced concrete », *Materials Chemistry and Physics*, vol. 93, no 2, p. 404-411, oct. 2005, doi: 10.1016/j.matchemphys.2005.03.043.
- [149] H. sadok Ahmed, « Effect of the microstructure of mortars with low hydraulicity slag on their behavior in aggressive environments », *MATEC Web Conf.*, vol. 149, p. 01025, 2018, doi: 10.1051/mateconf/201814901025.
- [150] A. Hadj-sadok, S. Kenai, L. Courard, et A. Darimont, « Microstructure and durability of mortars modified with medium active blast furnace slag », *Construction and Building Materials*, vol. 25, no 2, p. 1018-1025, févr. 2011, doi: 10.1016/j.conbuildmat.2010.06.077.