CEMENT MORTAR WITH VALUATION OF WWTP SLUDGE FROM THE TANNERY INDUSTRY

RAFAELA MULINARI CABRAL

Final dissertation to the Superior School of Technology and Management of Instituto Politécnico de Bragança to obtain the master's degree in Chemical Engineering in the ambit of the double diploma with Universidade Tecnológica Federal do Paraná.

Supervisor:

Prof. Ramiro José Espinheira Martins

Co-supervisor:

Prof. Juliana Martins Teixeira de Abreu Pietrobelli

Bragança

2023

DEDICATION

I dedicate this work to my mother,
Elisangela Clazer Cabral.
The person who inspires me, and who has always
encouraged and supported me in following my dreams.

ACKNOWLEDGEMENTS

To PhD. Prof. Ramiro José Espinheira Martins, for the guidance, support and help that were essential for the development of this study.

To Dra. Prof. Juliana Martins Teixeira de Abreu Pietrobelli, for the guidance that contributed to the development of this work for all support, teaching, and friendships.

A technician at the Chemical Processes Laboratory, Eng. Maria João Almeida Pinto Santos Afonso, for their support, suggestions, and friendship.

We would like to thank the analytical chemistry laboratory, Dr. Paula Marina de Sousa Plasencia Matos, for the support and suggestions given.

To the technicians of the Geotechnical Laboratory, João Augusto Pires and Octávio Manuel do Nascimento Pereira, for the help and information given during the tests.

To my boyfriend Juan Wiezbicki and all my friends for their support and friendships.

The dual diploma agreement between Universidade Tecnológica Federal do Paraná and Instituto Politécnico de Bragança.

To Universidade Tecnológica Federal do Paraná and Instituto Politécnico de Bragança.

ABSTRACT

The diverse and substantial quantity of waste generated by industries, combined with the scarcity of natural resources, necessitates the analysis, development, and implementation of treatment mechanisms to recover and reuse materials and substances to minimize the impacts of waste disposal in the environment. The leather tanning industry, which is responsible for leather processing, is a major polluter because hazardous and heavy materials are used in its processes. Among various alternatives, waste can be incorporated into cementitious matrices. The objective of this study was to investigate the valorization of sludge from Leather Tannery Wastewater Treatment Plants (WWTP) through its incorporation into cement, as well as technical and economic evaluation. Four scenarios were studied: low-moisture sludge, two types of ash obtained via incineration, and wet oxidation. Mortar specimens were prepared with different replacement proportions of cement (0%, 3%, 5%, 7% and 10%), which were evaluated for flexural and compressive strength, as well as two complementary water absorption and leaching tests. The results exceeded expectations, as in most cases, they demonstrated an increase in resistance, a decrease or stabilization in water absorption, and minimal release of pollutants and contaminants into the environment with an increasing percentage of replacement. Notably, the replacement of 10% of sludge using the incineration method yielded the most favorable outcomes, whereas the wet oxidation method produced the least favorable results.

Keywords: eco-friendly building materials, cement mortar, leather industry, sustainable construction, waste management, WWTP sludge.

RESUMO

A diversificada e a considerável quantidade de resíduos gerados pelas indústrias, juntamente com a escassez de recursos naturais, exigem a análise, o desenvolvimento e a implementação de mecanismos de tratamento para recuperar e reutilizar materiais e substâncias, com o objetivo de minimizar os impactos da eliminação de resíduos no ambiente. A indústria de curtumes, responsável pelo processamento de peles, é uma significativa poluidora devido à utilização de materiais perigosos e pesados em seus processos. Entre as várias alternativas, é possível incorporar os resíduos em matrizes de cimento. O objetivo deste estudo foi investigar a valorização do lodo proveniente das Estações de Tratamento de Águas Residuais de curtumes (ETAR) através da sua incorporação em cimento, bem como a avaliação técnica e econômica. Foram estudados quatro cenários: lodo com baixo teor de humidade, dois tipos de cinzas obtidas por incineração e, oxidação úmida. Foram preparados corpos de prova com diferentes proporções de substituição de cimento (0%, 3%, 5%, 7% e 10%), os quais foram avaliados quanto à resistência à flexão e compressão, bem como análises complementares de absorção de água e lixiviação. Os resultados excederam as expectativas, uma vez que na maioria dos casos demonstraram um aumento na resistência, uma diminuição ou estabilização na absorção de água e uma liberação mínima de poluentes e contaminantes no ambiente com o aumento da percentagem de substituição. De destacar que a substituição de 10% de lodo usando o método de incineração produziu os resultados mais favoráveis, enquanto o método de oxidação úmida produziu os resultados menos favoráveis.

PALAVRAS CHAVE: materiais de construção ecológicos, argamassa de cimento, indústria de curtumes, construção sustentável, gestão de resíduos, lamas de ETAR.

INDEX OF TABLES

INDEX OF FIGURES

INDEX OF ABBREVIATIONS

ABNT – Brazilian Association of Technical Standards
MS - Mortar specimens
AAS – Atomic Absorption Spectrophotometry
EPA – Environmental Protection Agency
ESTiG - Superior School of Technology and Management
FEPICOP - Portuguese Federation of the Construction Industry and Public Works
S/S – Stabilization and solidification
NBR – Brazilian technical standard
LI – Loss on ignition
FS – Fixed solids
TS – Total solids
TOC – Total Organic Carbon
WWTP – Waste Water Treatment Plant

SUMÁRIO

1 INTRODUCTION

The growing awareness of socio-environmental issues, stricter legal requirements, large quantities of waste generated by industries, and limited availability of energy and raw materials have prompted researchers to explore various industrial waste treatments and applications [1]. The circular economy is a production and consumption model that promotes value and extends the life cycle of products, thereby reducing greenhouse gas emissions and waste, while also enabling better utilization of raw materials. By encouraging the attribution of an alternative to products at the end of their life cycle, the circular economy enhances competitiveness, stimulates innovation, and fosters sustainable economic growth [2].

Industrial waste can be categorized into three phases: gas, liquid, and solid. However, this study specifically focused only on liquid and solid phases. In the liquid phase, different treatment methods can be employed, including preliminary processes such as the removal of coarse solids through fixed or rotating screens, as well as primary, secondary (biological), and tertiary treatments. These processes lead to the formation of a solid phase, commonly known as sludge, which was the main focus of this study. Sludge is characterized by its high content of organic matter and water, and its composition is primarily influenced by the source of the solid materials, the quantity of sludge generated, and the specific treatment processes involved [3].

The tanning industry employs numerous chemical substances that are harmful to the environment at various stages of the production process, from receiving hides to tanning [4]. During the transformation of animal skin into leather, chemicals are added to enhance the durability and physical properties. These substances may include vegetable tannins or mineral tanning agents such as chromium metal, which is most commonly used in the production of wet blue leather for commercial purposes. The waste generated from this process is hazardous and has a high potential for contamination, making it crucial to ensure proper environmental disposal [5, 6, 7].

The treatment of wastewater generated from tanning processes in wastewater treatment plants (WWTP) is of utmost importance because of the generation of large quantities of toxic waste. Legislative bodies have established legal limits for certain parameters, such as COD, BOD, total dissolved solids, and pH, for this type of industry to prevent the discharge of harmful substances into the environment [8].

An alternative approach to reduce solid waste from WWTP in the tannery industry involves its incorporation into a cementitious matrix. This is particularly relevant as the construction sector demands cost-effective, highly moldable materials, and both the cement and tannery industries are growing. Cement has a rich history dating back over 4500 years, with significant advancements made by the English civil engineer John Smeaton in 1756, who obtained a product with high resistance by calcining soft and clayey limestones. In 1824, entrepreneur Joseph Aspdin developed a fine powder by burning limestone and clay, that hardened into a rock-like substance when mixed with water and dried. It was named Portland cement due to its similarity in color and hardness to rocks from the British Isle of Portland [3].

The construction industry faces significant challenges in terms of waste management and the pursuit of sustainable practices. According to information from the Portuguese Federation of Construction and Public Works Industry, cement consumption in the national market has been steadily increasing since 2011, reaching its highest value in 2022 [9]

The aim of this thesis was to propose a technically and economically feasible solution for solid waste, involving its valorization and characterization. It also sought to introduce an innovative method for partially substituting sludge from WWTP in the Tanner industry by incorporating it into cement mortar and evaluating its integrity and durability.

2 OBJECTIVES

2.1 GENERAL OBJECTIVE

The technical viability and economic value of applying sludge from a tannery wastewater treatment plant to partially replace cement in mortar production were evaluated.

2.2 SPECIFIC OBJECTIVES

- Characterization of sludge generated in the tannery WWTP;
- To test the methodologies (reduction of moisture content, ash obtained by incineration, and wet oxidation) for the reduction of organic matter in sludge;
- Prepare specimens containing different concentrations of sludge in partial replacement in cement;
- Perform mechanical and complementary tests on the specimens produced;
- Analyze the technical and economic feasibility of the developed methodologies.

3 STATE OF THE ART

3.1 TANNERY INDUSTRY

The leather, one of the oldest traded goods in the world, has been used for millennia. Records indicate that prehistoric people used the skin of hunted animals to keep warm approximately 20,000 years ago, although without much durability. Approximately 6,000 years later, pieces of Egyptian leather were found to have remarkably preserved strength and color [10].

Primitive methods for preserving hides involve simply drying them in the air and sun, but over time people discovered the preservative effects of various oils and tannins found in leaves, branches, and different types of trees, which could be released through maceration in water. As technology advanced, the process for preserving this material continued to improve, culminating in the practical application of chromium in the tanning process in 1893. This introduced the tanning leather technique, which has since become a widely used and sophisticated industry [1, 10, 11].

Chemical substances are added during tanning of animal skin (such as bovine, goat, or sheep) to increase durability and enhance its physical characteristics. The addition of vegetable tanning agents, such as tannins, is one method, but the most commonly used is the addition of mineral salts, such as chromium, which produce Wet Blue leather that can be sold [5, 6]. Vegetable tanning can take up to four months to complete, whereas mineral processes reduce this time by approximately three weeks [11].

In 1989, according to data from the National Institute of Statistics, there were 103 tanneries in Portugal, with the majority concentrated in the districts of Santarém, Porto, and Braga, with 68, 14, and 4 establishments, respectively. From 2015 to 2018, Portugal exported 1.865 billion, 85 million, and 150 million euros, respectively, in various sectors that use leather, including bags, footwear, wallets, and belts [12]. Currently, there are approximately 180 companies in the sector, with Lisbon, Porto, and Santarém being the main hubs, hosting 78, 27, and 25 industries, respectively [13].

3.1.1 Production process

Although the leather manufacturing process is not the focus of this study, it is essential to have a basic understanding of it. The process involves a series of operations, and, depending on the desired outcome, certain steps may vary or undergo minor modifications from one industry to another. Figure 1 provides an overview of the primary steps and sub-steps involved in the process [8, 14].

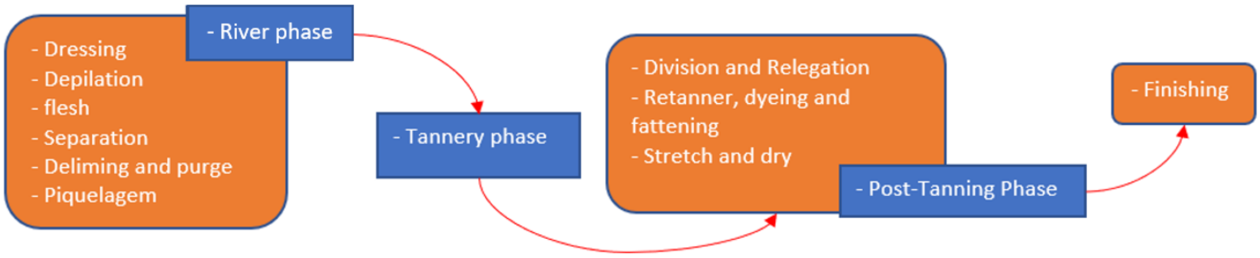


Figure 1: Stages of the production process of leather [8]

The leather production process encompasses several essential phases, each of which plays a fundamental role in the transformation of animal hides into a durable and versatile materials. The river phase serves as the starting point for the leather production process, where raw hides are received from supply sources. In this phase, the hides underwent a series of preliminary operations, including the removal of dirt, grease, and residual hair. The river phase may also involve the desalting process, in which the salt used for hide preservation is removed. Proper preparation of hides at this stage is crucial to ensure their readiness for tanning [8].

The tanning phase is one of the most critical parts of the leather production process. Here, hides are treated with tanning agents to stabilize the collagen fibers, making them resistant to deterioration. Tanning agents can be of vegetable origin, such as tannins, or mineral origin, such as chromium salts. The tanning process may also involve dyeing steps to achieve the desired leather color. Precise control of tanning conditions is essential for attaining the desired characteristics of leather [8].

In the post-tanning phase, various processes occur after primary tanning. This includes the removal of unreacted tanning agents, washing of the hides, and the application of chemicals that enhance the final properties of the leather. Post-tanning operations may also include stretching, smoothing, and drying of the hides. This phase is essential for preparing the hides for the final finishing step [8].

The finishing phase is the final stage of leather production, during which the material is refined and prepared for use in various products. Surface treatments are applied to improve the texture, shining, and durability of leather. This may involve the application of dyes, protective coatings, and polishing processes. Finishing completes the transformation of hides into leather ready for use in the manufacturing of a wide range of products, from footwear and clothing to luxury accessories [8].

3.1.2 Environmental impact

The leather industry is considered a major polluter and generates hazardous waste in liquid and solid form. One of the main concerns is the presence of potentially toxic chromium, which can be harmful to the environment. As a result, the European leather industry is under significant environmental pressure and faces market fluctuations. Portugal experienced significant growth in this industry during the 80s and 90s of the 20th century [1, 3, 8]. However, if not stored and treated properly, there is a risk of the oxidation of Cr III to Cr VI, which is a more toxic form of chromium, leading to soil and water contamination [15].

Although numerous studies have explored alternatives for decontaminating hazardous waste from the leather industry, the literature emphasizes that the treatment of its effluents poses significant environmental and technological challenges owing to their unique characteristics [1, 16].

The concentration of each element in the effluent from this industry varies depending on the production process, with high pH, large amounts of lime and free sulfides, high content of suspended solids, salinity, and BOD being some of the main characteristics, in addition to the presence of chromium. Maximum and minimum values of these parameters are shown in Table 1 [17].

Table 1: Characterization of effluent from the tanning industry (main parameters) * [17]

Parameters	**Minimum value ($mg\ L^{-1}$)**	**Maximum value ($mg\ L^{-1}$)**
pH	8.4	11.8
BOD	535	1500
COD	2500	3500
Suspended materials	2490	21350

* Values may vary depending on the process used by the industry.

Table 1 – Characterization of effluent from the tanning industry (main parameters) * [17] (cont.)

Parameters	Minimum value ($mg\ L^{-1}$)	Maximum value ($mg\ L^{-1}$)
Total nitrogen	190	260
Ammoniacal nitrogen	65	216
Chloride – Cl	400	3200
Sulfate – $S0_4{}^{2-}$	246	1650
Sulfides – S^{2-}	40	303
Chromium - Cr	24.2	160
Fatty substances	154	976

* Values may vary depending on the process used by the industry.

The tanning industry consumes approximately 30 to 40 liters of water per kilogram of leather produced [18], and with a processing of around 9 billion kilograms of hides, an estimated 300 to 400 billion liters of effluent are generated. Table 2 provides a breakdown of water consumption for each stage of the tanning process [8].

To produce approximately 350 kg of leather, the tanning industry requires one ton of salted skin, resulting in a substantial demand for water and energy and generating effluents with a high pollutant load, leading to severe environmental impacts. Typically, one ton of salt hide produces 650 kg of sludge on average [4].

Table 2: Amount of water consumed per ton of skin produced [8]

Process Step	Amount of water (m^3)
Dressing	9.0 – 1.0
Depilation	4.0 – 6.0
Descaling	4.5 – 2.0
Pickling	1.0 – 1.5
Tannery	1.0 – 2.0
Dyeing	1.0 – 1.5
Finishes	1.0 – 2.0
Washes	11.5 – 13.0

As previously mentioned, wastewater from leather industries contains a range of pollutants, including organic matter, suspended solids, sulfides, lime, chlorides, chromium salts, and ammoniacal compounds, which make their treatment difficult and expensive [1]. In addition, factories that use natural tannins may also contain natural phenols, tannins, and lignins, which are abundant in nature and present in their effluents [19]. Table 3 list some typical pollutant load values found in these industries effluents [20].

Table 3: Typical conditions found in stage tannery effluents* [20]

Process Step	BOD_5	COD	Total solids	Dissolved solids	Suspended solids	Chloride as Cl^-	Total chromium
Dressing	8.3-18.8	22.5-45.0	262.5-412.5	240-360	22.5-52.5	112.5-225	-
Depilation	17.5-35	35-87.5	105-175	84-105	21-70	14-28	-
Descaling	1.5-4.5	3.8-10.5	6.1-15	3.8-9	2.3-6.0	1.5-3.0	-
Pickling	0.3-0.5	0.8-2.3	26.3-52.6	25.5-50.3	0.8-2.3	1.5-3.8	-
Tannery	0.5-1.2	1.5-3.8	45.0-90.1	43.5-86.3	1.5-3.8	23.0-38.0	3.0-7.5
Global (with washes)	35.0-105.0	87.5-280.0	528.0-875.0	458,0-735.0	70.0-140.0	210.0-332.5	3.5-8.8
Dyeing/ Finishes	1.5-3.0	3.8-10.5	6.0-15.0	5.1-13.5	0.9-1.5	0.8-1.5	-

* Values expressed in kg/tonne of hide processed.

The most suitable place for depositing sludge is landfills that have a proper structure, typically containing waterproofing agents and collectors for gas and leachate, which helps to avoid soil contamination. However, this requires compliance with local legislation regarding all parameters [17]. Unfortunately, many metals such as Cd, Cu, Pb, Cr, Sn, and Zn can leach into the environment from landfills, causing soil pollution. Wastewater can also contain metals such as Zn, Cu, Pb, Cr, As, Mo, and Cd [21].

3.2 CIRCULAR ECONOMY

In the 1970s, the concept of a circular economy emerged, which presupposes the rupture of the linear economic model (extract, transform and discard), for the implementation of a model in which all types of materials are elaborated to circulate efficiently and can be reused in production without loss of quality [22].

This model distinguishes itself through its capacity for sustainable implementation, as it transforms end-of-life products into resources for other processes, effectively closing loops within industrial environments and greatly reducing waste. In essence, it provides the opportunity to repurpose what is viable, mend what is damaged, and recycle what cannot be repurposed [23].

In summary, the circular economy offers business opportunities that contribute significantly to social, economic, and environmental sustainability, with the goal of optimizing the circulation of products, components, and/or materials in technical and/or biological cycles in order to create a more efficient and sustainable system [24].

Figure 2: Circular Economy Model [2]

3.3 CIVIL CONSTRUCTION

The construction industry is recognized as a major consumer and exploiter of natural resources, and its intensive use of energy results in significant environmental impacts, according to the International Construction Council [3]. In Portugal, the Portuguese

Federation of the Construction Industry and Public Works (FEPICOP) reported that cement consumption in the national market has reached its highest level since 2011, with a 1.5% increase (year-on-year) to 3,836 thousand tons by 2022. Additionally, there has been a growth of 3.4% in the licensing of residential buildings and 10.3% for non-residential buildings, as of November 2022 [9].

3.3.1 Tannery sludge on cement

Countless waste materials generated by various industrial sectors, such as chemical, food, and metallurgy, which have been increasingly recognized for their environmental impact. These wastes can take different forms, such as ash, sludge, paper, ceramics, alkaline, and acidic residues, with global daily production reaching millions of tons. Therefore, it is necessary to limit the disposal of natural resources, to increase awareness, and to preserve the environment [4, 25].

In 1996, Weng conducted a study on the granulometric chromium residue generated during chromite mining. The residue, which has characteristics similar to sand and silt, was used as a filling material in concrete and steel structures, and its effect on corrosion was analyzed. The results indicated that the presence of the residue did not affect the corrosion of the steel or cause any problems in the structural integrity of the concrete, as confirmed by microscopic analysis [17, 29].

Solidification stabilization (S/S) is a viable alternative for the management of chromium residues, as the metal cannot be extracted or recovered. This technique involves immobilizing the residue within a solid matrix, with the exact amount determined in the laboratory. Different materials, such as cement, asphalt, polymer, and cement-polymer, can be used for S/S, with Portland cement being the most common because of its simplicity and water activation [17]. Park (2000) noted that Portland cement was first used for S/S of nuclear waste in the 1950s [26].

The S/S process involves the mixing of both liquid and solid wastes, including sludge, with cementitious material to form a binding system that creates a solid material with structural integrity and stability, thereby minimizing waste leaching [17, 27]. Physical parameters such as particle size, amount of solids, density, viscosity, temperature, and humidity, as well as chemical aspects like reactions between waste and cement (such as cation exchange), can influence the stabilization process [17]. Therefore, waste pretreatment is necessary to remove acids and oxidants, reduce volume, and prevent any potential interference with the S/S process [28].

Chromium sludge from the tanning industry can be mixed with clay at a weight percentage of 5-15% and utilized in brick manufacturing; however, special firing conditions must be applied [20, 30].

3.3.2 Portland Cement

According to NBR 16697 (ABNT, 2018), Portland cement is a hydraulic binder obtained by grinding Portland clinker. During its production, a predetermined amount of one or more forms of calcium sulfate and mineral additions was added, as presented in Table 4 of the standard [31]. Portland cement is a powdery material composed of complex silicates and aluminates that possess agglomerating, agglutinating, or binding properties. When mixed with water, it undergoes hydration, resulting in a hardened mass that exhibits mechanical resistance [17].

Table 4: Limits of the main compositions of Portland cements adapted from [27]

Portland cement designation (% mass)	**Acronym**	**Composition (%)**			
		Clinker + calcium sulfate (gypsum)	Blast furnace slag	Pozzolanic material	Carbonate material
Common	CP I	95 - 100		0 - 5	
Composed with granulated blast furnace slag	CP II - E	51 - 94	6 - 34	0	0 - 15
Composed with pozzolanic material	CP II - Z	71 - 94	0	6 - 34	0 - 15
Composed with carbonate material	CP II - F	75 - 98	0	0	11 - 25
blast furnace	CP III	25 - 65	35 - 75	blast furnace	CP III
Pozzolanic	CP IV	45 - 85	0	Pozzolanic	CP IV
high resistance starts	CP V	90 - 100	0	high resistance starts	CP V

A cement is a composite material comprising a clinker, which is made up of limestone and clay. When water is added to a clinker, it hardens and acquires strength and durability. Other materials are added to the mixture, such as gypsum, which increases the hardening time of the ground clinker, as well as blast furnace slag and pozzolanic materials, which have hydraulic binder properties. Fillers are also used to make materials more workable [17].

3.3.3 Addition of minerals

According to NBR 11172 (ABNT, 1990), any mineral substance added to cement, mortar, or concrete to modify its properties is classified as a mineral addition [32]. Mineral additives have been added to cementitious materials to improve their workability, strength, and durability [22]. As Anjos (2009) explains, the addition of minerals improves the consistency and cohesion of the mixture when fresh, and the resistance to compression and permeability when hardened. This is not only due to the chemical effect of the pozzolanic reaction, but also to the physical effect of pore-filling [33].

3.3.3.1 Pozzolans

Pozzolans refer to reactive mineral additions with a siliceous or silico-aluminous composition. During cement hydration, they react with calcium hydroxide, resulting in the formation of a secondary $C-S-H$, that enhances the durability of structures utilizing pozzolanic materials [31]. NBR 12653 (ABNT 2014) classifies pozzolans into three groups (Table 5) based on their physical and chemical properties. The materials under examination must meet the requirements outlined in Tables 6 and 7 to be identified as pozzolans [35].

Table 5: Classification of pozzolanic materials [35]

Class	Material description
N	Natural and artificial pozzolanas such as volcanic materials, siliceous cherts, diatomaceous earth and calcined clays
C	Fly ash from coal burning
E	Any pozzolana not included in the classes N e C

Table 6: Physical requirements for pozzolanic materials [35]

	Material Class		
Physical Requirements	**N**	**C**	**E**
Material retained on the 45μm sieve	<20%	<20%	<20%
Performance index with Portland cement at 28 days, in relation to the control	≥ 90%	≥ 90%	≥ 90%
Pozzolanic activity with lime at 7 days	≥ 6 MPa	≥ 6 MPa	≥ 6 MPa

Table 7: Chemical requirements for pozzolanic materials [35]

	Material Class		
Chemical Requirements	**N**	**C**	**E**
$SiO_2 + Al_2O_3 + Fe_2O_3$	≥ 70	≥ 70	≥ 70
SO_3	≤ 4	≤ 5	≤ 5
moisture content (%)	≤ 3	≤ 3	≤ 3
fire loss (%)	≤ 10	≤ 6	≤ 6
Alkalis available in Na_2O	≤ 1.5	≤ 1.5	≤ 1.5

3.3.3.2 Filler

The term "filler" can be defined as a finely divided material without any chemical activity, acting on the physical effect of granulometric conditioning and serving as nucleation points for the hydration of cement grains [36]. However, some authors, such as Matschei (2007), argue that besides the filling effect resulting from fillers, these materials can also interact chemically through their sometimes low reactivity and by accelerating the kinetics of hydration caused by the nucleation effect [37].

3.4 LITERATURE RESULTS

Searching the literature, the study "Eco-friendly Cement Mortar with Recovery of WWTP Sludge," conducted in 2020 at the Polytechnic Institute of Bragança (Grabowski, 2020), it was observed that three of the methods used by the author for reducing organic matter align with the principles adopted in this work, specifically referred to by the author as SA (sludge ashes), DS (oven-dried sludge), and WO (wet oxidized sludge), denoted as INC, SOD and WO, respectively, in this study. The results found by the author were not only comparable but also inferior to those achieved in this new work, Figure 3 illustrated the results obtained by the author, which were extracted from the original paper.

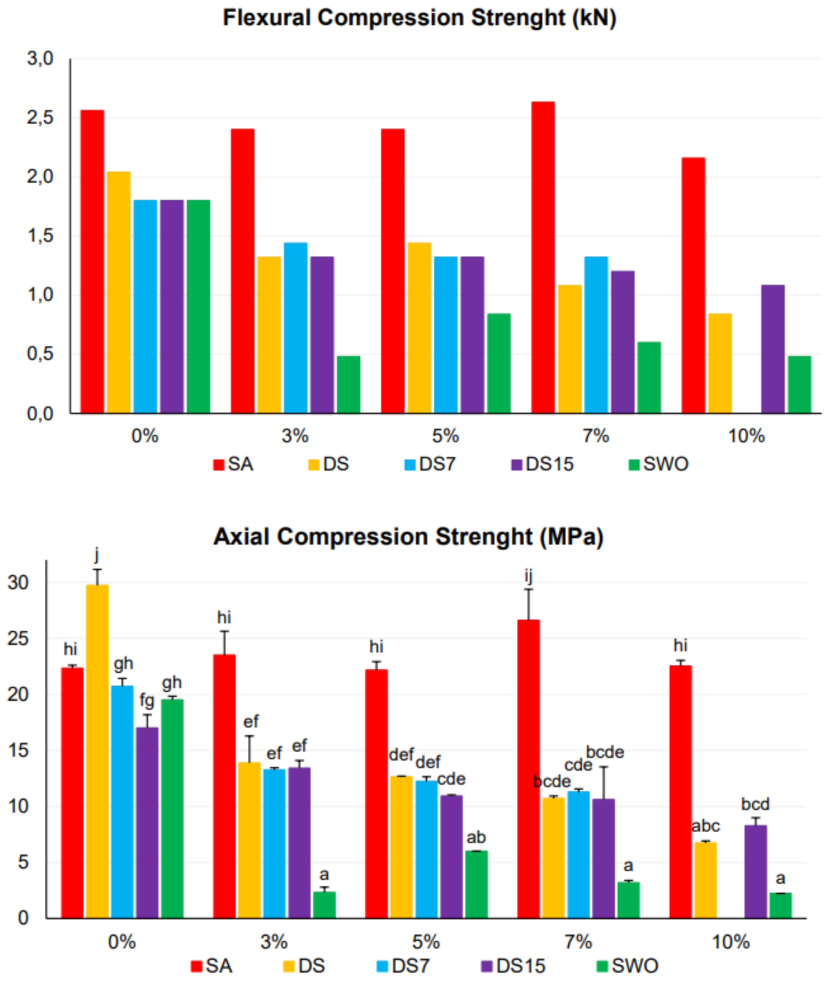


Figure 3: Final compressive flexural (kN) and axial compression (MPa) strength test result [3]

3.5 CHROMIUM

Belonging to the group of transition metals, chromium is the twenty-fourth element in the periodic table. Discovered by Louis-Nicholas Vauquelin in France in 1797, its name derives from the Greek word chroma meaning "color" due to the different colors of its salts.

Chromium is a shiny, silvery metal with oxidation states ranging from -2 to +6, although the most stable and commonly found in the environment are in the Cr^{3+} and Cr^{6+} formats. This element is hard and highly resistant to corrosion, with a molar mass of 51.996 g and density of 7.14 $g\ cm^{-3}$ [38].

Mining and industrial activities are the primary sources of chromium contamination, because they often release chromium-containing fumes and dust into the atmosphere and generate wastewater that may contain chromium [39].

3.5.1 Environmental and human impact

Trivalent chromium, one of the two biologically significant forms, Cr^{+3} and Cr^{+6}, is essential for human nutrition and is considered practically non-toxic at doses between 50-200 μg d^{-1} [36]. Its deficiency in the human body can cause disturbances in glucose metabolism, as it acts as an agent to potentiate insulin. However, it is important to carefully analyze the effects of this element as doses above adequate levels can lead to intoxication and a series of diseases. On the other hand, when transformed into Cr^{+6}, it becomes an extremely dangerous substance for humans, with highly toxic potential. Several studies have linked occupational exposure to this form of chromium to the appearance of lung cancer [38].

The concentration of chromium in plants is mainly associated with the presence of soluble forms of the element in the soil. The Cr^{6+} ion appears in the form of a soluble anion that can easily penetrate the cell membrane, exerting a negative and toxic effect due to its role as a potent oxidizing agent [38, 39].

Thus, it can be inferred that careful attention must be given to both the concentration of chromium and its treatment and analysis, to mitigate its potential impact on both the environment and human health.

4 METHODOLOGY

In this study, wastewater treatment plant (WWTP) sludge was obtained from the tanning industry in the Alcanena region of Portugal. This study was conducted at the Laboratory of Chemical Processes at the Polytechnic Institute of Bragança, and the collection of tannery sludge was collected on January 18, 2023.

4.1 SLUDGE CHARACTERIZATION

Incorporating sludge into cement can affect various parameters positively and negatively. For instance, the durability of the final product may be affected by the presence of high levels of organic matter and heavy metals. Therefore, it is essential to thoroughly characterize the material being studied [3]. For characterization, tests were conducted, including measurements of moisture content, total solids, fixed solids, organic matter content, organic carbon content, loss on ignition, and atomic absorption spectrophotometry (AAS) to confirm the concentration of an element in a sample, all tests were performed in triplicate.

4.1.1 pH test

The pH is a logarithmic scale used to measure the acidity, neutrality, or alkalinity of a solution. In this study, pH analysis was conducted using Embrapa methodology, with some modifications. Specifically, 100 mg of sludge was dissolved in 100 mL of distilled water and agitated for 15 min. After a 10 min rest period, the pH of the liquid supernatant was determined close to the interface of the phase change using a calibrated pH meter [3].

4.1.2 Moisture content

Moisture determination is the process of determining the percentage of water in a given sample. To calculate this value, approximately 3 g of sample was dried in porcelain containers in an oven for approximately 24 h at 105 °C. Until the entire sample was completely dry, it was necessary to mix the contents at equal intervals to provide better drying and prevent it from becoming completely dry [1]. The corresponding calculation performed using Equation 1.

$$M = \frac{(A-B)}{A} * 100 \qquad \text{Eq. 1}$$

where:

M percentage of moisture
A wet sample weight minus the dish, mg
B weight of the dry sample minus the container, mg

4.1.3 Total solids content

A solid is a state of matter characterized by its rigidity, ability to maintain its shape, and equilibrium with the liquid phase resulting from its fusion. By this generic definition, can specifically define any substance that retains the characteristics found in natural and wastewater, even after various operations such as drying and calcination, can be considered solid [40]. Table 8 outlines the different classifications of the solid types.

Table 8: Classifications of types of solids [40]

TYPE	CLASSIFICATION
Total solids (TS)	All the matter that remains in the container after the total drying of a given mass at 105 °C
Fixed solids (FS)	Total matter remaining in the vessel after a given mass has been calcined at about 550 °C
Volatile solids	All matter that is volatilized after calcination (subtraction between TS and FS)
Solids in Suspension	All matter that after filtration and drying remains retained in the membrane
Fixed Suspension Solids	All matter that after filtration, drying and calcination is retained in the membrane
Volatile Suspension Solids	Any material that values after calcination in the muffle furnace (subtraction between the two previous classifications)
Dissolved Solids	All matter that is not retained after filtration and remains after complete drying of the sample
Settleable solid	All substances present in a liter of sample that is settled by gravity

Among these, presented, in this work only two types have been addressed. To perform this analysis, the procedure began with weighing the crucibles, followed by placing them in a furnace at 550°C for 1 h. After this process, they were transferred to a desiccator until they reached room temperature, at which point their weights were recorded. Subsequently, approximately 3 g of the sample were added to each crucible and placed in an oven at 105 °C until a constant weight was achieved. After this period, the crucibles were returned to the desiccator until they reached room temperature, and the weights were recorded for total solids calculations (Equation 2). The same crucibles were then subjected to calcination in a furnace at 550 °C for 30 min. After this process, the cooling step was repeated until room temperature was reached, and the weights were recorded again for fixed solids calculations (Equation 3).

4.1.3.1 Total solids [40]

$$TS = \frac{(A-B)}{(C-B)} * 100 \qquad \text{Eq. 2}$$

where:

TS percentage of total solids

A mass of the dry material plus the crucible, g

B crucible weight, g

C mass of the material at the beginning plus the crucible, g

4.1.3.2 Fixed solids [40]

$$FS = \frac{(D-B)}{(E-B)} * 100 \qquad \text{Eq. 3}$$

where:

FS percentage of fixed solids

D mass of the material after calcination plus the crucible, g

B crucible weight, g

E mass of the material at the beginning plus the crucible, g

4.1.4 Organic matter content

To determine the organic matter content, an adapted version of the method by Sampaio (2017) was employed, in which approximately 100 mg of dried and ground sludge was transferred to a 500 mL Erlenmeyer flask, into which a 1N solution of potassium dichromate ($K_2Cr_2O_7$) and 20 mL of concentrated sulfuric acid (H_2SO_4) were added. The mixture was vigorously stirred for one minute to prevent residue accumulation from adhering to the bottom of the flask, and then allowed to stand for 30 min. After this period, 200 mL distilled water, 10 mL concentrated orthophosphoric acid, and 1% ferroin indicator were added. The solution was titrated with 0.5N ammonium ferrous sulfate until a greenish color was obtained [41].

Sampaio originally reported that the color obtained during the titration process should be green. However, subsequent tests and information found in the literature suggest that the color change can vary depending on the sample, ranging from blue to green (as observed by Sampaio) or from green to reddish-brown (as observed by Standard Methods) [41, 43]. The organic matter content was calculated using the Equation 4.

$$OM = 1{,}725 * \frac{\left(10-\left(V_2*\frac{10}{v_1}\right)\right)*0{,}4}{m} \qquad \text{Eq. 4}$$

where:

OM percentage of organic matter content

V_1 volume of ammonium ferrous sulfate spent in the blank titration, mL

V_2 volume of ammoniacal ferrous sulfate tasted in the sample titration, mL

m mass of the analyzed sludge sample, g

4.1.5 Organic carbon content

Soil carbon exists mainly in three forms: as a mineral component in structures such as carbonates ($CaCO_3, MgCO_3\ etc.$), as an organic component in animal and plant residues at various stages of transformation, and as charcoal (pyrogenic carbon) resulting from natural fire events or applied to the soil as biochar [42]. When determining the organic carbon content in moist soil using potassium dichromate oxidation, only the easily oxidizable organic matter is quantified [41, 42].

Two techniques were employed in this test: the first involved oxidation by potassium dichromate following Sampaio's methodology, it's noteworthy that this methodology mirrors the one utilized for organic matter, utilizing an Equation 5, that is part of the organic matter equation [41]:

$$\%C = \frac{(10-(V_2*\frac{10}{V_1}*0{,}4)}{m} \qquad \text{Eq. 5}$$

where:

$\%C$ percentage of organic carbon

V_1 volume of ammonium ferrous sulfate spent in the blank titration, mL

V_2 volume of ammoniacal ferrous sulfate tasted in the sample titration, mL

m mass of the analyzed sludge sample, g

In the second method was utilized measuring equipment known as TOC (Total Organic Carbon), located in the CIMO laboratory - Mountain Research Center of the Polytechnic Institute of Bragança. The TOC technique employs total oxidation and acidification of the sample at 720 °C to distinguish between organic and inorganic carbon. The objective of this study was to compare and verify the effectiveness of the results obtained using each method.

4.1.6 Loss on ignition

This test involves determining the percentage of mass lost or decomposed by a sample when subjected to a pre-established thermal heating cycle, which typically requires high temperatures and is performed in a furnace or muffle furnace. The observed mass loss is related to the presence of structural water and/or organic matter (which may be contaminants) in the sample [44].

This characterization is necessary because, according to NBR 12653, the material is considered pozzolanic class N when the loss on ignition is less than or equal to 20%, and classes C and E when the result is less than or equal to 6% [35].

The test involved placing 1 g of residue in porcelain containers positioned in a muffle furnace at 900 °C for 50 min. After cooling for approximately 2 h, the containers were removed and transferred to a desiccator to complete cooling. Once fully cooled, the final weight of the containers were recorded. The loss on ignition was calculated using Equation 6.

$$LI = \frac{(m1 - m2)}{m} * 100 \qquad \text{Eq. 6}$$

where:

LI represents the percentage of loss on ignition

$m1$ mass of the crucible plus the mass of the sample, before calcination, g

$m2$ mass of the crucible plus the mass of the sample, after calcination, g

m mass of the sample used in the analysis, g

4.1.7 Atomic absorption spectrophotometer

Atomic absorption spectrophotometry is used to determine the concentration of an element in the sample by measuring the radiation of the characteristic wavelength absorbed by the vaporized atoms of that element. The sample was vaporized by being sucked into a flame at an appropriate temperature, and the flame was then crossed by the characteristic radiation of the element. The radiation was then passed through a monochromator and detected, allowing the measurement of the radiation absorbed by the atomized element in the flame [17]. The Varian Spectr AA 220 equipment in the analytical chemistry laboratory of the Polytechnic Institute of Bragança was used to conduct this test, which aimed to characterize the materials under analysis.

4.1.8 Digestion with Parr Pump

To measure the metal concentration using AAS, complete dissolution of the sample was required, which was achieved via sample digestion using Parr Pumps. The procedure involved adding approximately 100 mg of the sample along with 2 to 4 mL of 65% nitric acid (HNO_3) 65%, and heating in a microwave at varying time intervals (30 or 60 s) and power levels (600 or 800 Watts), allowing it to cool for approximately 16 h and taking the reading at AAS.

4.2 SLUDGE PREPARATION

To ensure that the sample composition and presence of organic matter did not affect the properties of the final cement, it was necessary to degrade the organic matter before incorporating it into the cement mortar [41]. To perform this degradation, the material burning technique was chosen, which involved four methods of drying the sludge, being sludge oven drying, two types of incineration and wet oxidation.

4.2.1 Sludge oven drying (SOD)

The manufacture of mortar specimens using only sludge serves as a standard for other analyses because the sludge undergoes only water removal without any other physical or chemical changes [3].

To prepare the samples, they were dried in porcelain crucibles using a Scientific Series 9000 Laboratory Oven (model 972), at 105 °C for 24 h, which created a thin layer, increased the surface area in contact with the heat oven, and contributed to the efficiency of the drying process [41].

4.2.2 Incineration

Incineration was selected as the technique to achieve the best results, using two different methods. The first technique (INC-1) involved incineration in two stages, starting with pre-dried sludge at 105 °C for 24 h, followed by burning in a muffle furnace at 300 °C for 0.5 h, and then at 900 °C for 3 h [3]. The second method (INC-2), described by Swarnalatha et al., involves a temperature progression scale, starting at 100 °C and ending at 800 °C over 8 h [45].

4.2.3 Wet oxidation (WO)

The typical operating conditions for this analysis included temperatures ranging from 150 to 330 °C and pressures from 1 to 22 MPa using pure or atmospheric oxygen for 15 to 120 min. However, due to laboratory limitations, the samples were prepared at a pressure of 2.02 bar (0.22 MPa) and a temperature of 121 °C for 18 min in an autoclave at the Chemical Processes Laboratory - Polytechnic Institute of Bragança. The samples were then oven dried at 105 °C for 24 h.

4.3 MORTAR SPECIMENS

Prismatic molds with dimensions of 4 x 4 x 16 cm were used to manufacture the mortar specimens (MS), with each specimen containing approximately 600 g, as shown in Figure 3. Six MSs were produced for each sludge concentration, of which three were used for testing on the 7th day of mortar curing, and the remaining three were used for the 28th day of curing. The standard MS was prepared with a composition consisting of 14% distilled water, 54% sand that had been dried for 24 h at 105 °C with a particle size smaller than 0.4 mm, and 32% cement, forming a paste. In contrast, in the other MS-incorporated sludges, the only difference in the composition of the paste was the concentration of cement, as the replacement was carried out with 3, 5, 7, and 10% of cement with sludge, and its was through mass replacement.

Figure 4: Mold used in the manufacture of mortar specimens

The NBR 5738 (ABNT) standard was used to produce the mortar specimens, which specifies the use of a horizontal compactor for the mortar paste developed and applied to the prismatic molds. After this stage, the MS were placed on a laboratory bench in the Geotechnological Laboratory of the ESTiG for 48 h, removed from their respective molds and transferred to a humid chamber maintained at 20-25 °C with 90% humidity (Figure 4).

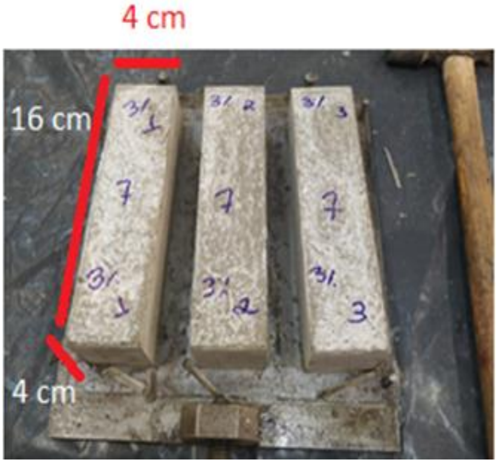


Figure 5: Mortar specimens after 48 hours on the bench

4.4 MECHANICAL AND COMPLEMENTARY TESTS

Four different tests were conducted on the produced MS, including flexural and compressive strength tests as well as leaching and water absorption tests. The strength tests were performed on the 7th and 28th days of cement mortar curing, compression tests were conducted, using the “Compression testing machine 3,000 kN type ST80L4”, this involved applying force at a point 4 cm from the end of the Mortar specimens until it reached the peak force applied, Figure 4 shows the equipment used.

Figure 6: Compressive strength testing equipment

Additionally, flexural tests were performed, using the “Prensa Marshall mod S212”, with the specimen positioned horizontally, applying force at its center until complete rupture as shown in Figure 6, Figure 7 shows the equipment used.

Figure 7: Mortar specimens after flexural test

Figure 8: Equipment for testing flexural strength

These two tests were aimed at detecting the effects of incorporating previously treated sludge into the cement mortar. The mortar was classified based on the compressive strength that the mortar specimen can withstand on the 28th day of curing, following the EN 998-1 standard, as illustrated in Table 9.

Table 9: Requirements for compressive strength applied to mortar [46]

CATEGORY	VALUES (N mm^{-2})
CS I	0.4 a 2.5
CS II	1.5 a 5.0
CS III	3.5 a 7.5
CS IV	≥ 6

Solid waste management and the assessment of its dangerousness are fundamental issues in environmental protection. Leaching and water absorption tests were conducted on the 28th day of curing [3, 41].

The water absorption test followed the LNEC E 394-1993 specification, aiming to determine the percentage of water absorbed by the prismatic mortar specimen after 48 h of immersion in distilled water. This percentage was calculated using Equation 7:

$$W_i = \frac{m_2 - m_1}{m_1} * 100 \qquad \text{Eq. 7}$$

where:

W_i represents the percentage of water absorption

$m1$ is the mass of the dry mortar specimen, g

$m2$ is the mass of the mortar specimen after 48 hours of saturation, g

The NBR 10005 standard was used to extract leachate from the solid waste, which is a crucial step in assessing the mobility and environmental impact of this waste. This procedure was carried out to determine the ability of the organic and inorganic substances contained in the solid waste to be transferred to an extraction medium through the leaching process [48]. The test was adapted because of the laboratory limitations.

To conduct this analysis, an initial assessment of the sample was essential to determine its physical state, whether it was a solid or a contained liquid, and whether a reduction in particle size was required. Initially, the sample was crushed and sieved through a 9.5 mm mesh. Subsequently, it was subjected to vacuum filtration, and finally, using Equation 8, the percentage of solids was calculated.

$$\mathrm{S}(\%) = \frac{final\ mass\ of\ filter\ residue}{\text{initial mass of residue}} * 100 \qquad \text{Eq. 8}$$

Subsequently, it was necessary to determine the optimal extraction solution. Approximately 5 g of the sample, with particle diameters ≤ 9 mm weas weighed and transferred to a beaker. To this, 96.5 mL of deionized water was added, and the mixture was vigorously shaken for 5 min using a magnetic stirrer. The pH was then measured. Meanwhile, when the pH exceeded 5.0, 3.5 mL of 1 N HCl was introduced, and the solution was thoroughly homogenized and, subsequently heated for 10 min at 50 °C. after cooling, the pH was measured again, and with the value still exceeding 5.0, it was determined that the appropriate extraction solution in compliance with the standard was nº 2. Extraction solution nº 2 involves mixing 5.7 mL of glacial acetic acid with distilled water to achieve a volume of 1 L, with a pH target of 2.88 ± 0.05.

Given that the sample comprised 100% solids and was nonvolatile, approximately 10 g of each sample was meticulously weighed and subsequently transferred into a leaching bottle. To this, extraction solution nº 2, in an amount 20 times the mass of the sample, was added, the bottle was securely sealed with adhesive tape to prevent leakage (Figure 8).

Figure 9: Sample with leached extract nº 2

The mixture was then placed into a horizontal agitator (Figure 9) and agitated for 18 ± 2 h. Shaking was conducted at a temperature not exceeding 25 °C, with a rotation speed of 150 ± 2 rpm. Following this, filtration was performed, leading to the formation of the liquid, called leached extract, from which the concentrations of residues in the sample were determined. For residue classification, the obtained data must be compared with the values outlined in Annex 1 [49].

Figure 10: Equipment used in leaching testing

4.5 TECHNICAL AND ECONOMIC FEASIBILITY

The evaluation of technical feasibility considers the energy expenditure required for each methodology to prepare sludge for its implementation in cement, as well as the energy savings achieved by partially replacing cement with sludge in the production of the cement matrix. The economic viability was also be assessed based on these criteria, taking into account the monetary aspects of these techniques, calculated according to Equation 9 [3], Table 10 shows some of the electricity demand values for the types of burning processes.

$$F = G - (G * h) + (I * j) \qquad \text{Eq. 9}$$

where:

F represents the economy or cost, $kWh.t^{-1}$ cement

G is the energy expenditure of tonne cement production, $kWh.t^{-1}$ cement

h is the cement concentration, fraction

I is the energy expenditure in the treatment of tonnes of particles, $kWh.t^{-1}$ particles

j is the concentration of sludge particles

Table 10: Energy demand for preparation of sludge

PROCESS	ELECTRICITY DEMAND
Cement production	100 $kWh.t^{-1}$ cement [58]
Drum or fluidized bed dryers	0.07 $kWh.kg^{-1}h20$ [3]
Drying operation	39 $kWh.t^{-1}$ dry sludge [3]
Dry sludge and incineration	275 $kWh.t^{-1}$ dry sludge [3]
	- 1024.5 $kWh.t^{-1}$ dry sludge (recovery)

Portland cement production is recognized as one of the main sources of carbon dioxide (CO_2) emissions in the global construction industry. Several studies highlight the significant contribution of the cement sector to global greenhouse gas emissions, largely due to the decarbonation of limestone during clinker production, which is responsible for approximately 90% of this industry's CO_2 emissions, being the main component of cement [51].

The consumption of a cement plant is approximately 100 kWh per ton of cement produced [52], in Portugal the monetary value for energy consumption in companies can be considered 0.15 $€/kWh$ and, for each ton of clinker produced 870 kg of CO_2 are released into the atmosphere [53]. Innovative strategies and technologies have been the subject of research to mitigate these emissions, including the use of clinker substitutes and the implementation of more efficient and sustainable processes [54].

In order to determine the reduction in cost and CO_2 emissions associated with the incorporation of sludge into the pasta, considering the production of one ton of cement as a reference, Equation 10 was used.

$$E = {}^{(C * p)}/_{1000} \qquad \text{Eq. 10}$$

where:

E represents the emission of CO_2, kg

C is the final concentration of cement with the partial substitution with sludge, kg

p is the CO_2 production in a ton of cement released into the atmosphere, kg

5 RESULTS AND DISCUSSION

Samples containing sludge oven drying (SOD), two stages incineration (INC-1), incineration involved a temperature progression scale (INC-2) and wet oxidation (WO) were prepared and tested.

5.1 SLUDGE CHARACTERIZATION

The sample exhibited a pH value of 8.46 and had high concentrations of various metals and minerals, with a chemical oxygen demand (COD) of 251 $g\ kg^{-1}$.

First, material characterization tests were conducted, encompassing measurements of moisture content, total solids, fixed solids, organic matter content, organic carbon content, loss on ignition, and atomic absorption spectrophotometry (AAS), to verify the elemental concentrations within the sample. The corresponding test values are presented in Table 11, and the concentrations of the elements are shown in annex 2.

Table 11: Results of sludge characterization tests

PARAMETER	VALUE
Moisture content	73.3%
Total solids	26.7%
Fixed solids	13.5%
Organic matter contente	29.9%
Organic carbon content	21.4 $mg\ L^{-1}$
Loss on ignition	89.1%

In accordance with Świerczek et al. (2018), the organic matter content was low, suggesting that the processed sludge had undergone stabilization. Furthermore, the moisture content of the sludge aligns with the values commonly reported in the literature, as demonstrated in Sampaio's study (2017), where it was recorded at 74.9%, and below the value found by Grabowski (2020) (83.2%).

A pH level above 7.0 indicates that chromium (Cr) is predominantly in its trivalent form (Cr^{3+}), which is its most stable state [55]. A study carried out by Muiz et al (2001), found a pH value of 8.5 for tannery sludge [56]. Additionally, when the pH is approximately 8, this suggests that chemical stabilization with liming products such as calcium carbonate ($CaCO_3$) or calcium hydroxide ($Ca(OH)_2$), does not occur, because the pH typically reaches a value near 12 in such cases [57, 58].

Because the sludge had a low total and fixed solid content, it was appropriate to use high temperatures to treat the material [59]. The total solids value closely corresponds to the findings reported by Gonçalves (2017), in author three-year study on several WWTP parameters, he recorded a value of 26.1% in the final year [58].

5.2 SLUDGE PREPARATION

Figure 10 shows the natural appearance of the sludge.

Figure 11: Sludge in natural

5.2.1 Sludge oven drying

Figure 11 shows the visual aspects of the sludge sample after drying in an oven. According to the SOD preparation methodology, it was assumed that all moisture was eliminated, resulting in an SOD humidity level of 0%.

Figure 12: Sample of sludge oven dried

5.2.2 Incineration

Figure 12 shows the results of the incinerations (INC-1 and INC-2). Since the burning model remains consistent, differing only in the execution technique, the visual appearance remains identical. The incineration process alters the color of the sludge and considerably diminishes its volume, by converting organic matter into carbon dioxide and water.

Figure 13: Sample of sludge incineration

5.2.3 Wet oxidation

The equipment used to prepare the sludge by wet oxidation is shown in Figure 13, and the appearance of the sludge before and after the autoclave process is presented in Figure 14.

Figure 14: Equipment used to prepare the sludge by WO

Figure 15: Sludge sample during the autoclave process

5.3 MORTAR

Mortar workability refers to the ease with which it can be mixed, transported, applied, and finished. As observed in the study of Grabowski (2020), this feature varies: in some cases, workability decreases when the mixture is homogenous, potentially due to porosity in the material, whereas in others, it increases with the addition of sludge [3].

For the INC-1 and INC-2 mortars, the workability and viscosity increased, with the latter exhibiting better results. The reduction in the workability of the mortar with SOD was not as significant as that of mortar with WO. Annexes 3 to 6 illustrate the visual condition of the samples following bench exposure. In some cases, the upper surface exhibited increased roughness, which was attributed to specific particles of the treated sludge. In others cases it was possible to verify the porosity of the material. These parameters were not measured but only for visual perception.

5.4 MECHANICAL TESTS

The results of the compressive tests on days 7th and 28th of curing are listed in Table 12. Additionally, Figure 16 illustrate the average compressive strengths on 28 days of the curing. The values of the standard deviations values in percentage were performed for each percentage of substitution in the Excel software, resulting in 0.00, 4.64, 9.40, 11.68 and 15.84 for 0, 3, 5, 7 and 10% of substitution respectively.

Table 12: Compressive test results by treatment and concentration (MPa)

DAY OF CURING	METHOD	0%	3%	5%	7%	10%
7th	SOD	21.19	20.20	17.64	15.88	13.75
7th	INC-1	21.19	24.00	24.61	22.69	27.59
7th	INC-2	21.19	25.68	23.03	25.21	26.34
7th	WO	21.19	15.00	10.81	6.31	3.69
28th	SOD	23.56	2.12	1.71	1.63	1.44
28th	INC-1	23.56	2.13	2.57	2.71	2.20
28th	INC-2	23.56	2.79	3.06	3.00	4.10
28th	WO	23.56	1.66	0.94	0.43	0.34

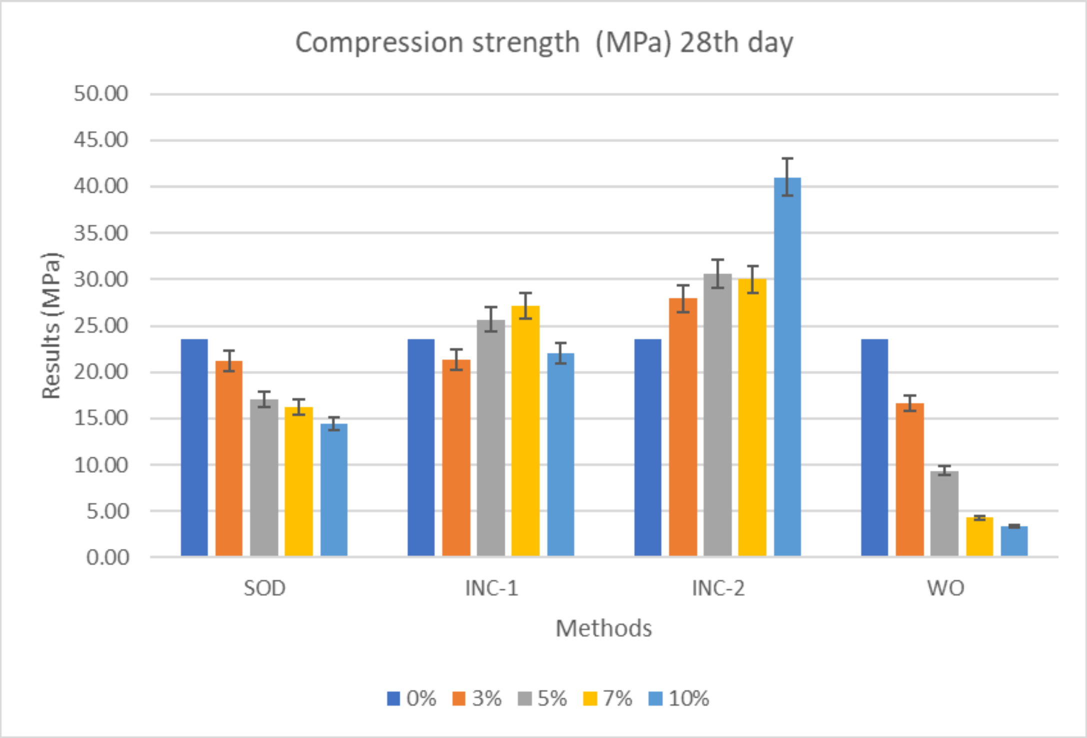


Figure 16: Compressive strength test at 28th days of curing

Solidified materials exhibiting compressive strengths exceeding 1 MPa hold significant potential for diverse applications, including their use as base and surfacing materials in road construction and as components in civil engineering, such as brick and block manufacturing, aggregates, mortar and various concrete structures, for both structural or non-structural purposes [4]. Brito supported this concept, asserting that cement matrices with compressive strengths exceding 1 MPa offer robust physical integrity, thus expanding the material's utility from paving bricks to a wide array of applications, as base and surfacing materials, aggregate components, and various concrete elements, both with and without structural functions [60].

Additionally, Dias [61] and Patel and Pandey [62] affirmed that the decrease in compressive strength may be attributed to the presence of specific lead salt compounds within the residue, which can interfere with cement hydration reactions that which are pivotal for the development of strength.

The outcomes of flexural tests on the 7th and 28th days of curing are presented in Table 13, while Figures 17 and 18 depict the average flexural strength on the 7th and 28th days of curing.

Table 13: Flexural test results by treatment and concentration (kN)

DAY OF CURING	METHOD	0%	3%	5%	7%	10%
7th	SOD	1.5	1.6	1.7	1.6	1.4
7th	INC-1	1.5	1.6	1.9	1.8	1.8
7th	INC-2	1.5	1.8	1.8	1.7	1.8
7th	WO	1.5	1.6	1.3	0.7	0.7
28th	SOD	1.8	1.8	1.7	1.8	1.6
28th	INC-1	1.8	1.9	2.0	2.0	2.0
28th	INC-2	1.8	2.2	2.3	2.2	2.7
28th	WO	1.8	1.6	1.5	1.0	0.8

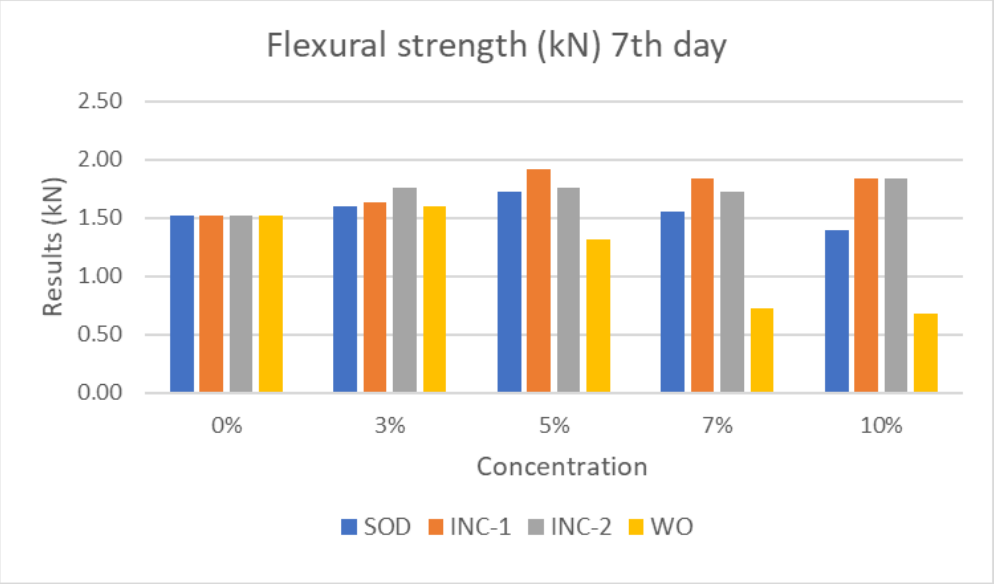


Figure 17: Results of flexural strength test at 7th days of curing

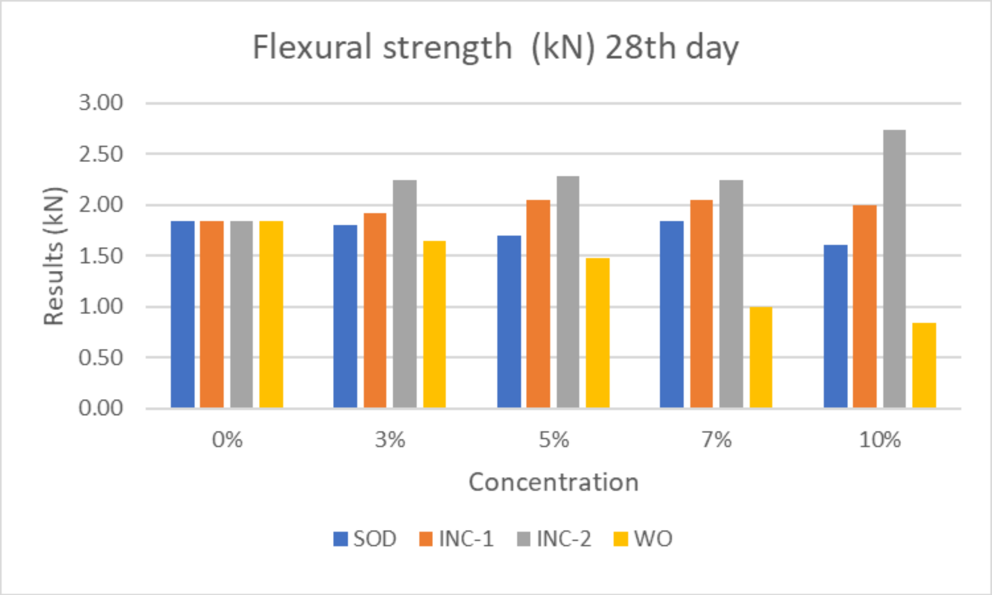


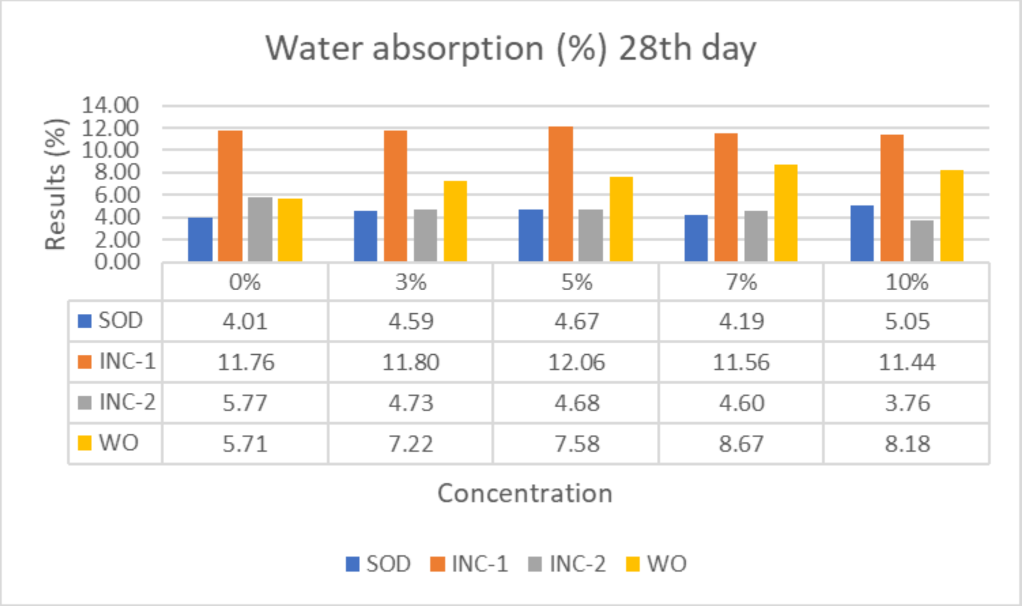
Figure 18: Results of flexural test at 28th days of curing

Based on the results presented in Figures 16 and 18, it is evident that the incineration methods achieved the expected results and yielded the best outcomes. Therefore, it was concluded that the mortar specimen that exhibited the best mechanical resistance was the specimen with a 10% substitution of INC-2 in the sludge. This observation can be attributed to the slow burning process employed, which effectively degraded all the organic matter in the waste. The dried sludge samples exhibited similar values and behaviors in terms of strength profiles and strength values. In contrast, the WO samples yielded less favorable results.

The flexural test exhibited a highly consistent behavior with the compressive test, as all sludge treatment methods (excluding WO, which showed divergent results) applied for cement substitution demonstrated a positive correlation between the substitution percentage and the corresponding increase in values.

5.5 COMPLEMENTARY TESTS

Complementary tests were carried out only with samples within 28 days of curing, in accordance with the standards followed. For the water absorption test, Equation 7 was used for the calculations, and the results are shown in Figure 19. In Annex 7, it is possible to see the place where the test was carried out and some samples after the absorption period.



	0%	3%	5%	7%	10%
SOD	4.01	4.59	4.67	4.19	5.05
INC-1	11.76	11.80	12.06	11.56	11.44
INC-2	5.77	4.73	4.68	4.60	3.76
WO	5.71	7.22	7.58	8.67	8.18

Figure 19: Water absorption at 28th days of curing

For leaching, according to Equation 8, it was concluded that the samples were 100% solid and that the extraction solution used was extraction solution nº 2. After agitation, filtration was carried out, and with the filtered liquid, the concentration of metals in the sample was measured, to compare with the initial concentrations and verify whether the samples were in accordance with the imposed standards. The reading was carried out in the laboratory analytical chemistry laboratory of the Polytechnic Institute of Bragança and the analyzed elements were iron, manganese, chromium, lead, cadmium, nickel, aluminum, arsenic and magnesium with all concentration results falling below the limits specified by NBR 10004, some results are illustrated in Figure 21 and 22, with the rest found in Annex 8.

SLUDGE OVEN DRYING		Elements (concent. ± prec.)		
Day of curing	**Composition**	**Cr**	**Pb**	**As**
28th	0%	0.048 mg/L ± 1.4%	≤ 0.10 mg/L ± 0.5%	≤ 1 mg/L ± 6.4%
	3%	1.451 mg/L ± 1.0%	≤ 0.10 mg/L ± 0.5%	≤ 1 mg/L ± 6.4%
	5%	1.358 mg/L ± 0.9%	≤ 0.10 mg/L ± 0.5%	≤ 1 mg/L ± 6.4%
	7%	2.754 mg/L ± 0.8%	≤ 0.10 mg/L ± 0.5%	≤ 1 mg/L ± 6.4%
	10%	6.322 mg/L ± 0.8%	≤ 0.10 mg/L ± 0.5%	≤ 1 mg/L ± 6.4%

INC-1		Elements (concent. ± prec.)		
Day of curing	**Composition**	**Cr**	**Pb**	**As**
28th	0%	≤ 0.05 mg/L ± 0.7%	≤ 0.10 mg/L ± 0.7%	≤ 1 mg/L ± 5.2%
	3%	≤ 0.05 mg/L ± 0.7%	≤ 0.10 mg/L ± 1.2%	≤ 1 mg/L ± 6.3%
	5%	≤ 0.05 mg/L ± 0.7%	≤ 0.10 mg/L ± 0.9%	≤ 1 mg/L ± 7.2%
	7%	≤ 0.05 mg/L ± 0.7%	≤ 0.10 mg/L ± 1.5%	≤ 1 mg/L ± 8.4%
	10%	≤ 0.05 mg/L ± 0.7%	≤ 0.10 mg/L ± 0.8%	≤ 1 mg/L ± 7.9%

Figure 20: Leaching test results for SOD and INC-1 methodologies

INC-2		Elements (concent. ± prec.)		
Day of curing	**Composition**	**Cr**	**Pb**	**As**
28th	0%	≤ 0.05 mg/L ± 0.7%	≤ 0.10 mg/L ± 0.9%	≤ 1 mg/L ± 8.5%
	3%	2.176 mg/L ± 0.4%	≤ 0.10 mg/L ± 0.2%	≤ 1 mg/L ± 7.4%
	5%	3.233 mg/L ± 0.5%	≤ 0.10 mg/L ± 0.3%	≤ 1 mg/L ± 7.2%
	7%	5.661 mg/L ± 0.7%	≤ 0.10 mg/L ± 0.5%	≤ 1 mg/L ± 8.1%
	10%	7.908 mg/L ± 0.6%	≤ 0.10 mg/L ± 0.7%	≤ 1 mg/L ± 8.3%

WET OXIDATION		Elements (concent. ± prec.)		
Day of curing	**Composition**	**Cr**	**Pb**	**As**
28th	0%	0.085 mg/L ± 0.9%	≤ 0.10 mg/L ± 12.8%	≤ 1 mg/L ± 5.2%
	3%	2.840 mg/L ± 0.3%	≤ 0.10 mg/L ± 13.6%	≤ 1 mg/L ± 6.3%
	5%	5.706 mg/L ± 0.3%	≤ 0.10 mg/L ± 9.3%	≤ 1 mg/L ± 7.2%
	7%	7.100 mg/L ± 0.5%	≤ 0.10 mg/L ± 13.1%	≤ 1 mg/L ± 8.4%
	10%	7.683 mg/L ± 0.3%	≤ 0.10 mg/L ± 10.7%	≤ 1 mg/L ± 7.9%

Figure 21: Leaching test results for INC-2 AND WO methodologies

The aim of leaching tests is to assess the ability of substances, whether pollutants or contaminants, to be released from a solid sample into a liquid medium. The analysis involved examining various liquids to ensure that all concentration results remained below the limits set by NBR 10004.

Upon reviewing the outcomes of this test, it became evident that the obtained values fell below the stipulated limits of the standards. Additionally, the concentrations of various analyzed elements were notably low and, in some cases, even non-existent. This indicates that the material presents no environmental hazard.

The best result was achieved for the specimen with 10% replacement of INC-2 by sludge, consulting the leach (Annexe 8) and water absorption data (Figure 19), indicating that this specimen presented the lowest result when compared to the standard. However, tests carried out with WO indicated higher water absorption values in all areas, indicating lower performance than the standard (0% replacement).

When we compare the values obtained in this research, with the results presented in topic 3.4, were not only comparable but also superior to those found by the author, as illustrated in Figure 3, extracted from the original work. While the author's best result achieved a 7% substitution using the SA method, in this study, a 10% substitution was achieved using the same method, resulting in a significant increase in cement waste substitution and improved compression results. Additionally, the results of the DS method (SOD in this study) were very similar to those obtained. Finally, the worst performance in both studies was attributed to the WO method, which yielded less favorable results.

5.6 ECONOMIC VIABILITY

Between 2010 and 2020, the average thermal energy intensity of clinker decreased annually by 0.2%, subsequently stabilizing at approximately 3.6 GJ/t clinker. This reduction coincided with an increase in the sector's electricity intensity, reaching approximately 100 $kWh.t^{-1}$ cement by 2022 [63]. According to Cochez and Nijs (2010), the efficiency and type of cement production process result in variations in electricity demand, ranging from 90 to 150 kWh per ton of cement [64].

In a study conducted by Shnell et al. (2020), drum or fluidized bed dryers, which transfer heat to the sludge through conduction and convection, usually using hot gas or steam, exhibited an energy consumption rate of approximately 0.07 kWh per kilogram of water removed [64]. Given that each ton of dry sludge requires the evaporation of 683 kg of water (reducing humidity from 73.3% to 5.0%), the electric energy demand for this process is estimated to be 47.81 kWh per ton of dry sludge.

For the sake of clarity, energy savings calculations were performed for concentrations of both 3% and 10%, with the remaining replacement percentages falling within this range.

In this scenario, the electrical consumption for the portion corresponding to cement in the mortar was 97 $kWh.t^{-1}$ cement at a concentration of 3%, and 90 $kWh.t^{-1}$ cement to 10%. Considering the value of 100 $kWh.t^{-1}$ cement for the production of cement, the energy savings would be 5.22 $kWh.t^{-1}$ cement and 1.57 $kWh.t^{-1}$ cement, replacing 10% and 3% respectively. According to Grabowski (2020), with the same replacement percentage, the energy savings were 8.6 $kWh.t^{-1}$ cement (10% sludge) and 2.6 $kWh.t^{-1}$ cement (3% sludge) [3].

The same author explored the perspectives of other researchers, who suggested that the incineration process consumes 275 $kWh.t^{-1}$ dry sludge, but the operation has an energy recovery of 1024.5 $kWh.t^{-1}$ dry sludge and the drying operation consumes 39 $kWh.t^{-1}$ dry sludge [3]. In these scenarios, consumption was 15.05 $kWh.t^{-1}$ cement (10%) and 74.51 $kWh.t^{-1}$ cement (3%), resulting in energy savings 84.95 $kWh.t^{-1}$ and 25.48 $kWh.t^{-1}$ cement, respectively, for the incineration process. In the drying process 98.17 $kWh.t^{-1}$ cement (3%) and 93.9 $kWh.t^{-1}$ cement (10%) for the portions of sludge plus cement resulted in energy savings of 1.83 $kWh.t^{-1}$ and 6.1 $kWh.t^{-1}$ cement. The results were very close to what the author found, with consumption of 100.1 $kWh.t^{-1}$ and 95.7 $kWh.t^{-1}$ cement and electricity savings 1.9 $kWh.t^{-1}$ and 6.3 $kWh.t^{-1}$, respectively.

Table 14 presents the energy savings results, computed using Equation 9, for each of the considered processes.

Table 14: Energy savings according to literature values

		Energy saving ($kWh.t^{-1}$ cement)	
Process	**Eletricity demand**	**3%**	**10%**
Drum or fluidized bed dryers	0.07 $kWh.t^{-1}{}_{H20}$ [65]	1.6	5.2
Drying operation	39 $kWh.t^{-1}$ dry sludge [3]	1.8	6.1
Dry sludge and incineration	-749.5 $kWh.t^{-1}$ dry sludge [3]	25.5	85.0

According to the European Central Bank, the carbon price is projected to rise from €85 in 2021 to €140 per tonne of CO_2 emission by 2030 [66]. Information gathered from Carbon Credits indicates that the average value for carbon emissions in 2023 was €90 per ton of CO_2 emitted [67]. Considering the energy consumption of 100 kWh and a cost of 0.15 euros per kWh for the production of one ton of cement, along with the emission of 870 kg of CO_2 per ton, Table 15 visually represents the reduction in costs and CO_2 emissions (Equation 10) associated with the integration of sludge into the mixtures. These reductions were based on the quantity of one ton of cement.

Despite each MS weighing around 600 g, with 192 g attributed to cement, the production potential is noteworthy. With 1000 kg of cement, approximately 5208 specimens can be generated, leading to the production of 3125 kg of mortar per ton of cement, these values represent the standard specimen with 0% sludge replacement. Table 15 presents the "Final mortar concentration (kg)" column, displaying the concluding mortar production figures for each percentage of sludge replacement per ton of cement.

Table 15: Reduction in cost and CO_2 emissions with the partial replacement of sludge

% of substitution by sludge	Final cement concentration (kg)	Final mortar concentration (kg)	Cement production cost (€)	CO_2 reduction emission (kg)	CO_2 profit (€)	Overall gain (€)	Overall cost (€)
0%	1000	3125.0	15.0	0	0	0	15.0
3%	970	3221.6	14.5	26.1	2.3	1.9	12.2
5%	950	3289.5	14.2	43.5	3.9	3.2	10.3
7%	930	3360.2	13.9	60.9	5.5	4.4	8.5
10%	900	3472.2	13.5	87	7.8	6.3	5.7

These findings highlight not only the achievement of monetary and energy savings through the partial replacement of cement with sludge from a WWTP tannery industry but also a concurrent reduction in CO_2 emissions into the atmosphere due to the diminished utilization of cement.

6 CONCLUSIONS AND FUTURE RESEARCH

6.1 CONCLUSIONS

The study involved evaluating the mechanical and chemical properties of mortar samples containing sludge from the tanner industry wastewater treatment plants (WWTP), investigating the technical feasibility of these methods. Additionally, a comparative analysis of energy production costs, both in cement production and sludge preparation for use in mortars, allowed for an assessment of the economic viability of these practices.

Except for the WO methodology, the incorporation of small proportions of sludge ash did not adversely affect the mechanical and/or chemical resistance of the mortar. The most favorable results, as presented in data, were achieved through the INC-2 methodology, especially at a 10% replacement rate. This approach demonstrated superior performance in mechanical tests and lower values in complementary (chemical) assessments than the standard. Conversely, autoclaving sludge has not proved to be an unattractive option. It failed to fully degrade all organic matter, resulting in reduced mechanical strength and higher water absorption test results when compared to the dry sludge approach, leaving the mortar porous and crumbly.

Mortar substitutions of 7% and 10% cement with WO particles fell into category CS III, whereas all other treatment types and substitution rates fell into category CS IV.

In terms of energy costs, the low organic matter content in the sludge results in energy savings, as it requires a relatively short burning time to effectively degrade the material. In the context of CO2 emissions, the incorporation of sludge yields positive effects as it diminishes the need for cement, resulting in a reduction of CO2 emissions and thereby contributing to a financial gain for the cement industry. Therefore, this material holds significant potential for use in civil construction.

These findings emphasize the potential and effectiveness of the techniques applied in this study to enhance cement mortar properties by incorporating WWTP sludge from the tannery industry. This approach aligns perfectly with the principles of the circular economy, providing benefits to various stakeholders. It allows the construction sector to adopt a novel product, lowering production costs. It introduces a novel product to the construction sector, reducing production costs, addressing waste issues within the tanning industry, diverting waste from landfills, and reducing environmental impact. Additionally, it minimizes the extraction of raw materials from the environment and contributes to sustainability.

6.2 FUTURE RESEARCH

In this study, several standards were considered to characterize and assess of mortar quality. However, there are numerous other standards available for exploration, including NBR 9778, EN 13755, and the National Normative Collection on Concrete and its Constituents, among others. A combination of European and Brazilian standards can provide a more comprehensive and reliable dataset.

One of the standards discussed, EN 998-1:2017, encompasses various parameters for evaluating mortar quality, including compressive and flexural strengths, both of which were addressed in this study. However, there is potential for further investigation of this standard achieve a more detailed assessment of mortar quality and safety.

Additionally, there is an opportunity to delve into metal recovery, conduct additional tests, such as flow table testing and pull-out testing, and explore the interaction of binder materials within the mortar, including their microscopic behavior. New drying methods can be considered, as well as research into novel mortar mixing formulas, involving the introduction of new components and varying proportions. This exploration could pave the way for fresh avenues of improvement and innovation in the field of mortar production.

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8 ANNEXES

Annexe 1: Maximum limit concentration in the extract obtained in the leaching test [49]*

Parameter	Maximum limit on leachate ($mg\ L^{-1}$)
Arsenic	1,0
Barium	70,0
Cadmium	0.5
Lead	1.0
Total Chrome	5.0
Fluoride	150.0
Mercury	0.1
Silver	5.0
Selenium	1.0

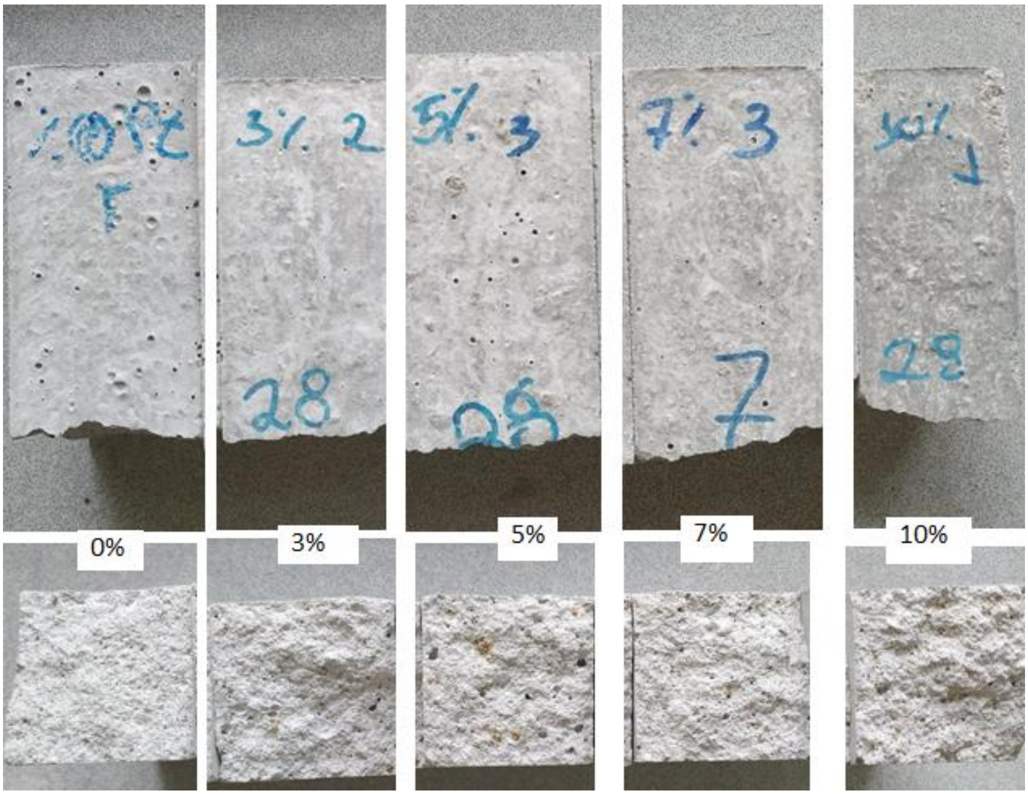
* Adapted

Annexe 2: concentrations of the elements in the sample

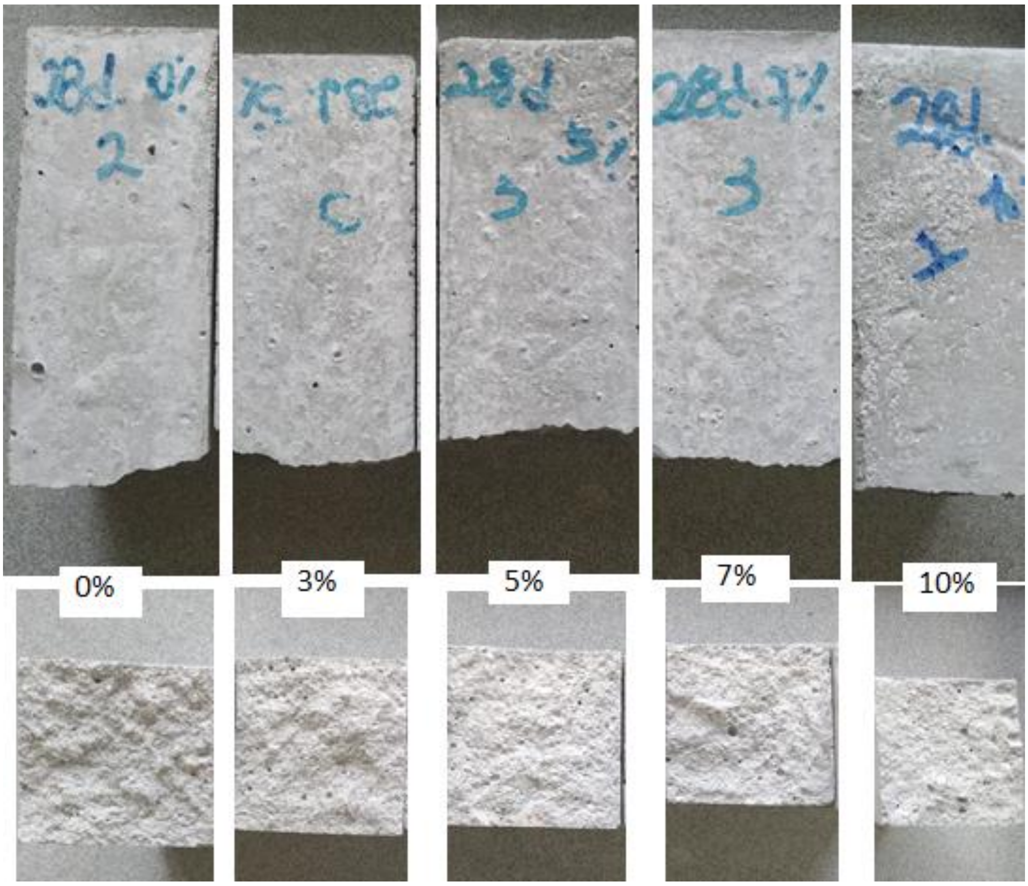
ELEMENT	CONCENTRATION ($mg\ kg^{-1}$ dry matter)
Lead	17.2
Manganese	890
Phosphorus	6210
Strontium	133
Arsenic	6.14
Zinc	86.3
Cobalt	5.08
Chromium	4100
Iron	8880
Nickel	13.8
Sodium	5760
Magnesium	8100
Aluminum	14500
Titanium	298
Sulfur	8670

Potassium	12600

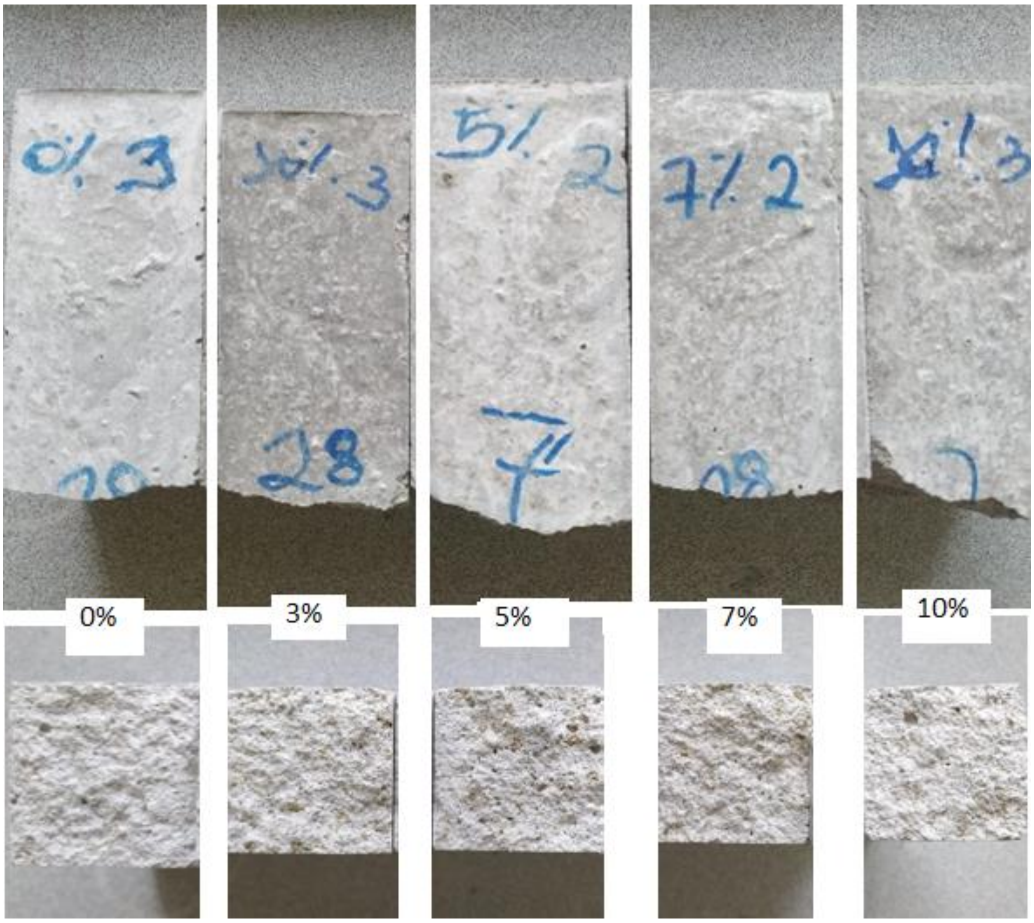
Annexe 3: Images of specimens with sludge oven drying



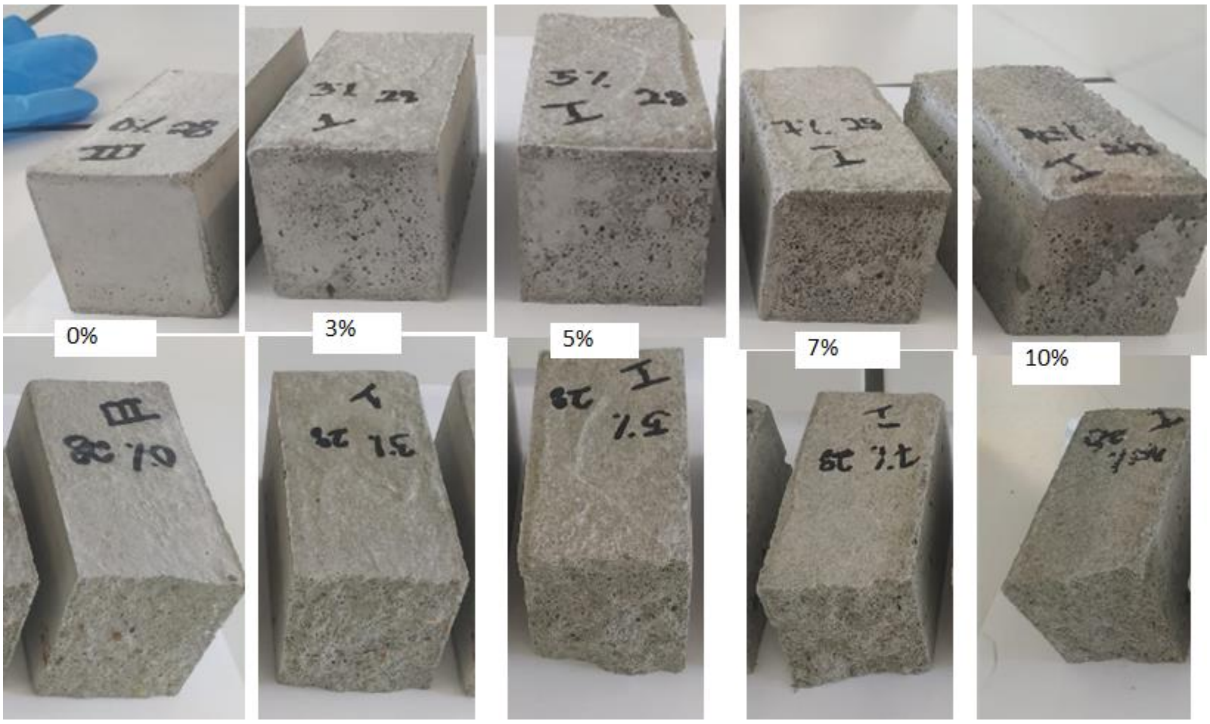
Annexe 4: Images of specimens with incineration on two steps



Annexe 5: Images of specimens with incineration by scale



Annexe 6: Images of specimens with wet oxidation



Annexe 7: Images of water absorption test

Specimens during water absorption

Specimens after water absorption

Specimens during water absorption

Annexe 8: Leach test results

- SOD

SLUDGE OVEN DRYING		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Cr**	**Mn**	**Fe**
28th	0%	0.048 mg/L ± 1.4%	0.056 mg/L ± 2.9%	0.146 mg/L ± 4.0%
	3%	1.451 mg/L ± 1.0%	0.094 mg/L ± 1.7%	0.199 mg/L ± 3.4%
	5%	1.358 mg/L ± 0.9%	0.082 mg/L ± 2.1%	0.151 mg/L ± 3.6%
	7%	2.754 mg/L ± 0.8%	0.091 mg/L ± 1.9%	0.176 mg/L ± 3.6%
	10%	6.322 mg/L ± 0.8%	0.0167 mg/L ± 1.1%	0.168 mg/L ± 3.6%

SLUDGE OVEN DRYING		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Pb**	**Mg**	**Ni**
28th	0%	≤ 0.10 mg/L ± 0.5%	≤ 0.15 mg/L ± 0.7%	≤ 0.1 mg/L ± 20.7%
	3%	≤ 0.10 mg/L ± 0.5%	≤ 0.15 mg/L ± 0.7%	≤ 0.1 mg/L ± 20.7%
	5%	≤ 0.10 mg/L ± 0.5%	≤ 0.15 mg/L ± 0.7%	≤ 0.1 mg/L ± 20.7%
	7%	≤ 0.10 mg/L ± 0.5%	≤ 0.15 mg/L ± 0.7%	≤ 0.1 mg/L ± 20.7%
	10%	≤ 0.10 mg/L ± 0.5%	≤ 0.15 mg/L ± 0.7%	≤ 0.1 mg/L ± 20.7%

SLUDGE OVEN DRYING		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Cd**	**As**	**Al**
28th	0%	≤ 0.05 mg/L ± 15.3%	≤ 1 mg/L ± 6.4%	≤ 0.05 mg/L ± 1.7%
	3%	≤ 0.05 mg/L ± 15.3%	≤ 1 mg/L ± 6.4%	≤ 0.05 mg/L ± 1.7%
	5%	≤ 0.05 mg/L ± 15.3%	≤ 1 mg/L ± 6.4%	≤ 0.05 mg/L ± 1.7%
	7%	≤ 0.05 mg/L ± 15.3%	≤ 1 mg/L ± 6.4%	≤ 0.05 mg/L ± 1.7%
	10%	≤ 0.05 mg/L ± 15.3%	≤ 1 mg/L ± 6.4%	≤ 0.05 mg/L ± 1.7%

- INC-1

INC-1		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Cr**	**Mn**	**Fe**
28th	0%	≤ 0.05 mg/L ± 0.7%	0.002 mg/L ± 36.7%	0.120 mg/L ± 4.9%
	3%	≤ 0.05 mg/L ± 0.7%	0.000 mg/L ± 59.8%	0.153 mg/L ± 4.2%
	5%	≤ 0.05 mg/L ± 0.7%	0.001 mg/L ± 35.4%	0.134 mg/L ± 5.1%
	7%	≤ 0.05 mg/L ± 0.7%	0.005 mg/L ± 23.0%	0.625 mg/L ± 1.4%
	10%	≤ 0.05 mg/L ± 0.7%	0.003 mg/L ± 27.75	0.150 mg/L ± 4.2%

INC-1		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Pb**	**Mg**	**Ni**
28th	0%	≤ 0.10 mg/L ± 0.7%	≤ 0.15 mg/L ± 1.2%	≤ 0.1 mg/L ± 30.2%
	3%	≤ 0.10 mg/L ± 1.2%	≤ 0.15 mg/L ± 0.8%	≤ 0.1 mg/L ± 33.1%
	5%	≤ 0.10 mg/L ± 0.9%	≤ 0.15 mg/L ± 1.3%	≤ 0.1 mg/L ± 24.2%
	7%	≤ 0.10 mg/L ± 1.5%	≤ 0.15 mg/L ± 0.7%	≤ 0.1 mg/L ± 18.4%
	10%	≤ 0.10 mg/L ± 0.8%	≤ 0.15 mg/L ± 0.5%	≤ 0.1 mg/L ± 21.3%

INC-1		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Cd**	**As**	**Al**
28th	0%	≤ 0.05 mg/L ± 29.1%	≤ 1 mg/L ± 5.2%	≤ 0.05 mg/L ±1.7%
	3%	≤ 0.05 mg/L ± 23.4%	≤ 1 mg/L ± 6.3%	≤ 0.05 mg/L ±1.7%
	5%	≤ 0.05 mg/L ± 30.1%	≤ 1 mg/L ± 7.2%	≤ 0.05 mg/L ± 1.5%
	7%	≤ 0.05 mg/L ± 19.3%	≤ 1 mg/L ± 8.4%	≤ 0.05 mg/L ± 1.3%
	10%	≤ 0.05 mg/L ± 21.7%	≤ 1 mg/L ± 7.9%	≤ 0.05 mg/L ± 1.8%

- INC-2

INC-2		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Cr**	**Mn**	**Fe**
28th	0%	≤ 0.05 mg/L ± 0.7%	0.000 mg/L ± 0.0%	0.223 mg/L ± 2.8%
	3%	2.176 mg/L ± 0.4%	0.001 mg/L ± 64.6%	0.216 mg/L ± 4.2%
	5%	3.233 mg/L ± 0.5%	0.001 mg/L ± 76.2%	0.279 mg/L ± 3.1%
	7%	5.661 mg/L ± 0.7%	0.000 mg/L ± ≥100%	0.270 mg/L ± 3.0%
	10%	7.908 mg/L ± 0.6%	0.000 mg/L ± ≥100%	0.303 mg/L ± 0.6%

INC-2		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Pb**	**Mg**	**Ni**
28th	0%	≤ 0.10 mg/L ± 0.9%	≤ 0.15 mg/L ± 2.2%	≤ 0.1 mg/L ± 47.4%
	3%	≤ 0.10 mg/L ± 0.2%	≤ 0.15 mg/L ± 1.9%	≤ 0.1 mg/L ± 30.7%
	5%	≤ 0.10 mg/L ± 0.3%	≤ 0.15 mg/L ± 1.1%	≤ 0.1 mg/L ± 27.2%
	7%	≤ 0.10 mg/L ± 0.5%	≤ 0.15 mg/L ± 0.7%	≤ 0.1 mg/L ± 20.7%
	10%	≤ 0.10 mg/L ± 0.7%	≤ 0.15 mg/L ± 0.4%	≤ 0.1 mg/L ± 26.2%

INC-2		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Cd**	**As**	**Al**
28th	0%	≤ 0.05 mg/L ± 20.3%	≤ 1 mg/L ± 8.5%	≤ 0.05 mg/L ± 3.2%
	3%	≤ 0.05 mg/L ± 27.3%	≤ 1 mg/L ± 7.4%	≤ 0.05 mg/L ± 3.9%
	5%	≤ 0.05 mg/L ± 33.9%	≤ 1 mg/L ± 7.2%	≤ 0.05 mg/L ± 1.5%
	7%	≤ 0.05 mg/L ± 22.4%	≤ 1 mg/L ± 8.1%	≤ 0.05 mg/L ± 1.6%
	10%	≤ 0.05 mg/L ± 18.8%	≤ 1 mg/L ± 8.3%	≤ 0.05 mg/L ± 1.8%

- WO

WET OXIDATION		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Cr**	**Mn**	**Fe**
28th	0%	0.085 mg/L ± 0.9%	0.000 mg/L ± 0.6%	0.222 mg/L ± 8.7%
	3%	2.840 mg/L ± 0.3%	0.000 mg/L ± 0.9%	0.254 mg/L ± 7.4%
	5%	5.706 mg/L ± 0.3%	0.000 mg/L ± 0.7%	0.210 mg/L ± 8.1%
	7%	7.100 mg/L ± 0.5%	0.000 mg/L ± 0.8%	0.252 mg/L ± 6.6%
	10%	7.683 mg/L ± 0.3%	0.000 mg/L ± 0.6%	0.284 mg/L ± 6.7%

WET OXIDATION		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Pb**	**Mg**	**Ni**
28th	0%	≤ 0.10 mg/L ± 12.8%	≤ 0.50 mg/L ± 0.6%	≤ 0.1 mg/L ± 60.0%
	3%	≤ 0.10 mg/L ± 13.6%	≤ 0.50 mg/L ± 0.8%	≤ 0.1 mg/L ± 29.2%
	5%	≤ 0.10 mg/L ± 9.3%	≤ 0.50 mg/L ± 0.6%	≤ 0.1 mg/L ± 12.1%
	7%	≤ 0.10 mg/L ± 13.1%	≤ 0.50 mg/L ± 1.7%	≤ 0.1 mg/L ± 8.8%
	10%	≤ 0.10 mg/L ± 10.7%	≤ 0.50 mg/L ± 0.3%	≤ 0.1 mg/L ± 6.3%

WET OXIDATION		**Elements (concent. ± prec.)**		
Day of curing	**Composition**	**Cd**	**As**	**Al**
28th	0%	≤ 0.05 mg/L ± 29.6%	≤ 1 mg/L ± 7.4%	≤ 0.1 mg/L ± 1.4%
	3%	≤ 0.05 mg/L ± 21.8%	≤ 1 mg/L ± 7.6%	≤ 0.1 mg/L ± 1.6%
	5%	≤ 0.05 mg/L ± 17.2%	≤ 1 mg/L ± 5.5%	≤ 0.1 mg/L ± 1.5%
	7%	≤ 0.05 mg/L ± 12.8%	≤ 1 mg/L ± 8.1%	≤ 0.1 mg/L ± 1.2%
	10%	≤ 0.05 mg/L ± 15.1%	≤ 1 mg/L ± 8.0%	≤ 0.1 mg/L ± 1.8%