

Review

Using Calcined Marls as Non-Common Supplementary Cementitious Materials—A Critical Review

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Abstract: This review summarizes the major research and scientific findings on the relevance of using calcined marl as supplementary cementitious material in developing eco-friendly cement for the next generation. Incorporation of calcined marl into cement can result in changes in the properties of these binders, and thus compatibility with other additions could be potential challenging, particularly at higher replacement ratios. From the reviewed literature, a detailed investigation on the characterization of calcined marls, activation methods, influencing parameters, along with studies on the hydration and microstructure was discussed, the overall objective aimed at coming up with the optimal physical and chemical parameters to generate highly reactive marl.

Keywords: calcined marls; supplementary cementitious material; activation methods; hydration



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1. Introduction

In the coming years, cement companies will be seeking to reach the concept of scale economies by increasing production, lowering costs, and reducing CO₂ emissions. The need for alternative strategies is becoming urgent as the cement industry is the third largest emitter of carbon dioxide [1] just behind energy production for housing and fuel for transportation. Moreover, continuous population growth over the past few years has resulted in the need to increase domestic infrastructures. This would not be feasible without cement: 4.6 billion tons of cement were globally produced only in 2015 [2]. This amount is much higher than the human food consumption [3]. According to a scenarios analysis of the China TIMES model [4], cement demand is expected to reach 2.3 billion tons by 2030 in China alone. Energetically speaking, to produce a ton of cement requires 80 to 100 kWh of electrical power [5], and it releases an average of 0.95 tons of CO₂. Nowadays the trend is to reduce this value to half of the current level. About 40% of this energy comes from the chemical reaction of clinker, while fuel combustion is responsible for the rest [6]. Moreover, cement-based materials made up around 30% of the overall use of materials worldwide [7].

In light of this, the cement industry has been long known to investigate several ways to mitigate the harmful effects on the environment. The World Business Council for Sustainable Development suggested many mitigation scenarios [8] through energy efficiency, alternative fuels, carbon capture and storage (CCS), and clinker substitute. Meanwhile, many challenges are faced by the industrial communities to efficiently implement these strategies in the cement plants and to measure the benefits from an environmental and economic perspectives.

Among the most effective strategies for energy efficiency is integrating a pre-calciner with the kiln which allows more than a half of released energy to be recovered [9]. Also, tires, animal meals, waste oils, and other organic materials can be considered as an effective alternative fuel regarding their high calorific capacity [10]. For instance, 80% of the thermal needs in Europe, are covered by organic waste [11]. The estimated gained energy from the combustion of these alternative fuels is about 30–45 kWh/t of clinker [12].

Nonetheless, CO₂ capture and storage (CCS) is the key technology to make major savings in carbon dioxide emissions. Barker et al. claimed that CCS-free production concentrates more than 60% of CO₂ in the air from mineral decomposition [13]. Such a problem can be avoided using this modern technology. However, many issues are still limiting the use of this technology at large scales due to treatment costs that may vary from 24–70 € per ton of cement [12]. CCS is not affordable for many countries with low-income and where population growth is still high. These poor communities constitute around 40% of the world's population. Therefore, more affordable cementitious materials must be adopted to meet the needs of these developing countries.

Clinker substitute has proven to be a very effective way to reduce greenhouse gas (GHG) emissions through the use of supplementary cementitious materials (SCMs) (e.g., fly ashes, slags, silica fumes, calcined clays, etc.). These materials are generally used due to their pozzolanic behavior and through potential recycling as most of them are wastes [14]. However, the availability of these materials is a big concern. The upcoming resources that have received much interest are calcined clays. Their availability, their pozzolanic reactivity after calcination, make them an efficient material for clinker replacement. In the same category, calcined marl is an example, and because of its weak use in conventional applications, marl is therefore also regarded as a waste product that can be recovered in large amounts at minimal cost [15].

The current paper aims to highlight the literature related to the different types of used SCM, and to focus particularly on the formulation, use, effectiveness, and pozzolanic performance testing of marls, in the view of suggesting the optimal parameters that will ensure their compatibility with other components in blended cement and overcome their limitations if any.

2. General Background of Supplementary Cementitious Materials (SCMs)

2.1. Introduction

SCMs describe a variety of materials which are widely used in concrete in addition to Portland cement. They were used to improve the long-term strength of the concrete [16]. A broad range of materials can be used as SCMs; some are widely available like calcined clays (Si-Al) and natural pozzolans. Other materials can also be used such as silica fume, blast furnace slag, coal fly ash, and other industrial pozzolanic by-products [17]. SCM-based cements often require a higher amount of water than conventional cements. Their use offers tremendous potential in cement production to reduce CO₂ emission. Life-cycle analysis shows that using SCMs in the concrete mixtures has a substantial reduction in greenhouse gas emissions and lowering the costs by decreasing the calcination energy [18–20]. Several parameters are improved by using SCMs such as particle packing, and pore refinement [21]. However, the limited supply of those materials in many regions is a barrier to broader utilization.

In the future, mitigating environmental issues will include the use of specific SCMs in conjunction with their local availability. Some materials like fly ash will continue to be used, but their use shall be more limited as they are not accessible. Today, cement plants are already consuming about 90% of available blast furnace slag [22]. These materials are not widely available to meet the market challenge. Hence it is now essential to use SCMs based on calcined clays.

Calcined clays are certainly key materials in this respect, they are proven to be abundant in almost every corner of the world, and so they have become the most promising

source of additional SCMs which can make a substantial contribution to lower further the environmental impact of cement and concrete [23].

2.2. Types of SCM

2.2.1. Fly Ash (FA)

Fly ash (FA) is an industrial byproduct generated by coal combustion-based power stations [24]. The use of fly ash as a cement replacement can enhance the strength and durability of concrete and affect setting time in complex ways. It works as a filler and as pozzolan at the same time, dilutes the material of cement, and chemically reacts with products from cement hydration.

The replacement of 25% of ordinary Portland cement with FA showed that the greenhouse gas emissions of concrete (25 MPa/32 MPa) mixtures were reduced by 13–15% [25]. Less than one-third of the available FA is suitable for blending in cement due to the presence of unburned organic matter [22]. Moreover, burning coal for electricity is being debated in many countries because of the environmental burdens. Therefore, FA availability is an issue in the long term [26].

2.2.2. Blast Furnace Slag

Blast furnace slag (BFS) is one of the most widely used and effective SCMs. It is a by-product of the pyrometallurgical iron industry mainly composed of non-ironic products, fluxes, and coke ashes. The production of one ton of steel leads to the generation of about 300 kg of BFS [27]. Unlike cement, the slag does not develop binding properties at room temperature underwater. A soda treatment is often required to activate this inert material [28]. The influence of the various activators on the slag hydration was studied by Lognot et al. [29]. Two other methods are used for further BFS treatment, air-cooling and water-quenching. The first is usually used in applications at a low level, like fill for bitumen, and so granulated blast furnace slag is formed by water-quenching slag. It can then be ground with gypsum to create this ground-granulated blast furnace slag (GGBFS), with the presence of an alkali activator, GGBFS can be used by itself. Furthermore, it is often added to pure Portland cement clinker, followed by an inter-grinding of the two materials to create blended cement [30]. GGBFS has a similar composition to calcium silicate hydrate, and it can be incorporated in cement formulation with a high level of replacement. This hydraulic latent material may reach a proportion of 70% of the cement [12]. In addition, GGBFS will lead to a 47.5% decrease in greenhouse gas emissions in case of using it as a cement substitute in concrete [31]. However, the amount of slag available couldn't keep up with the high demand for cement. Moreover, nowadays more steel is being recycled because of environmental pressures, and therefore slag's accessibility is limited.

2.2.3. Calcined Clays

There is already a great history of using calcined clays to replace a part of cement [32]. Mielnez et al. [33] examined pozzolan calcination in the early 1950s, and the possibility of using it as concrete additions in the US. In Brazil in the Jupia dam was first construction with 30% of replacement by metakaolin using it as supplementary cementitious material (SCM) in the 1960s; the same country has produced 2 Mt per year of calcined clays since the 1970s [20]. These materials are known to have pozzolanic properties. Depending on the source and chemical composition of these clays, the calcination process is widely variable. Some require a high thermal treatment, others do not [34]. Their reactivity relies on making the right choices in terms of calcination conditions and particle size distribution. According to Taylor-Lange et al. [35], the calcination of kaolin remains one of the most effective choices for SCMs. The pozzolanic reaction improves the compressive strength values, reduces the porosity and enhances the durability of concrete. A high replacement of clinker by metakaolin presents an extra alumina that will react with more limestone enhancing the properties of the cement [36]. Moreover, in the early stages, calcined clays act as a filler and diluent, but when hydrated, their pozzolanic activity partially consumes calcium hydrates,

resulting in a reduction in coarse porosity, hence the late resistance [37]. Nevertheless, such clays are hardly accessible in many regions and costly, and this reduces the widespread use and production of metakaolin.

2.2.4. SCM Based on Calcined Clay and Limestone

According to Scrivener et al. [38], a mixture of limestone and calcined clay is used to replace part of the clinker in blended cement, and these products are named LC3-Limestone calcined clay cement. In the designation LC3-X, X refers to the portion of clinker content of the mixture. With that kind of combined substitution, it will be possible to achieve good mechanical properties with a higher substitution rate compared to the other pozzolans [39], especially at a very young age, and because the clay is finely divided, it can react faster and easier than fly ash. In earlier investigations, it was shown that the LC3 cement has good protection of reinforcement, excellent resistance to chloride penetration, and sulfate stability [26].

2.2.5. Natural SCMs

Several natural pozzolans can be use as SCMs. Perlite, pumice, and zeolite are examples. Their structure and properties are presented in the Table 1.

Table 1. Examples of natural supplementary cementitious materials (SCMs) [40].

Natural SCMs	Structure	Features
Perlite	Siliceous and amorphous hydrated volcanic glass	Good pozzolanic reactivity
Pumice	Amorphous and porous volcanic rock	Low density and high absorption capacity
Zeolite	Hydrated aluminosilicate mineral	Chloride resistance

3. Calcined Marls as SCMs

3.1. Characteristics of Marls

Marl is often referred to as ‘evil clay’ because it is rendered as undesirable for the manufacturing of fired clay materials such as bricks and lightweight aggregate due to its high calcium carbonate content [15]. Nevertheless, this material becomes an efficient pozzolan at the calcined state that contain both calcined clay and calcium containing compounds. It can be obtained competitively in large quantities to make blended Portland cements. Figure 1 represents the conventional mineralogical composition of the marls. The yellow shadow is to highlight the three sections where the marls are located. Clay mineral and calcium carbonate range between 25–75%. The rest is mostly in the form of quartz and feldspar. Few authors have studied the clay with a high content on calcium carbonate. The relative chemical composition of marl samples is depicted in a CaO-SiO₂-Al₂O₃ ternary phase diagram in Figure 2. As can be seen, the marl samples dominate a large part of the diagram. However, this category has not been given as much interest as the other spots. Therefore, the investigation on these materials is essential, which will broaden the variety of available SCMs especially with the accessibility of this type of material in the world.

3.2. Activation Methods

To get a reactive material, a variety of thermal, mechanical and chemical paths or a mix of them can be used to reach this purpose. The thermal treatment requires a heating process at high temperatures ranging between 700 and 900 °C, while mechanical methods depend on an extended grinding. Activators such as acid or alkaline compounds are used for chemical methods. The technical characteristics of the three activation methods are shown in Table 2.

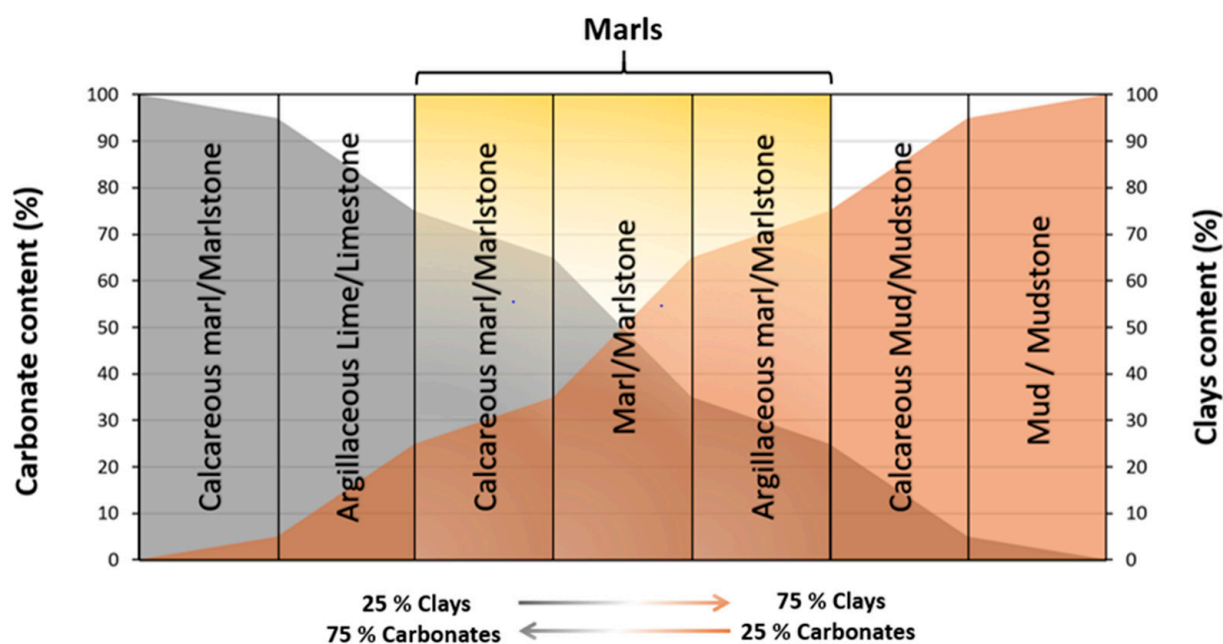


Figure 1. Conventional marls classification.

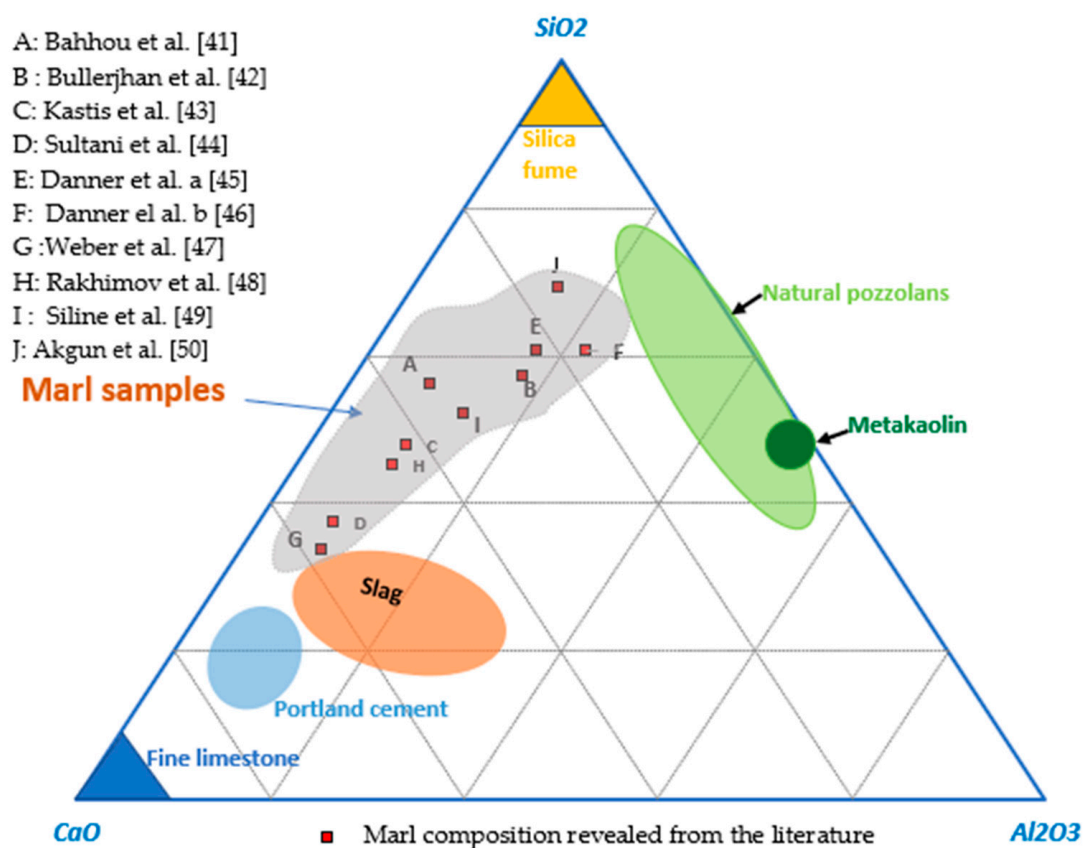


Figure 2. Chemical composition of different marls plotted in a CaO-SiO₂-Al₂O₃ ternary phase diagram. (A): Bahhou et al. [41]; (B): Bullerjhan et al. [42]; (C): Kadtis et al. [43]; (D): Sultani et al. [44]; (E): Danner et al. a [45]; (F): Danner et al. b [46]; (G): Weber et al. [47]; (H): Rakhimov et al. [48]; (I) Siline et al. [49]; (J) Akgun et al. [50].

Table 2. Features of the existing activation method.

Activation Method	Technological Features	Advantages	Disadvantages
Mechanical	Different types of mills—ball, vibratory, vario-planetary	Simplicity	High energy costs
Chemical	The use of activators such as acid or alkaline compounds	Low curing time	Complexity, not scalable
Thermal	Heating with post-cooling following several patterns	A relatively simple and effective way	Environmental issues

3.2.1. Thermal Activation

In their natural state, clay minerals with their crystalline structure do not possess pozzolanic properties. However, when calcined at temperatures between 600 and 900 °C they exhibit the required pozzolanic activity [51]. Thermal activation is performed considerably under the glass forming temperatures. The collapse of structural layers is featured by the removal of OH groups typically known as the dihydroxylation [52]. This transformation makes the clay mineral highly recommended as SCMs. For instance, the structural disorder of kaolinite leads to the formation of a metastable state, called metakaolin, and the higher the reactivity of metakaolin is, the higher the content on penta-coordinated aluminum ions occurring during the dihydroxylation [53]. A higher calcination temperature is needed to reach an excellent reactivity with clay that they have a high degree of order, in general, the activation temperature is between the structural reorganization and recrystallisation [54].

Calcined clays could be more or less reactive depending on clay mineralogy, in fact, this parameter mainly affects the calcination temperature, for that reason this temperature should be chosen carefully to obtain the highest pozzolanic activity [35,55].

Among the natural clays, illite clays have a high activation temperature, with some crystallinity remaining even after dehydroxylation [34], for kaolinite or montmorillonite, the gap between the temperature of dehydroxylation or structural reorganization and the recrystallisation temperature is much larger compared to the illite when both phenomena happen almost at the same temperature. It should be mentioned that the recrystallization may take place if this temperature is exceeded and as a result, the reactivity decreases. Therefore, in order to obtain the pozzolanic activity, the temperature must not reach the sintering point because at this particular level, the clay minerals may partially melt [52], the disordered structure must also be fixed quickly so that there is neither time nor energy to reorganize.

When marl calcined to the proper temperature, it is an effective pozzolan providing an adequate strength for mortars. Results revealed that the pozzolanic reactivity of marls has increased since the formation of a glass phase during the calcination of clays containing high amounts of calcite. This amorphous phase leads to a structural disorder, which mainly depends on the clay mineralogy [56].

According to Figure 3, it can be concluded that most of marl samples reach their highest pozzolanic reactivity at around 800 °C. Interestingly, most of the marls studied in the literature contain montmorillonite together with other minerals such as kaolinite, palygorskite or illite. The illustration shows a great correlation between the clay minerals containing in the marl and their optimal calcination temperature. They were all pointing to 800 °C as an activation temperature. The choice of 800 °C is justified by the formation of a glassy phase at this temperature while avoiding the recrystallisation of new minerals. Some calcium carbonate minerals could remain after the thermal treatment [57], and will react latter with the calcium aluminate hydrates to form essential products namely carboaluminate phases [58].

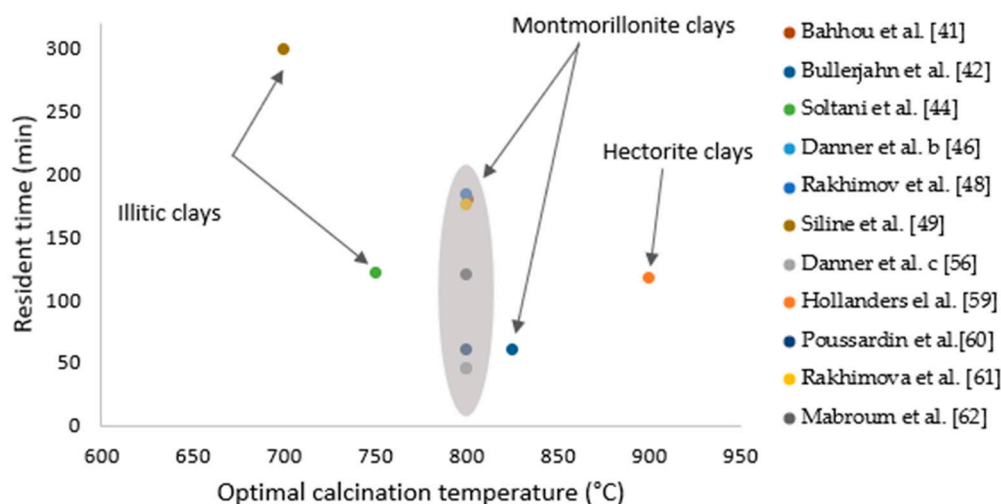


Figure 3. The resident time as a function of the optimal activation temperature for the studied marl used as SCMs. Bahhou et al. [41], Bullerjahn et al. [42], Soltani et al. [44], Danner et al. b [46], Rakhimov et al. [48], Siline et al. [49], Danner et al. c [56], Hollanders et al. [59], Poussardin et al. [60], Rakhimova et al. [61], Mabroum et al. [62]

Research findings [63] showed that pozzolan activity of marl decreased when the sintering temperature was higher than 900 °C. This was related to crystallizations of inactive phases namely anorthite, diopside and gehlenite. Moreover, the amount of periclase and free lime decreased as the calcination temperature increased, indicating that calcium and magnesium contribute to the formation of various phases at high temperatures [42].

3.2.2. Chemical Activation

Chemical activation is among the most widely used methods to activate the clays for industrial and research objectives. It can be undertaken either through the acid or alkali methods. Usually, the acid treatment involves the use of HCl or H₂SO₄, and its major function is to get a partly dissolved material with a high number of active sites and increased specific surface area [64]. The mechanism is all about the exchange between the proton H⁺ and the mineral cations (Al³⁺, Mg²⁺, Fe²⁺) which leads to the alteration of the mineral substrate and high absorption capacity [65].

On the other hand, major progress has been made recently regarding the basic mechanisms of the alkaline activation process. A high enough concentration of hydroxide anions is needed to dissolve large amounts of the precursor, typically the aluminosilicate source, while additional metal cations are essential for charge compensation in the product phase. NaOH and KOH compounds are employed as alkaline activators for clays [66]. The marls or calcareous clays were chemically treated only with the alkali activation path. Most of the starting materials were pre-treated, before proceeding to the synthesis step. Usually, thermal treatment is required to ensure the high degree of amorphicity. Several studies have investigated the use of carbonated rocks mostly extracted from the mine waste [67,68], they were all pointing on the effectiveness of those materials as a precursor and how they improve the mechanical properties of activated blended systems by forming under alkaline activation C-(A)-S-H and/or N-A-S-H gels and a strong transition zone between the silicate phases of the pulp and the calcined marl particles. In this way, calcined marl provides a valuable material for alkali-activated mixed systems.

3.2.3. Mechanical Activation

As the reactivity of the materials relies on structural disorder, the mechanical activation tends to enhance it by prolonging the grinding [69], this physical process leads to a change in particle size influencing its chemical aspect by boosting the amorphization, thus the process is called mechanochemical activation [70], bearing in mind that the strength development is mainly affected by the physical features especially at an early age, and so

mechanochemical treatment is a great way to increase the chemical reactivity by reducing the crystallinity and the increase in surface energy [71]. The type of grinding used in this type of activation is attrition milling. Even the literature here seems to be very limited, and the data available related to the use of this process on clays are very scarce, and for the marl non-existent.

3.3. Factors Impacting the Quality of Calcined Marls

It is noteworthy that the selection of the activation temperature would not be meaningful without an appropriate correlation with the circumstances that are presented as part of the calcination process. The resident time, the particle size, the heating and the cooling rate are examples. These parameters can help to enhance the efficiency of the productivity of calcined marls at the hydration process. Table 3 presents their influence on the final properties of the calcined marl-based cement. A recent study by Danner et al. [72], has shown the impact of these parameters on the marl reactivity. It was found firstly that heating clays at lower residence times (30 min) was more useful and leads to a higher pozzolanic reactivity. Secondly, it was suggested that a finer particle size has a strong tendency to significantly increase the consumption of lime when it declines from 50 to 10 μm . Finally, the cooling rate reported having no significant influence on the pozzolanic reactivity. This work delivers an approach about how important it is to choose these parameters properly all along with the activation temperature.

Another crucial factor is the water/cement ratio. Its elevation due to the dilution effect [73], results in a high dissolution rate of the clinker phases. A lower w/c ratio (0.38) has led to the most compressive strength development with a 20% substitution of calcined marl. Blends with higher w/c ratios are usually less effective at a certain age, as the viscosity and the pore improvement are reduced, which finally leads to a lower compressive strength [44].

Among the most effective ways to overcome the calcined marl limitations and its ability to be incorporated within the blended cement is the implementation of additives. Adding plasticizers is an overriding procedure to compromise the amount of water absorbed by the calcined marl, thus controlling the fluidity of the paste. The flash set results from the C_3A reaction, which accelerates the early hydration of clinker phase, this can be boosted when adding LS (lingosulfanate) as additive [74].

The topochemical hydration is prevented when plasticizers are absorbed on the cement grain surfaces, and they act as retarders by delaying hydration. The delay is not affecting ettringite, because at the beginning of hydration, the plasticizers immediately uptake by non-hydrate phases. However, there is a problem, smectite clays can make the plasticizer useless as poly (ethylene oxide) interposes itself between the residual smectite layers of the calcined marl [75], and therefore, a new approach of formulating new plasticizers needs to be found for these particular materials in order to minimize intercalation.

Table 3. Factors influencing the performance of calcine marl-based binders.

Factors		Major Observation	References
Grinding	Particle size	Finer particle size (50 to 10 μm) is followed by a high consumption of the lime which leads to a higher reactivity.	[72]
Dosage	Calcined marl Content	When adding calcined marl, the porosity and the water absorption increase, also the lack of C_3S and C_2S phases at higher substitution will alter the hydration properties.	[49]
	W/C	-Low w/c: A well-developed compressive strength due to high dissolution rate of clinker phases. -High w/c: Lower compressive strength due to the weak pore refinement.	[73] [44]

Table 3. Cont.

Factors		Major Observation	References
Calcination	Activation Temperature	The pozzolanic activity drops once the sintering temperature is reached, as a result of the inactive phases crystallization. The amount of periclase and free lime decreases as the calcination temperature increases.	[63] [42]
	Resident time	-The dehydroxylation and decarbonation degrees increase with an extended holding time. -The time to retain the sample under treatment of the targeted temperature. It is a decisive factor against the pozzolanic aspect of the calcined marl. -Heating clays at lower residence times of 30 min claimed to be more useful and it leads to a higher pozzolanic reactivity.	[49] [76,77]
	Cooling rate	No significant influence on the pozzolanic reactivity of the calcined marls.	[72]
	Heating rate	To guarantee homogeneous spread of the temperature within the sample, the increase should be as low as possible.	[78]
Additives	Superplasticizers	-The early hydration of the clinker phases is boosted when adding lingosulfanate as additive. -The retarder effect of plasticizers prevents the topochemical hydration being absorbed on the cement grain surfaces. -The poly(ethylene oxide) intercalates between the semectite interlayers of the calcined marl, the role of plasticizers is no longer shown.	[74,75]
	Limestone	Systems with limestone is known to be an ettringite stabilizer, it enhances the formation of carboaluminate hydrate AFm phases (mono-sulphate phases).	[15]

When adding limestone, the nucleation of hydrate phases is boosted through the ion-exchange reactions which creates additional surface for the C-S-H nucleation and thus the hydration process is accelerated [79]. Moreover, Ca^{2+} ions are adsorbed on the surface of the limestone. The limestone has a high affinity for these ions resulting in the stable nuclei formation and subsequently in the growth of C-S-H [80].

It is noteworthy that in the presence of limestone, the transformation of ettringite to monosulphate will not take place as the limestone provides more space filling and good pore refinement and the ettringite is stabilized. These properties are well-known to guarantee the overall durability [81]. Moreover, when comparing limestone to other carbonates, dolomite for instance, its reactivity was reported to be correlated with portlandite availability, otherwise, its addition acts as filler and remains unreactive [82]. Krishnan et al. [81] have studied the calcined marl behavior, in both carbonate additions, calcium hemicarboaluminate was the main AFt phase (Ettringite). It shall be noted that after 28 days, the hemicarboaluminate was transformed to monocarboaluminate only in system with limestone additions.

3.4. SCMs Characterization Techniques and Reactivity Tests

Alternative SCMs are inorganic substances that are incorporated into the cement or concrete formulation, achieving the pozzolanic reaction needed for gaining the strength, workability, and long-term durability required. In order to evaluate whether these materials are suitable for use as SCMs or not, several actions need to be taken. ASTM C1709 [83] (American Society for Testing and Materials) is a standard that provides a complete guide for assessing their reactivity and confirming the compatibility of SCMs in concrete uses.

First of all, particular attention should be paid to chemicals that may affect cement hydration. For instance, lead (Pb) and other heavy metals are chemical components which can slow or prevent the hydration of Portland cement [84]. Other chemical substances such as chloride, sulfate, and alkali ions affect negatively the long-term performance of concrete [85] and thus, it must be ensured that the contents do not contain any contaminants damaging to the environment and health.

Secondly, the fineness needs to be determined properly because this physical property controls several parameters that are mainly in charge of the protection of the concrete

against aggressive ions (the particle packing, pore refinement, and connectivity of the pores). Finally, it has to be checked if the physical and chemical properties are in agreement with the standards; then the material is tested in concrete; and finally the long-term performance is examined.

Considering all steps described in Table 4, the previous method can be quite exhausting, (time, cost, and effort) and therefore, rapid testing methods are nowadays receiving significant research interest. First, the marl clay has to be characterized. The marls are commonly reactive when they contain more amorphous phase rather than crystalline phases. X-ray diffraction can simply measure its content on amorphous phases and determine their reactivity performance [86]. Thermal analysis by TGA/DTA (ThermoGravimetric Analysis/Differential Thermal Analysis) is also employed to identify optimal calcination temperatures by assessing the degree of dehydroxylation. Nuclear magnetic resonance (NMR), for silicon and aluminum, offers a valuable insight into calcined marls, monitoring the changes in the state of coordination after calcination, which can be later correlated to SCM properties [34].

Table 4. Complete guide for assessing the suitability of a new SCM.

Stages	Why Going through this Step?	Tests	Standards	Recommendations
Characterization of the Material (Stage I: ASTM C1709)	Some chemicals may affect negatively the cement hydration and they are also damaging to the environment and health. Specific tests are required to identify and dispose of these elements before proceeding with the evaluation.	Determination of: the loss on ignition water soluble alkalis total chloride ions Determination of the amount of available alkalis. Mineralogical characterization	ASTM C114 [87] ASTM C311 [88] A3004-E1 [89]	Proceed with the high-pressure method to extract the pore solutions.
Determination of Suitable Fineness (Stage II: ASTM C1709)	The fineness of the material is among the most key properties for improving concrete efficiency	No specific standard for testing the fineness. Measurement of compressive strength.	ASTM C1709 [83]	Mortar samples are preferably stored in limewater to compensate for the difference in pH between the cement and the solution
Testing for Specification (Stage III: ASTM C1709)	Verify the conformity of the chemical and physical aspects of the ASCMs	The chemical properties: SiO ₃ , moisture, and LOI (Loss on ignition) contents. The sum of the three oxides content SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ The physical properties: the fineness strength activity index water requirements volumetric stability The chloride contents. Free calcium oxide content, soluble alkali content. leachable heavy metals content.	ASTM C618 [90] ASTM C618 [90] ASTMC1218/C1218M [91] ASTMC114 [87] ASTM D3987 [92]	The author suggests that the standard should refer to the phase structure rather than focusing on the content of the three oxides.
Concrete Performance Tests (Stage IV: ASTM C1709)	Predict environmental behavior of concrete materials through empirical studies.	Fresh state of concrete: The slump test Air content The time of setting fresh density bleeding Hardened state of concrete: Compressive strength Flexural strength Length change Air void system parameters Modulus of elasticity Sulfate resistance Length change of the mortar bars owing to the alkali–silica reaction Additional tests: the resistance to rapid freezing and thawing the heat of hydration	ASTM C143/C143M [93] ASTM C231/C231M [94] ASTM C403 [95] ASTM C138/C138M [96] ASTM C232/C232M [97] ASTM C39/C39M [98] ASTM C78 [99] ASTM C157/C157M [100] ASTM C457/ C457M [101] ASTM C469 [102] ASTM C1012/C1012M [103] ASTM C1567 or C1293 [104] ASTM C666/C666M [105] STM C186 [106]	The present tests are mainly developed to be used in Portland cement systems. In certain cases, the curing process is not suitable for concrete containing ASCMs and will have a significant impact on the results analyzed.
Field Trials and Long-term Performance (Stage V: ASTM C1709)	This stage is intended to confirm the results collected in the laboratory experiments	—————	—————	Rapid assessment methods are urgently needed

Within the past few years, several tests have already been developed to assess the reactivity of the elaborated cements. Figure 4 shows the different rapid methods used to follow the progression of hydration reaction. The evaluation of isothermal calorimetry or the determination of bound water is needed within the first days [107]. Avet et al. first applied the R3 test method on the calcined kaolinite clays, which showed strong correlations between all the tests included in the protocol. X-ray diffraction is used as a direct quantification of the amorphous phases with the help of PONKCS analysis [108], or most likely by analyzing scanning electron microscopy (SEM) backscattered electron (BSE) images [109], or solid-state nuclear magnetic resonance (NMR) spectroscopy [110,111].

It is interesting to note that the R3 protocol, is a rapid screening procedure, that can indirectly determine the reaction degree, by measuring the consumption of $\text{Ca}(\text{OH})_2$, and since almost all the testing approaches for pozzolanic reactivity rely on the chemical reaction of SCM with $\text{Ca}(\text{OH})_2$ [112]. The existing methods could not be meaningful in the calcined marl evaluation, as these materials have great content on calcium carbonate, the portlandite consumption is no longer attributed to the reactive silicate and aluminate, but it is also related to the reaction between quicklime (CaO) and water. Samples with a high amount of carbonate consume more calcium hydroxide [57]. Therefore, the test methods are significantly altered.

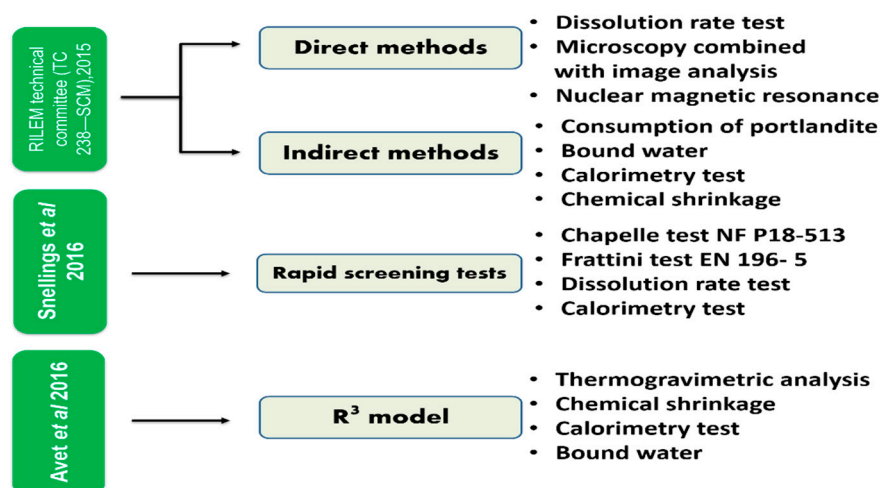


Figure 4. Rapid evaluation methods. Avet et al. [107,113].

Additionally, in basic tests, the reaction level of calcined marl in real Portland cement mixtures can be quite different from the traditional SCMs. This may be the reason why compressive strength tests are still commonly used to evaluate calcined marl materials.

Consequently, new methods or complementary tests need to be established to effectively assess the calcined marl-based cement firstly, to guarantee the occurrence of the reactive phases after the calcination with a high $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content [90], while not having a full decomposition of calcite; and secondly, to ensure that the hydration process was efficient by the production of well-compacted hydrates.

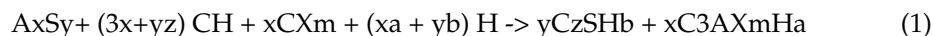
3.5. Calcined Marl Hydration and Pozzolan Reactions

The chemical reaction behind the formation of hydration products is called the “pozzolanic reaction” influenced mainly by the dissolution-precipitation mechanisms. Three key factors being responsible are the solid reactants, the solid hydrate reaction products, and the pore solution [82].

When a SCM is incorporated within cement blends, it causes the dilution effect, which negatively affects the early strength development [114], in particular within the first 24 h. The impact becomes more prominent, as the substitution rate increases. On the other hand, a system with a high replacement rate leads to a strong decrease of portlandite at later ages, because SCMs chemically react with calcium hydroxide (CH) to form additional CSH [115].

Thanks to their finer particle size, SCMs may improve the nucleation of particles allowing more space to the growth of the hydration products [116]. Thus, the degree of reaction of clinker phases is increased which is typically called the “filler effect”. Finally, and as a consequence of these effects the later compressive strength is improved [117].

The literature often presents the equation corresponding to the pozzolanic reaction as follows:



where the A_xS_y stands for the alumina- silicate species dissolved from SCM and X stands for a mono- or divalent anion group, that can be incorporated into the AFm structure, i.e., sulfate, carbonate, hydroxide, chloride [112].

Marl as a material rich in carbonate, has gained attention lately as a promising source for the production of SCMs. Scientists have carried out experiments and investigations to understand the basic process of cement-calcined marl hydration. Table 5 represents a summary of the main products formed in the reviewed studies. Different behaviors may occur depending on the nature and content of clays minerals. As highlighted in Table 5, the calcination of marls results in the formation of mainly silicate and aluminate phases, CaO, MgO, and amorphous phase, nearly all the different investigations do not include the carbonate addition as a part of calcite remains uncalcined after the thermal treatment. Later on, the calcium aluminate hydrates (CAHs) from the pozzolanic reaction react with calcite remaining after calcination to form calcium carboaluminate hydrates [58], and therefore a full decomposition of calcite may not be desirable in terms of clay reactivity [72].

According to Bullerjahn et al. [42], free lime was depleted in the first 24 h of hydration, indicating the high reactivity of CaO. By contrast, periclase seemed to be reactive only when it comes from calcined dolomite. In other words, the dissolution is quite stagnant with periclase presented in the clinker composition. The calcium-rich phases favor the formation of gehlenite-type glass in contact with aluminosilicate whereas it was akermanite-types (melilite-type) and magnesium silicates for magnesium-rich phase. Schwiete et al. [118] demonstrated that gehlenite was more reactive than akermanite, the latter leads to the formation of C-S-H, potentially (C,M)-S-H or M-S-H, and contrarily, calcium aluminate hydrates or ettringite and monosulfate were the main hydrates occurred in the gehlenite type binder.

Moreover, these highly carbonated clays result in calcium carbo-aluminate formation instead of mono- sulfoaluminate hydrates. Danner et al. [46,119] has investigated intensively in this field, not surprisingly, the main product that has been occurred in the paste enriched with calcined marl was the carboaluminate hydrate phases. The occurrence of this phase is mainly attributed to the reaction between the AFm phases and the limestone present in the cement blend, although the pozzolanic reaction of calcined kaolinite and marl is quite similar with respect to the formation of monocarboaluminate and hemicarboaluminate through the remaining calcium carbonate. However, Danner et al. [56] revealed a slight difference. Stratlingite was not observed in the crystalline hydration products of the marl clay, it was related to the lower reactivity of alumina, and so the total AFm phases was smaller than in the clay-rich kaolinite. Moreover, the amount of carboaluminate hydrates increased with increasing clinker substitution. It was explained by the additional content of limestone and, therefore, the content of CH is reduced. A brief resume of key hydration mechanism of the clinker with SCMs and calcined marl is shown in Figure 5.

Table 5. Summary of the main phases occurred after the calcination and hydration for the reviewed papers.

Reference	Mineralogical composition (Content %)	Additives		Calcination		Hydration	
		Are the carbonates added or not?	Optimal activation T	Phase formed	Physical properties	W/C Ratio	Phase formed after hydration
Danner et al. [57]	Montmorillonite (54), Calcite (25), Kaolinite (8)	No	800 °C	Anorthite $\text{CaAl}_2\text{SiO}_8$ Wollastonite CaSiO_3 Diopside $\text{CaMgSi}_2\text{O}_6$ Gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$	$d_{50} < 10 \mu\text{m}$	0.5	Carbo-aluminate hydrates and Ettringite
Weber et al. [47]	Smectite (24), Calcite (71), Quartz (4).	No	800 and 1100 °C	CS; C3S2; C2S, C2AS (gehlenite); C3A; C4AF	$d_{50} = 30 \mu\text{m}$ SSA = 33.0 m ² /g	0.65	calcium silicate hydrates (CSH-phases) and calcium aluminate hydrates (AFm, Aft-phases)
Soltani et al. [44]	calcite, quartz, and clay minerals particularly illite	No	750 °C	Crystalline silicate and aluminate minerals	$D_{90} < 100 \mu\text{m}$	0.45	C-S-H phases
Rakhimov et al. [48]	Kaolin (7.12), montmorillonite (12.4), chlorite (4.00), calcite (46.9), quartz (13.44), albite (7.83), mica (6.90), and gypsum (1.40)	No	800 °C	Hatruirite Ca_3SiO_5 Larnite $\text{Ca}_2(\text{SiO}_4)$	SSA = 200 m ² /Kg		Calcium silicate hydrate gel (CSH). Calcium hydrocarboaluminates
Bahhou et al. [41]	Montmorillonite (27.4) Dolomite (56.2) Quartz (12.3)	Limestone (15)	800 °C	Lime, periclase, amorphous phase		–	–
Kastis et al. [43]	Calcite, Amorphous silica phase, Quartz	No			$d_{50} = 6.3 \mu\text{m}$.	0.4	calcium aluminate hydrates and carboaluminates, CaCO_3 , and $\text{Ca}(\text{OH})_2$
Justen et al. [15]	Smectite (60), illite (30), kaolin (30) and calcium carbonate (10-20)	No	800 °C		$d_{50} \approx 7 \mu\text{m}$.	0.5	(CSH, CAH and CASH)
Hollanders et al. [59]	Hectorite, Quartz	No	900 °C	Enstatite and a triclinic MgSiO_3 phase	SSA = 1.47 m ² /g		Portlandite
Siline et al. [49]	Calcite (30.5), Dolomite (16.5), Illite/muscovite (20), Chlorite (09), Quartz (7), Gypsum (02)	No	700 °C	CaO	Blaine = 3630 cm ² /g	0.5	CSH, CaCO_3 and CH products
Poussardin et al. [60]	Palygorskite (17.45) Smectite (15.58) Dolomite (53.58)	No	800 °C	belite (C2S), Am (Amorphous), lime, periclase		–	—
Danner et al. [45]	Smectite (70), calcium carbonate (20), the remainder being quartz and feldspars.	No	800 °C	Silicate and aluminate phases	$d_{50} = 7 \mu\text{m}$	0.5	CAH, CASH, Hydrogarnet
Bullerjhan et al. [42]	Montmorillonite, Palygorskite, amorphous, Calcite	Marl co-calcined with Dolomite Marl blended with calcined Dolomite	950 °C	Åkermanite types (melilite-type) C_{33}MS_2 Magnesium silicates	$D_{90} < 110 \mu\text{m}$ $D_{90} < 110 \mu\text{m}$	0.6	Strätlingite, Ettringite, CASH Hemi and mono carboaluminate/etteingite, CASH

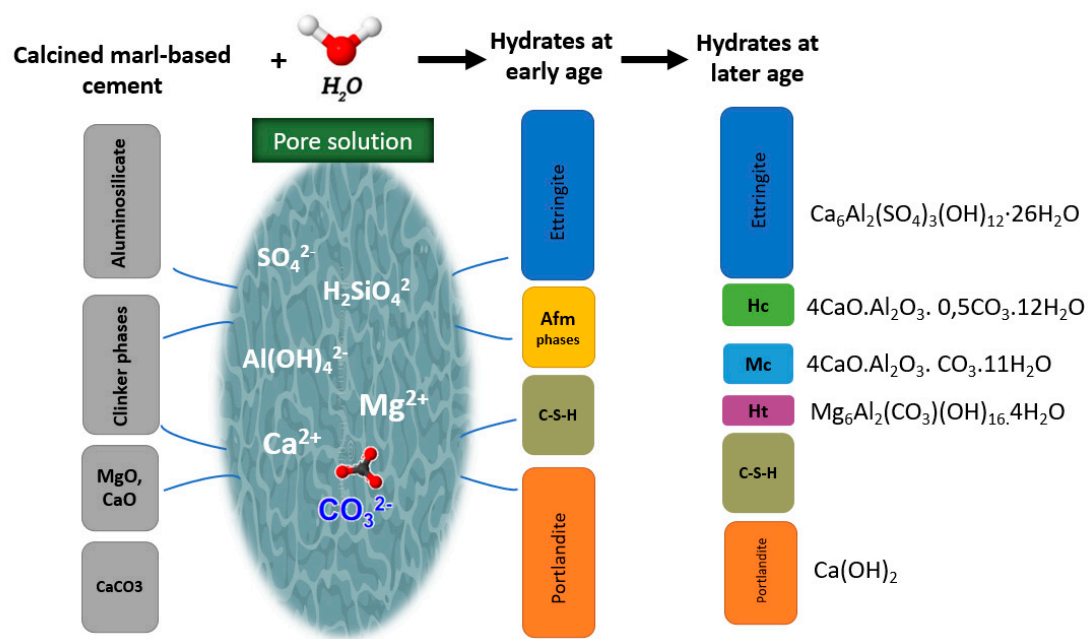


Figure 5. Schematic representation of the difference between the SCMs and the calcined marl hydration mechanism C-S-H: calcium silicate hydrates, Hc: hemi-carboaluminate hydrates, Mc: mono-carboaluminate hydrates, Ht: hydrotalcite.

3.6. Kinetic of Calcined Marl-Based Cements

The hydration of cement is extremely exothermic and unlike other reactions in the solid state. The rate of hydration cannot be explained by simple chemical equations. The hydration of cement is still partially unclear as precipitation or diffusion are involved in this mechanism. The calorimetry is usually used to examine such a complicated phenomenon. Several stages form this process. First, the so-called induction period, which usually lasts about three hours. Then the rate of hydration accelerates rapidly and crosses its maximum after around 10 h. At this stage, two main peaks appear; first, the exothermic peak is related to the silicate reaction. C_3S and C_2S react with water and form C-S-H and CH. The second appears later and it is related to the aluminate reaction, the conversion of Aft (ettringite) to AFm (mono-sulphate) phases [120]. This second peak is also attributed to the sulphate depletion [121] more precisely when the content on calcined clays increases. This peak often occurs early, and the systems become under sulphated [53]. The same author suggests that it might even occur before the main silicate reaction, and the same investigation reported that a slight gypsum addition controls the rapid reaction of aluminates, which significantly affects the early age strength.

Several studies have demonstrated that the filler effect has a strong effect on the acceleration peak, the filler effect may include a higher heat flow and accelerate the aluminum reaction, Calcined clays serve as nucleation sites and enhance hydrate nucleation [122], system with a high replacement rate shows a strong decrease of portlandite, and thanks to the extra hydrate space available, the degree of reaction of clinker phases is increased [116], Limestone, for example, is widely used as a filler knowing that it reacts with a certain amount of alumina and it generates carbo aluminate phases required for obtaining better strength and durability [123].

Moreover, during the acceleration period, as the replacement level of Portland cement by calcined clays increases the time between the two maxima seems to be reduced [56]. After that, the hydration rate begins to slow down progressively. The process goes into a decelerating period where the hydration products grow up around the un-hydrated cement core, and so the rate of hydration is controlled by the diffusion mechanism. The rate of hydration is decisive on the durability of the final products, and this is something that is steadily related to the heat released during the process.

Similar trends were noticed in kinetic hydration of calcined marl, when the system hydration starts, calcined marl is competing with cement particles. Consequently, the proper balance between the proportion of clinkers that can be hydrated at early hydration and the amount of calcined marl in the system will define the actual fluidity of the paste. Although the cumulative heat released from cement with a high replacement level of calcined marl decreases, the initial hydration time is unchanged [75], which means that calcined marl does not delay the hydration process of the clinker phases. Also, Justnes et al. [124] claimed that the rise of a second peak is mainly due to the sulfate depletion as it was consumed from the silicate reaction by calcined marl and C_3A .

3.7. Impact of Calcined Marls on Mechanical Performance and Durability

One of the effective ways to evaluate whether the elaborated cements are suitable for the application or not, is the compressive strength tests, the effectiveness of a test assessment would not be meaningful without a strong correlation with compressive strength results [125]. It is a well-recognized feature that calcined marls can improve mechanical performance of concrete over the long term and have the potential to greatly enhance durability as well, which is one major driving interest in their application in the production of concrete. The European cement standard considered the calcined marl as an industrial pozzolan that can be used within cement formulation [126]. Up to 55% clinker replacement, this material can ensure the pozzolanic reaction needed to have the required 28-day strength.

Beyond this point, up to 50% of substitution with calcined marl, the compressive strength (CS) at 28 days was equal or even higher than the reference mortar [127]; similar results regarding strength improvement can be taken from different studies, Rhakhimov et al. [48] claimed that the mechanical properties of the calcined marl base cement were much better than those with metakaolin. Similarly, Justnes et al. [15] found that when marl is calcined at 800 °C, systems with 20% replacement of OPC with marl calcined give the best result after 28 days of curing. However, once the substitution level reaches a high portion, the mechanical performance drops significantly, perhaps because all calcium hydroxide has been consumed. Ostner et al. [1] have concluded that mortars fall consistently under the reference value once the replacement level reaches 65%.

The contributions of calcined marl towards compressive strength development can be categorized into a physical effect and chemical effect; The first one involves (fineness and pore solution) [82], whereas the second relies on the amount of reactive components in the calcined marl. Figure 6 shows the development of the compressive strength as a function of $(Al_2O_3 + SiO_2)/(MgO + CaO)$. Only cements with the same substitution level and mortar condition were considered for plotting in this curve. It can be seen that the CS values increase with increasing $Al_2O_3 + SiO_2$ content. In fact, the lengths of the calcium silicate hydrate will stretch with time due to a low C/S favoring C-S-H polymerization [128], which explains the higher CS obtained. Not surprisingly, an excess of carbonate oxides at the expense of $(Al_2O_3 + SiO_2)$ has surely caused the CS development drop. This indicates that the correction of the marl composition in some cases is strongly needed to ensure the desired CS value. The plot represents a model for estimating the CS value as a function of the chemical content of the starting materials. Moreover, and unlike OPC which develops its final strength at a very early age, the calcined marl reaches its full strength in a few months. This difference in the long-term performance is attributed to the paucity of C_3S and the presence of belite (C_2S) in calcined marl [129], and also, it is well known that calcined marl has a slow hydration rate during the dormant period which lasts several months [128].

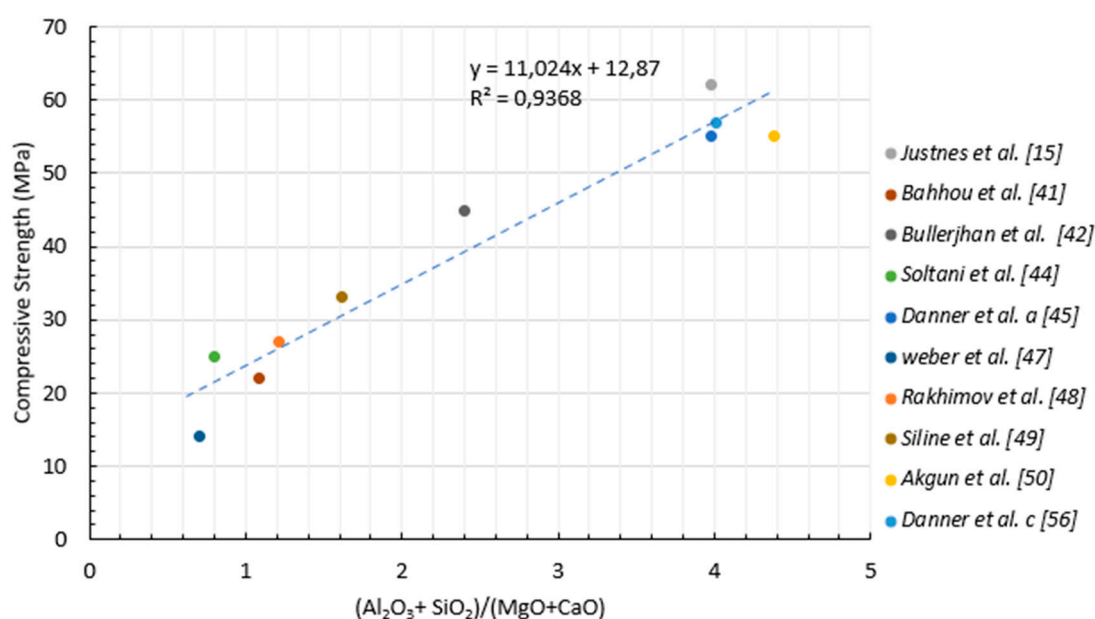


Figure 6. Correlation between the compressive strength and the ratio $(\text{Al}_2\text{O}_3 + \text{SiO}_2)/(\text{MgO} + \text{CaO})$. Justnes et al. [15], Bahhou et al. [41], Bullerjhan et al. [42], Soltani et al. [44], Danner et al. a [45], Weber et al. [47], Rakhimov et al. [48], Siline et al. [49], Akgun et al. [50], Danner et al. c [56].

Calcined marl usually promotes long-term development of mechanical performance and durability signs. They are a great reducer of corrosion rate, because with increasing cement replacement by calcined marl. The capillary porosity is increased knowing that more amorphous “gel” is formed from crystalline calcium hydroxide during the pozzolanic reaction. Also, the unreacted calcined marl could be another reason. Bearing in mind that the volume of capillary porosity expands with electrical resistivity. Thereby the ionic strength is reduced [127]. This property allows them to be integrated in reinforcing steel after passivity collapse [44] and, therefore, they are a powerful SCM for sustainable development goals.

Unfortunately, the latter property increases the porosity resulting in weaker strength, not greater strength, except when the product is naturally stronger.

Moreover, their occurrence is well proven for helping porosity refinement in the early ages [81]. Possible reasons for less chloride penetration maybe both the refinement of pores due to calcined marl as a substitute for cement and the increase in chloride binding due to the higher CAH content formed by the pozzolanic reaction, resulting in reaction with chlorides and, therefore, the formation of Friedel’s salt [1]. Another study revealed that replacing cement with a portion of calcined marl reduces the chloride ingress [127].

Further troubles such as carbonation and post-hardening swelling are expected to occur when the calcined sample contains the lime and periclase [60]. As the substitution of cement by calcined marl increases, the carbonation rate goes up [1]. The reduced carbonation resistance is apparently the major limitation of cement replacement by calcined marl in practice.

3.8. Environmental Benefits of Using Calcined Marl as SCMs in Cement Production

To meet cement demand without excessively affecting the environment, the challenges are quite significant since CO₂ emission is derived from several steps during the production process: the decomposition of calcium carbonate and the combustion of fuels. Despite the complexities mentioned so far, the use of calcined marl as SCM is a real benefit because the overall CO₂ emissions will be cut down. The calcination temperature will drop from conventional clinkerization temperature (1450 °C) to around 800 °C temperature for marl calcination. Moreover, the calcination of marls does not release a major portion of CO₂ because the calcite does not decompose fully.

Viewed from another perspective, marls are considered an effective alternative resource for cost-effective and green cement production. They are easily accessible through regional infrastructure projects and do not have the related supply problems which will reduce the burden on the consumption of natural resources and extending a quarry's lifespan. Despite that, using calcined marl as SCM can yield significant energy and carbon emission savings. Building structure must be viewed across its entire life cycle to mitigate carbon emissions.

4. Insights, Recommendations, and Conclusions

Calcined marls included in cements can result in significant modifications in the properties of these binders. In the light of this, the present work gathers all the findings related to the use of clays with a high amount of carbonates within the blended cement formulation. After investigating these studies, the following conclusions can be drawn:

- The findings have used thermal treatment as an activation method: 800 °C was often the effective calcination temperature, which guarantees both maximum dehydroxylation and moderation of decarbonation.
- The type of clay minerals existing in the marl matters. Their dehydroxylation, linked to a deterioration of the crystalline structure, is a preliminary requirement for highly effective reactions to generate reactive compounds.
- Many different parameters strongly affect the pozzolanic activity, including its fineness, w/c, chemical composition, calcination conditions and additives.
- Adding plasticizers is an overriding procedure to compromise the amount of water absorbed by the calcined marl, thus controlling the fluidity of the paste. However, a new approach of formulating new plasticizers needs to be found for this particular material in order to overcome intercalation issues.
- Complementary tests are needed to evaluate the reactivity of these calcined marl-based cements, as the existing ones may be affected by the high calcium carbonate content.
- Most of the calcined marls generate reactive silica and alumina phases after their calcination. Those phases are implicated in the production of calcium silicate hydrates through hydration of Portland cement along with the formation of calcium hydrocarboaluminates hydrates.
- A strong correlation between compressive strength values and $(\text{Al}_2\text{O}_3 + \text{SiO}_2) / (\text{MgO} + \text{CaO})$ was established. Higher carbonate oxides at the expense of $\text{Al}_2\text{O}_3 + \text{SiO}_2$ content caused a drop in CS values. A careful balance between the chemical composition of the marls should be considered in accordance with the proposed model to ensure the desired CS development.
- Corrosion and chloride resistance are the major advantages of using calcined marl as SCMs, while the carbonation seems to be the only drawback in terms of its durability.

Unlike other pure clays, the development of calcined marl-based cements is more complicated, given the mineralogical variety that these marls can represent. The best working temperature for a certain mineral can be the worst one for others, and some would recrystallize or have a full carbonate decomposition. It appears to be challenging to achieve, in one go, a total dehydroxylation of the clay phase while maintaining a certain amount of calcite without decomposition. Nonetheless, it is essential to comprehend the reactivity of these types of natural material, to sharpen our expertise, and to propose new innovative solutions to reduce CO₂ emissions from OPC production.

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