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Effects of Slag Addition on the Properties of Slag Cement (CEMII), And Blast Furnace Cement (CEM III).

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Abstract – This experimental study aims to investigate the advantages and feasibility of partially substituting clinker with slag in cement. The study involves preparing cement with mineral additives by replacing a certain percentage of clinker with added slag: [0%, 6%, 10%, 20%, 25%, 30%, 35%, 40%, 50%, 65%, 70%, 80%, 85%, and 90%]. The percentage of slag added to the cement was varied using the substitution method (partial replacement of clinker by slag) to examine its impact on the physico-chemical properties of the cement, as well as the mechanical behavior of mortar and concrete. The study includes an analysis of the anhydrous and hydrated states of the cement (chemical composition, grinding time, specific weight, fineness, particle distribution, cement paste consistency, heat of hydration, and setting time), as well as the characteristics of mortars prepared using the cement, such as shrinkage, swelling, mechanical behavior (compressive strength), and durability tests (acid attack and absorption test). The experimental data indicate that the quantity of added slag and the chemical composition of the cement are the main factors influencing the variation in mechanical strength (compression) of the tested mortars and concrete.

Keywords – Slag cement, Blast furnace slag cement, fineness, consistency, hydration, shrinkage, swelling, compressive strength

I. INTRODUCTION

The use of mineral additives in the production of Portland cement, specifically slag and blast furnace cement (C.P.J-C.E.MII/A-S, C.E.MII/B-S, C.E.MIII/A, C.E.MIII/B, C. E.MIII/C), has greatly addressed the issue of national self-sufficiency and reduced energy costs [1].

By adjusting the amount of additives, a variety of cements with the desired physical and mechanical properties can be achieved for different applications. Mineral additives are widely utilized in the production of mineral-added cements worldwide. Economically, they play a crucial role in the production of Portland cement with slag and blast furnace cement, as the use of clinker decreases with higher addition rates of slag. The contribution of mineral additives to the binding activity of cement is primarily due to two effects: physical-chemical and mechanical [2,3].

On the one hand, mineral additives are likely to modify the cement hydration process and the structure of hydrated products, and on the other hand, certain mineral additives with pozzolanic or latent hydraulic properties can react in a cementitious environment and form new hydrated products. These two effects act simultaneously and complementarily on the final performance of hardened materials.

Portland cements with slag and blast furnace with mineral additives are characterised by slower hardening in their initial period compared to ordinary Portland cement without additives, i.e. without secondary constituents (C.P.A-C.E.M I) [4,5]. .

This latent property of cement with mineral additives (C.P.J-C.E.M II – CEM III) [6, 7, 8], requires the use of a good activator, whether chemical (use of alkaline solutions that modify setting and hardening), mechanical (extensive grinding of the hydraulic binder) or thermal (acceleration of chemical reactions by raising the temperature).

Cements composed of mineral slag additives (CEMII–CEMIII) have slightly longer setting times than pure Portland cements (CPA-CEMI), especially when concreting in cold weather.

Mineral slag additives are widely used in the manufacture of Portland cements compounded with slag and blast furnace cement.

From an economic point of view, they are a very important factor in the production of cement with mineral additives (CEMII–CEMIII), as clinker consumption decreases in line with the rate of addition used (slag).

Reducing the proportion of clinker in the manufacture of cement with mineral additives (slag) has the following advantages[9,10]. :

- Reduced energy requirements for production (less clinker).
- Reduced CO2 emissions (lower clinker consumption).
- Improved properties of cementitious materials (mortar and concrete).

II. RESEARCH SCOPE :

The strategy of this study is based on examining the effects of mineral additives (in our case, slag) on the properties of slag cement in order to improve them and obtain activated slag cement without clinker or with less clinker, with properties similar to or better than those of ordinary Portland cement.

The objective of our study is to experimentally evaluate the influence of slag addition rates (0%, 6%, 10%, 20%, 25%, 30%, 35%, 40%, 50%, 65%, 70%, 80%, 85% and 90%) on the physical, chemical and mechanical properties of mortar and concrete.

The research study in this thesis aims to achieve the following main objectives:

1- Study of the effects of incorporating mineral additives: slag on the physical, chemical and mechanical properties and durability of mortars and concretes made from binary and ternary cements.

2- Selection of the optimum dosage of slag addition to Portland cements composed of slag and blast furnace cement that perform best in terms of both mechanical strength and durability.

This work contributes to improving the properties of mortars and concretes through mechanical activation of cement (CEM II – CEM III) from the Lafargeholcim M'sila Hammam Dalaa cement plant (cement manufactured with slag additives – 65% slag).

III. CHARACTERISATION OF USED MATERIALS

Different types of cement were formulated according to the content of slag and blast furnace slag addition. The aim of preliminary tests was to examine the principal properties of cement constituents. The clinker was replaced partially at various percentages by slag giving its following content: 0%, 6%, 10%, 20%, 25%, 30%, 35%, 40%, 50% 65%, 70%, 80%, 85%, and 90% by mass.

III.1. ***Cement with slag added***

The preparation of cements with and without slag additions, as well as the determination of their chemical and physical characteristics and mechanical testing of mortars made from them, were carried out at the Lafarge laboratory (Hammam Dalâa cement plant) in the province of M'sila.

III.2. Slag ***Mixture and its chemical and mineralogical composition***

The slag used in our experimental study as an additive is imported dried slag. The cement was partially substituted at different percentages (0%, 6%, 10%, 20%, 25%, 30%, 35%, 40%, 50%, 65%, 70%, 80%, 85%, and 90%) relative to the mass weight of clinker by a slag additive.

The chemical composition is shown in Table 1. It was determined by X-ray fluorescence spectrometry testing at the Lafargeholcim Hammam Dalâa cement plant laboratory. The analysis was performed on a finely ground sample to determine its chemical composition.

The mineralogical composition is shown in Table 2. It was determined by XRD testing at the Lafargeholcim Hammam Dalâa cement plant laboratory. The analysis is performed on a finely ground sample to determine its mineralogical composition.

- Glass phase (glass content) ≥ 2/3 of the total mass (calculated by XRD)
- (Ca0 + MgO + SiO2) ≥ 2/3 of the mass of the constituents
- (CaO + MgO) / SiO2 ≥ 1 (basicity index).

Table 1 The chemical composition of slag.

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	L.O.I
%	35.28	12.27	0.88	42.36	8.03	0.15	0.13	0.54

Tableau 2. Mineralogical Composition of slag

Elément	Merwinite	Melilite	Bredigite	Quartz	Calcite	BFS_amorphous
Laitier	0.38	0.45	0.09	0.01	0.72	98.35

III.3.Clinker

The chemical composition of the raw material determines the mineralogical composition of the clinker, so great care must be taken with the materials fed into the kiln in order to obtain a high C_3S content.

The raw materials used to manufacture clinker at the Hammam Dalâa cement plant and their physical characteristics are shown in Table 3. Figure 1 shows the clinker kilm as prepared in the cement plant.

Table 3 Main constituents of the vineyard of clinker, its specific gravity and its hardness

Clinker	**Clinker de Hammam Dalaa(H/D)**
Constituants	limestone, Clay, Dune sand, iron mineral
Specific gravity	1,43
hardness	37

Fig. 1. Clinker kiln (Lafargeholcim, M'sila)

III.4. Gypsum

The dosage of the natural gypsum (sulfate of dehydrated calcium, CaSO4. 2H2O) was maintained constant to 5% in the preparation of all the cements, for two reasons: Regulate the setting and permit the assessment of the effect of the limestone additions on the mechanical properties of the cement. Its chemical composition is given in table 4

Table 4. Chemical composition of the gypsum

Elements (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P.F	CL
Gypsum of BISKRA	3.11	0,68	0,38	31.06	3,31	40.05	0.02	0	23,57	0,015

IV. Cement Formulation

IV.1.Ponderal Composition of different cements

Slag was added at various percentages: 0%, 6%, 10%, 20%, 25%, 30%, 35%, 40%, 50%, 65%, 70%, 80%, 85%, and 90% (Table 5) . The purpose of this study was to investigate the effects of varying the percentage of added slag in cement through the substitution method (partially replacing clinker with slag) on the physico-chemical properties of the cement and the mechanical behavior of the mortar.

The study examined the anhydrous and hydrated states of the cement (chemical composition, grinding time, specific weight, fineness, particle distribution, consistency of cement paste, and setting time), as well as the characteristics of mortars prepared with the cement, such as shrinkage, swelling, mechanical behavior (compressive strength and flexural strength), and microstructure. The incorporation of slag at different percentages (0%, 6%, 10%, 20%, 25%, 30%, 35%, 40%, 50%, 65%, 70%, 80%, 85%, and 90%) into clinker increases the percentage of oxides (SiO2, Al2O3, MgO, SO3) and decreases the content of lime oxide (CaO, Fe2O3, PAF). According to standard NA 442 [11]. , the percentage of added slag in prepared cements should not exceed 95%, as CPJ-CEM III/C composite cements must contain a minimum of 81% slag and a maximum of 95% slag, with a minimum of 5% clinker and a maximum of 19% clinker.

Table 5. Pondered composition of the fourteen prepared cements

Types de cements	Clinker (%)	Gypse (%)	Laitier (%)
CEM I	95	5	0
CEM II/A-S	89	5	6
CEM II/A-S	85	5	10
CEM II/A-S	75	5	20
CEM II/B-S	70	5	25
CEM II/B-S	65	5	30
CEM II/B-S	60	5	35
CEM III/A	55	5	40
CEM III/A	45	5	50
CEM III/A	30	5	65
CEM III/B	25	5	70
CEM III/B	15	5	80
CEM III/C	10	5	85
CEM III/C	5	5	90

IV.2.*Chemical analysis of the various prepared cements.*

It is well known that the chemical composition of cement is a determining factor in the resistance of cement to aggressive agents and other properties. For this reason, the chemical composition of the all prepared cement was determined by X-ray fluorescence (XRF) according to NF P15-467]12]. , and the conformity of obtaining cement results was deemed with the EN 197-1 standard [13]. .

The results obtained from the tests carried out on the fourteen prepared cements are presented in Table 6. Some samples of prepared cements are presented in Fig.2. It can noted also that the slag addition was substituted at various percentages 0%, 6%, 10%, 20%, 25%, 30%, 35%, 40%, 50%, 65%, 70%, 80%, 85%, and 90%).

Figure.2 some samples of the prepared cement

Table.6. Chemical composition of the prepared cements

Slag content (%)	Elements (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K2O	Na_2O	CL	LOI
0	CEM I	21,95	5,12	4,12	69,64	1,84	2,25	0,60	0,16	0,014	1,61
6	CEM II/A-S	22,75	5,63	4,09	65,27	2,28	2,28	0,59	0,16	0,014	1,58
10	CEM II/A-S	23,23	5,97	4,00	61,50	2,58	2,31	0,59	0,15	0,015	1,55
20	CEM II/A-S	24,39	6,78	3,89	61,06	3,27	2,32	0,58	0,15	0,015	1,48
25	CEM II/B-S	25,04	7,20	3,79	60,07	3,63	2,35	0,58	0,14	0,015	1,46
30	CEM II/B-S	25,55	7,58	3,68	60,00	3,93	2,41	0,56	0,14	0,016	1,43
35	CEM II/B-S	26,56	8,06	3,57	59,96	4,28	2,42	0,56	0,14	0,016	1,40
40	CEM III/A	27,41	8,51	3,54	59,88	4,64	2,43	0,56	0,14	0,016	1,38
50	CEM III/A	28,02	8,89	3,33	59,73	4,72	2,48	0,55	0,14	0,017	1,31
65	CEM III/A	28,62	9,32	3,28	59,52	4,75	2,52	0,55	0,13	0,018	1,19
70	CEM III/B	29,01	9,55	3,22	59,38	4,81	2,58	0,54	0,13	0,018	0,99
80	CEM III/B	29,62	9,68	3,19	59,21	4,86	2,62	0,53	0,13	0,018	0,85
85	CEM III/C	29,82	9,74	3,15	59,12	4,89	2,69	0,52	0,13	0,018	0,81
90	CEM III/C	30,20	9,87	3,11	59,03	4,93	2,72	0,52	0,13	0,018	0,76

V. Results and Discussion

V.1. *Influence of Slag Addition Content on Cement Density*:

The results in Table 7 and Figure 3, show the effect of the addition of slag on the cement density.
In the light of the tests carried out, the following conclusions can be drawn:
- A reduction in density with an increase in the percentage of added slag in the cement.
- Increase in setting times.

The results show that increasing the amount of added slag in the cement has a significant effect on the specific weight of the cement. This may be due to the porosity created by the partial substitution of clinker by slag (slag substitution rate) and the low density of slag (slag density = 2.8±0.1 g/cm^3) lower than the clinker density (3.15±0.1 g/cm^3).

Table 7. Specific weight of prepared cements

Slag content (%)	Elements (%)	Density (g/cm^3)
0	CEM I	3.15
6	CEM II/A-S	3.13
10	CEM II/A-S	3.11
20	CEM II/A-S	3.1
25	CEM II/B-S	3.1
30	CEM II/B-S	3.08
35	CEM II/B-S	3.07
40	CEM III/A	3.05
50	CEM III/A	3.03
65	CEM III/A	3.03
70	CEM III/B	3.00
80	CEM III/B	2.97
85	CEM III/C	2.95
90	CEM III/C	2.91

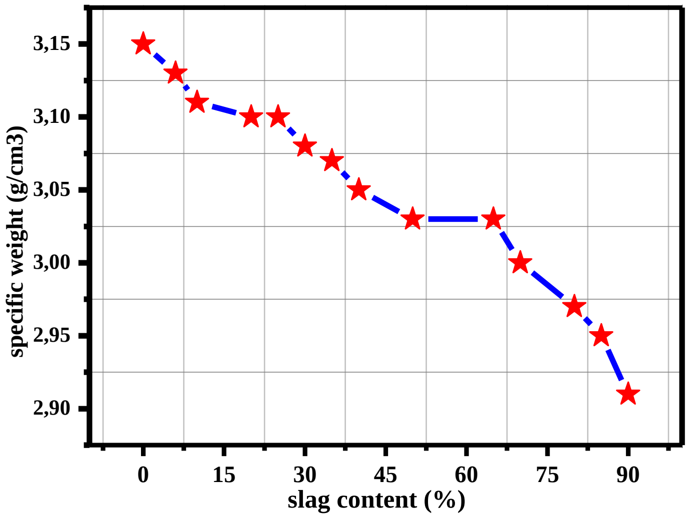

Fig.3 Variation of specific weight of prepared cements in function of slag content

V.2. *Influence of Slag Addition Content on Cement Specific Surface Area*:

The results presented in Table 8 demonstrate the impact of slag addition on the specific surface area of the cement. From these findings, it can be concluded that there is a decrease in specific surface area as the percentage of slag added to the cement increases. This is supported by the data shown in Table 8, which clearly indicates that the quantity of slag incorporated into the cement has a significant effect on its specific surface area (Blaine).

The lower strength of the concrete can be attributed to the porosity resulting from the partial substitution of clinker with slag, as well as the density and grind ability of the slag additive. Slag has a density of approximately 2.8 g/cm3, which is lower than the density of clinker at 3.15 g/cm3. Additionally, the grind ability of slag is more challenging compared to clinker. The fineness of the cement plays a crucial role in achieving a dense concrete structure and, ultimately, in the development of its mechanical strength.

A higher fineness level guarantees increased contact between cement grains leading enhanced reactivity, and long-term mechanical strength. By increasing the specific surface area of the slag from 2400 cm^2/g to 4000 cm^2/g, the activity of the cement within the slag is heightened, resulting in a corresponding in a corresponding increase in mechanical strength.

Table 8. Effect of slag addition content on the cement specific surface area

Type of cement	CEM I	CEM II/A-S	CEM II/A-S	CEM II/A-S	CEM II/B-S	CEM II/B-S	CEM II/B-S	CEM III/A	CEM III/A	CEM III/A	CEM III/B	CEM III/B	CEM III/C	CEM III/C
Slag (%)	0%	6%	10%	20%	25%	30%	35%	40%	50%	65%	70%	80%	85%	90%
SSA (cm^2/g)	4000	3950	3920	3900	3880	3820	3780	3740	3700	3680	3610	3500	3480	3380

V.3. The Effect of Slag Addition Content on The Prepared Cement Paste.

V.3.1. The Effect Of Slag Addition Content On The Cement Consistency.

The results of the experiment, as shown in Table 9 and Figure 4, clearly demonstrate the impact of slag addition rate on the normal consistency of cement. The water demand of cement pastes with varying percentages of added slag (ranging from 0% to 90%) was measured using the manual Vicat needle test. The effect of the amount of additive (slag) on the cement paste is reflected in the changes in the water demand ratio needed to achieve a normal consistency. The results, as depicted in Figures 4-4, indicate that as the percentage of slag in the cement increases, the amount of water required to achieve a normal consistency decreases.

Table 9 Effect of slag addition content on the cement consistency

Prepared cement	CEM I	CEM II/A-S	CEM II/A-S	CEM II/A-S	CEM II/B-S	CEM II/B-S	CEM II/B-S	CEM III/A	CEM III/A	CEM III/A	CEM III/B	CEM III/B	CEM III/C	CEM III/C
Slag (%)	0%	6%	10%	20%	25%	30%	35%	40%	50%	65%	70%	80%	85%	90%
E/C (%)	35	34.7	34.2	34	33.8	33.5	33.5	33.2	33	32.5	31.7	31	29.6	28

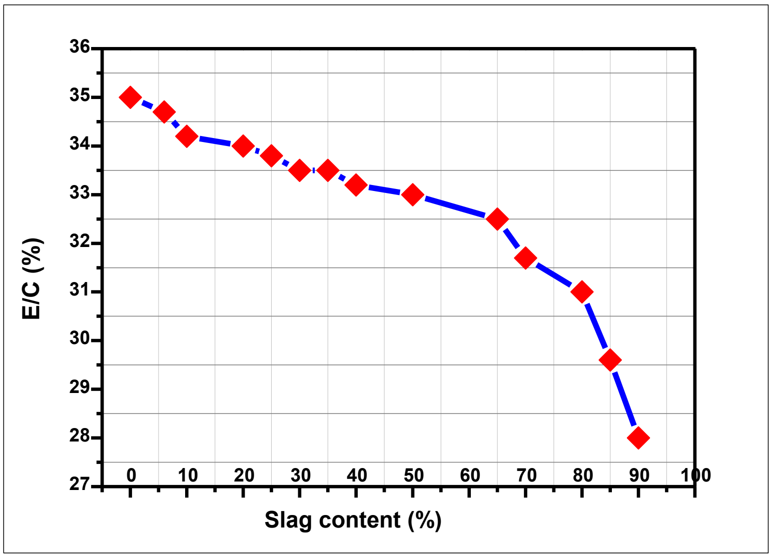

Fig.4. Variation of cement consistency of prepared cements in function of slag content

V.3.2. The Effect of Slag Addition Content On The Cement Setting Time.

The results of the experiment, as shown in Table 10 and Figure 4, clearly demonstrate the significant impact of the slag addition rate on the setting time of the cement paste. The test involved monitoring the viscosity of the paste using an automatic Vicat apparatus. The results, as depicted in Figures 4, indicate that as the percentage of slag additive in the cement increases, there is a noticeable increase in both the setting start and end times.

Table 14. Effect of slag addition content on the paste setting time

Prepared cement	CEM I	CEM II/A-S	CEM II/A-S	CEM II/A-S	CEM II/B-S	CEM II/B-S	CEM II/B-S	CEM III/A	CEM III/A	CEM III/A	CEM III/B	CEM III/B	CEM III/C	CEM III/C
Slag (%)	0	6	10	20	25	30	35	40	50	65	70	80	85	90
Initial setting time(min)	120	130	140	148	153	160	165	170	175	180	190	202	215	230
Final setting time (min)	180	200	220	230	235	247	253	260	270	275	280	294	300	320

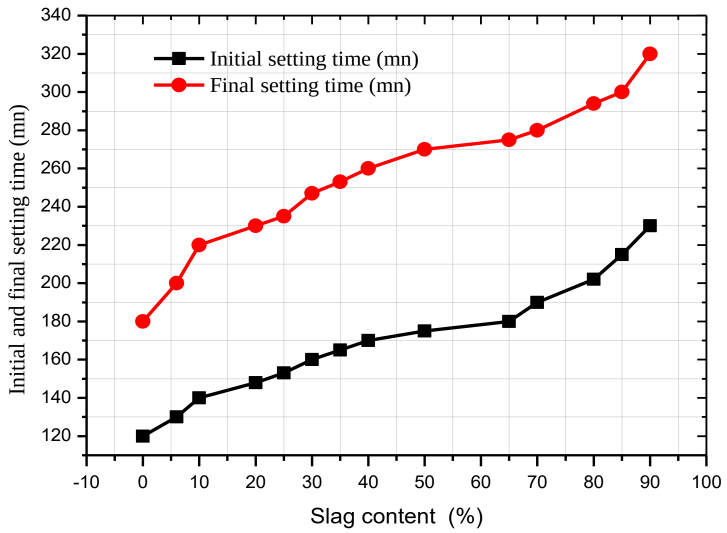

Fig.5. Effect of slag addition content on the paste setting time of prepared cements

V.3.3. The Effect of Slag Addition Content on The Cement Stability:

The results from Table 4-8 and Figure 4-6 show that hot expansion, which is the acceleration of hydration through heat treatment at 100°C, increases in a linear manner with higher slag content. This increase does not have a significant impact on cement stability and remains below the maximum limit set by EN 196-3 [14] , which is 10 mm. The rise in expansion can be attributed to the presence of impurities and other elements, such as free lime and MgO, which are harmful to the cement and typically result in higher expansion.

Table 14. Effect of slag addition content on the cement stability

Cement types	**CEM I**	**CEM II/A-S**	**CEM II/A-S**	**CEM II/A-S**	**CEM II/B-S**	**CEM II/B-S**	**CEM II/B-S**	**CEM III/A**	**CEM III/A**	**CEM III/A**	**CEM III/B**	**CEM III/B**	**CEM III/C**	**CEM III/C**
Slag %)	0%	6%	10%	20%	25%	30%	35%	40%	50%	65%	70%	80%	85%	90%
Hot expansion (mm)	0.5	0.5	0.5	1	1	1	1.5	1.5	1.9	2.0	2.0	2.4	2.4	2.4

VI. Conclusion

Slag cement, also known as CEM II - CEM III, is a type of cement that contains added slag. This results in a slower initial hardening process compared to ordinary Portland cement, which does not contain added slag and is known as CEM I. This slower hardening is due to the presence of secondary constituents, also known as CPA. To compensate for this, a good activator is necessary. This can be achieved through chemical means, such as using solutions containing chlorinated adjuvants to modify the setting and hardening process and increase the strength at a young age. Mechanical methods, such as crushing and pushing hydraulic binders, or thermal methods, which involve increasing the temperature to accelerate chemical reactions, can also be used as activators. Experimental results have shown that the amount of slag added and the physical properties, such as specific surface and granulometry, play a significant role in improving the reactivity of mineral additions and the mechanical strength of mortars and concretes.

The various results presented in this work clearly show the major influences of the mechanical activation of cements with added slag (CEM II - CEM III) on the hydration kinetics of cements (consistency - setting times and heat of hydration), on the mechanical properties of mortars and concretes and also on the dimensional (shrinkage) and volumetric (swelling) variations of the mortar pastes tested. The results obtained in this experimental study also allow us to draw the following conclusions:

- Increasing the amount of slag added to cement has a significant effect on the water required to achieve a normal consistency.
- As the proportion of slag in the cement increases, the water demand (W/C) decreases proportionally. This is due to the fact that slag is a supplementary cementing material that can improve the workability of the cement paste.
- The fineness (specific surface) of cements is also significantly affected by the addition of slag. As the proportion of slag increases, the specific surface of the cement decreases. This is because slag particles are finer than cement particles, resulting in a more finely ground mixture.
- The setting start and end times of the cement are also affected by the amount of slag added. As the proportion of slag increases, the setting times increase proportionally. This is because slag particles require more time to hydrate and contribute to the setting process.

Mechanical activation, achieved through extensive grinding on BB10, of cements with added slag has two essential advantages.

- Firstly, it improves the workability of the cement paste, making it easier to handle and place.
- Secondly, it enhances the reactivity of the slag particles, resulting in a more efficient use of the supplementary cementing material.

The rate of supplementary cementing materials, such as slag, also has a significant impact on the heat of hydration and physical and mechanical properties of the cement. By controlling the rate of slag addition, cements with low heat of hydration can be produced, making them suitable for use in special applications. Furthermore, the addition rate of slag can also affect the physical and mechanical properties of mortars and concretes. This can result in a change of cement type and class, such as from CEM II/A to CEM II/B or CEM III/A to CEM III/B or CEM III/C. This highlights the importance of carefully controlling the rate of slag addition in order to achieve the desired properties in the final product.

Cements with added slag must be finely ground to between (3400 cm^2/g - 4000 cm^2/g) and specific weight between (2. 90 g/cm^3 - 3.15 g/cm^3) in order to accelerate the hydration kinetics of cements in the short term (improvement of slag reactivity) and ensure good mechanical strength of the material: Mechanical activation (thorough grinding) of cements with added slag greatly accelerates the hydration kinetics after 2 days of hardening (very rapid reactivity of the hydration reaction).

Slag in general reduces the rate of cement hydration and therefore:

- An increase in the initial and final of setting.
- A decrease in initial strengths.

-Finally, to ensure good quality cements with different percentages of added slag (CEM II/A - CEM II/B - CEM III/A - CEM III/B - CEM III/C) with different strength classes, the following must be used:

- A clinker with good grind ability and good reactivity stored in a place protected from humidity.
- A medium-hard slag (easy to grind).
- A slag with good reactivity (slag rich in chlorine).
- Good quality SO_3 gypsum > 38%.
- Ensures good cement grinding (thorough grinding)

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