

Article

Hydration and Microstructural Evolution of Cement Pastes Incorporating Submerged Arc Welding Slag

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Abstract

The valorisation of industrial by-products as supplementary cementitious materials is a promising strategy to reduce clinker consumption and improve the sustainability of cement-based materials. In this study, the influence of submerged arc welding (SAW) slag on the hydration behaviour and microstructural evolution of cement pastes was investigated. Two SAW slags from different industrial sources were incorporated as partial replacements of ordinary Portland cement at 5%, 15%, and 30% by mass. Cement pastes were prepared with water-to-binder ratios of 0.3 and 0.4 and characterised through setting time, water demand, mercury intrusion porosimetry (MIP), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The results showed that SAW slag systematically delayed both initial and final setting times, while having only a negligible effect on water demand. Under the fixed mix conditions adopted in this study, this retardation is interpreted as the combined effect of clinker dilution and modified fresh-state conditions. MIP analysis revealed higher early-age porosity in SAW-containing pastes, particularly at high replacement levels and higher water-to-binder ratios, although mixtures with up to 15% slag approached the reference pore structure at later ages. Thermal analysis indicated lower bound water and portlandite contents at early ages, mainly due to clinker dilution, while long-term hydration development remained comparable at moderate replacement levels. At higher slag contents, some mixtures showed higher calcium carbonate contents, suggesting a tendency toward increased carbonate formation under the investigated conditions. Overall, the results indicate that SAW slag primarily affected early paste behaviour and pore structure development, with clinker dilution appearing to be the main mechanism, although weak secondary physical or chemical contributions cannot be completely excluded.



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1. Introduction

The current transition toward a more sustainable industrial model has intensified the need to reduce energy consumption, raw material depletion, waste generation, and greenhouse gas emissions across all productive sectors. The construction industry is one of the most relevant in this context due to its high environmental burden. It is responsible

for a substantial share of global raw material extraction, energy consumption, and waste generation, while also contributing significantly to worldwide CO₂ emissions. Among construction materials, ordinary Portland cement (OPC) plays a dominant role because of its good mechanical performance, durability, and cost-effectiveness [1,2]. However, its manufacture remains highly energy-intensive and is associated with large CO₂ emissions, mainly due to clinker production. Consequently, reducing clinker content in cement-based materials has become one of the most effective strategies for improving sustainability in the construction sector [3].

The partial replacement of Portland cement with supplementary cementitious materials (SCMs) and industrial by-products is widely recognized as a viable route to lower the environmental impact of cementitious systems. Conventional additions such as fly ash, ground granulated blast furnace slag, metakaolin, and silica fume have been extensively studied and successfully applied in a wide range of cement-based materials. Nevertheless, the limited availability of some traditional SCMs and the growing interest in circular economy strategies have encouraged the search for alternative industrial residues with suitable chemical composition and microstructural characteristics [4,5].

In addition, recent studies on blended cement systems have highlighted that Supplementary Materials can strongly affect both hydration development and pore structure evolution, which ultimately governs durability-related performance [6–8].

Submerged arc welding (SAW) slag is one such residue with increasing potential for cementitious applications. It is generated during the submerged arc welding process and is generally characterized by a high content of oxides such as SiO₂, Al₂O₃, CaO, MgO, and Fe-containing phases, together with a significant amorphous fraction. These characteristics have motivated growing interest in SAW slag as a constituent of cement-based materials. However, most published studies have focused on its use as a partial replacement for natural fine aggregates in concrete [9]. Similar findings were reported by Singh et al., who observed that concrete mixtures incorporating welding waste slag as a fine aggregate reached optimum compressive and split tensile strengths at 10% replacement, while higher dosages negatively affected mechanical performance [10]. Likewise, Ramesh et al. compared welding slag and furnace slag as sand substitutes and identified an optimum response at low replacement levels, particularly around 5% welding slag, which resulted in higher 28-day compressive strength than the control mixture while still maintaining acceptable performance up to 15% replacement [11]. Collectively, these studies indicate that SAW-related residues can be successfully incorporated as partial sand replacements at low dosages, with mechanical performance generally peaking in the range of 5–10%.

By contrast, the use of SAW slag as a partial replacement of Portland cement has received much less attention, despite its greater environmental relevance. Among the few available studies, Castro-Lopes et al. reported that SAW slag replacement levels between 5% and 10% were able to maintain or even improve mechanical strength compared with the reference mixture, whereas higher dosages led to strength reductions [12]. Their findings were supported by microstructural analyses, including X-ray diffraction and thermal analysis, which revealed modifications in phase assemblage and suggested that SAW slag may not behave as a completely inert filler. In addition, the authors highlighted the importance of considering durability-related properties, such as carbonation resistance, since higher slag contents may compromise long-term performance [12]. However, the available evidence remains limited, and it is still unclear to what extent SAW slag contributes through physical filling, clinker dilution, or only limited supplementary reactivity.

A key limitation in the available literature is the lack of detailed investigations on the influence of SAW slag on hydration development and microstructural evolution at the paste scale. In particular, there is still insufficient information regarding its effect on

setting behaviour, chemically bound water, portlandite evolution, pore refinement, mercury retention, and carbonation-related phase formation. These parameters are essential to determine whether the incorporation of SAW slag mainly delays hydration through clinker dilution, promotes any measurable secondary reaction, or modifies the pore structure in a way that may later influence transport-related durability.

This issue is particularly relevant because pore structure refinement, carbonate formation and CH consumption are closely interrelated in blended systems, and their combined interpretation generally requires complementary techniques such as MIP, TGA and XRD [6,7,13].

In this context, the present study investigates the influence of two submerged arc welding slags from different industrial sources on the hydration and microstructural evolution of cement pastes. The slags were incorporated as partial replacements of OPC at 5%, 15%, and 30% by mass, and the pastes were prepared with water-to-binder ratios of 0.3 and 0.4. The study combines setting time, water demand, mercury intrusion porosimetry (MIP), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) to clarify the role of SAW slag in hydration development, pore structure evolution, and phase assemblage. The novelty of this work lies in its combined paste-scale approach, whereas previous studies have mainly focused on SAW slag at mortar or concrete scale. Its importance lies in providing a more fundamental basis for understanding whether the observed behaviour is mainly governed by clinker dilution, possible fineness-related physical effects, or weak supplementary interactions, thereby supporting a more rigorous evaluation of SAW slag as a candidate material for low-clinker cementitious systems.

2. Materials and Methods

2.1. Materials

Ordinary Portland cement (OPC), classified as CEM I 42.5R, was supplied by Cementos Cruz (Murcia, Spain). Two submerged arc welding (SAW) slags from different industrial sources in Spain were used as partial cement replacements. One slag was supplied by Talleres Mecánicos Galicia S.L. (A Coruña, Spain) and is hereafter referred to as T slag (TS), while the second slag was supplied by NOKSEL ESPAÑA S.A. (Murcia, Spain) and is referred to as N slag (NS). Tap water was used for paste preparation. The physical properties of OPC and both slags are shown in Table 1. The two slags exhibited densities comparable to OPC, whereas their Blaine fineness values were higher, indicating a finer particle size after grinding.

Table 1. Properties of OPC and SAW slags.

Properties	OPC	T Slag	N Slag
Density (g/cm ³)	3.08	3.07	3.18
Blaine (cm ² /g)	3420	4783	4875

The SAW slags were ground in a ball mill for 3 h at a constant speed of 60 rpm before use. The Blaine fineness values reported in Table 1 correspond to the slags after this grinding process.

Their chemical composition was determined by X-ray fluorescence (XRF) using a Bruker S8 Tiger spectrometer, as shown in Table 2. OPC was mainly composed of CaO and SiO₂, while both slags were characterized by significant amounts of MgO, Al₂O₃, SiO₂, and CaO, together with noticeable MnO contents.

The amorphous contribution was estimated semiquantitatively by fitting the diffuse background and amorphous halo of the XRD patterns using DIFFRAC.EVA V4.2. The fitting was performed over the 2θ range of 5–70°, considering the identified crystalline phases

individually. Since no internal standard was used, the resulting values were employed only as comparative estimates.

Table 2. Main components detected in OPC and SAW slags by XRF (wt.%).

Oxides (%)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	P ₂ O ₅	SO ₃	F	MnO
OPC	0.37	2.51	4.09	16.89	1.33	64.74	0.26	3.51	0.18	4.06	-	-
TS	2.34	20.22	17.06	21.77	1.23	17.17	0.85	3.95	0.05	0.05	8.16	10.11
NS	2.64	16.14	15.09	22.95	1.30	23.72	2.54	2.55	0.04	0.08	9.86	6.51

Note: The values reported in Table 2 correspond to XRF analytical results expressed mainly as oxide equivalents, while fluorine (F) is reported separately as an element. Therefore, the table does not represent a strictly normalized oxide balance, and the direct sum of the listed components may exceed 100%, mainly because of the high fluorine content of both slags. Minor deviations may also arise from analytical uncertainty and rounding.

The mineralogical characterization of the ground SAW slags was additionally assessed by XRD, and the corresponding diffractograms are shown in Figures 1 and 2. Semiquantitative fitting of the diffuse background and amorphous halo indicated approximate amorphous contributions of 78% for TS and 80% for NS. The remaining crystalline fraction was mainly associated with spinel, periclase, phlogopite, fluorite, and fayalite, with some differences in relative phase proportions between the two slags. Since no internal standard was used, these values should be regarded as indicative comparative estimates rather than absolute quantitative phase contents. The results nevertheless indicate that both slags exhibit a predominantly vitreous character. However, the estimated amorphous contribution should be interpreted only as an indicator of potential reactivity and not as direct evidence of supplementary cementitious behaviour.

Cement pastes were prepared by partially replacing OPC with TS or NS at replacement levels of 5%, 15%, and 30% by mass. A reference paste (R-0) containing only OPC was also prepared. Two water-to-binder ratios ($w/b = 0.3$ and 0.4) were investigated in order to evaluate the influence of water availability on hydration development and pore structure evolution. The mix proportions of the pastes are presented in Table 3. All pastes were prepared under laboratory conditions at 20 ± 2 °C and $40 \pm 5\%$ relative humidity, demoulded after 24 h, and then cured in a controlled chamber at 21 ± 2 °C and $95 \pm 2\%$ relative humidity until the testing age.

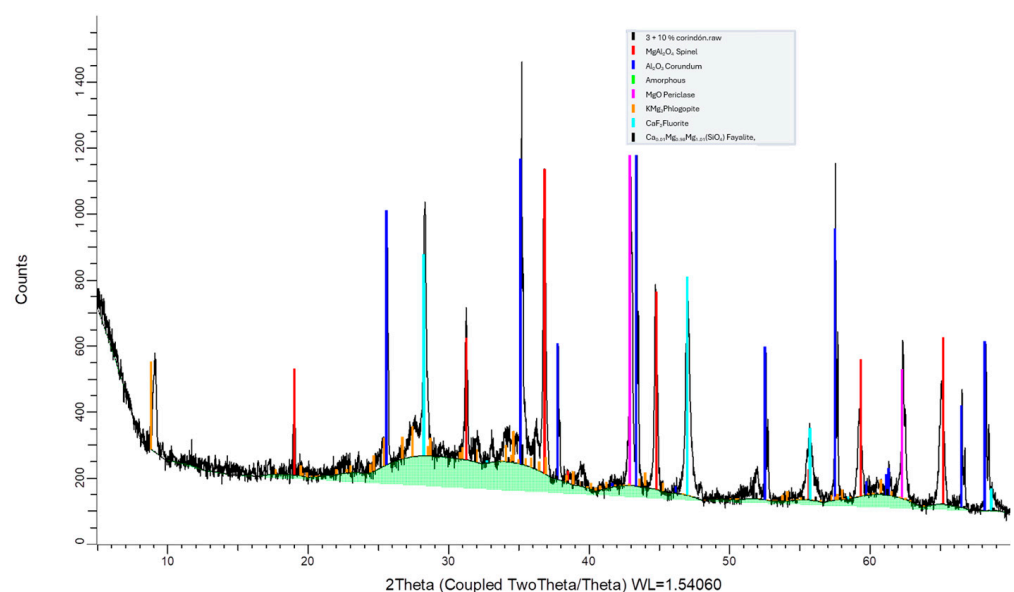


Figure 1. XRD pattern of ground T slag, including the identified crystalline phases and the fitted amorphous contribution.

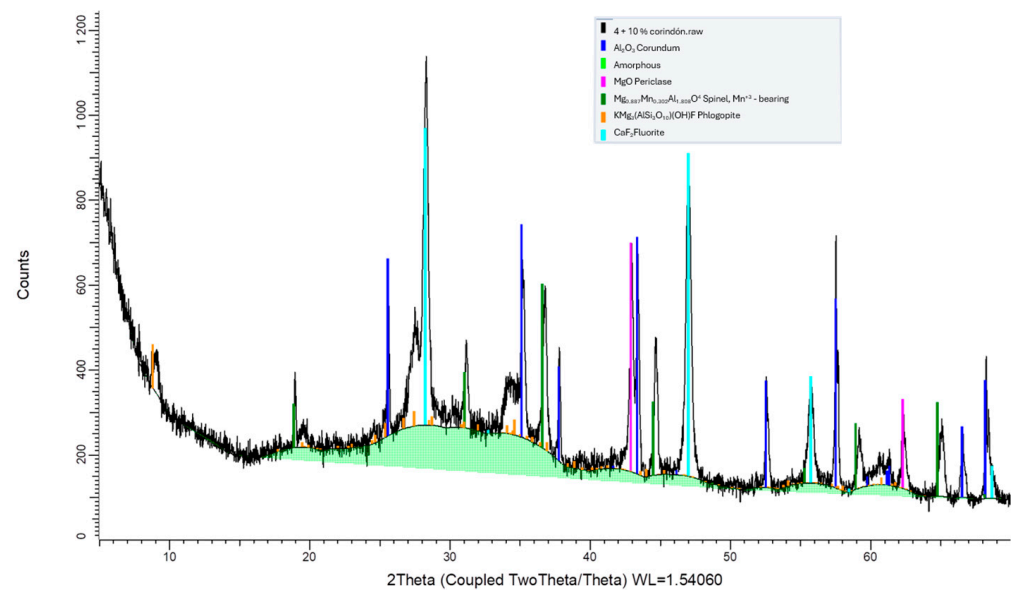


Figure 2. XRD pattern of ground N slag, including the identified crystalline phases and the fitted amorphous contribution.

Table 3. Mix proportions of cement pastes (weight %).

Mixture	TS	NS	OPC
R-0	-	-	100
PT-5	5	-	95
PT-15	15	-	85
PT-30	30	-	70
PN-5	-	5	95
PN-15	-	15	85
PN-30	-	30	70

2.2. Methodology

Below, the tests carried out on the cement pastes can be seen.

2.2.1. Setting Time and Water Demand

Water demand and setting time were assessed using a Vicat apparatus following the general test principle of UNE-EN 196-3 [14]; however, in the present study the measurements were performed as a comparative evaluation under fixed mix conditions rather than on pastes adjusted to standard consistency.

2.2.2. Mercury Intrusion Porosimetry (MIP)

MIP was carried out using Micromeritics Autopore IVA 9500 (Micromeritics Instrument Corporation, Norcross, GA, USA), which reaches pressures of up to 3200 psi, equivalent to the determination of pore size of up to 0.0067 μm . The resolution of the volume was 0.1 mm^3 , and the accuracy was $\pm 0.2\%$. For each specimen, two fragments were analyzed. The reported values correspond to the mean of the two measurements, and the error bars represent the standard deviation. The parameters examined include total porosity, reflecting the overall volume of accessible pores, and cumulative mercury retention, defined as the fraction of pore volume not intruded by mercury and used as an indicator of pore refinement and connectivity.

Before MIP testing, the specimens were oven-dried at 50 $^{\circ}\text{C}$ for 48 h until constant mass. This relatively low drying temperature was selected to limit drying-induced microcracking

and minimise alteration of temperature-sensitive hydration products [15]. After drying, the samples were stored for one week in an airtight container with silica gel to prevent moisture uptake before testing.

Since the interpretation of MIP results may also be affected by accessibility effects such as the ink-bottle effect, total porosity and pore size distribution were analyzed together with mercury retention in order to obtain a more reliable description of the pore network [16].

2.2.3. Thermal Analysis (TGA)

Thermogravimetric analyses (TGA) were carried out using a SDT Q600 TA Instruments device (TA Instruments, New Castle, DE, USA) in order to evaluate hydration development, portlandite evolution, and carbonation-related phase formation in the cement pastes. Prior to testing, the hydrated samples were dried at 50 °C until constant mass in order to remove most of the free water. Approximately 10 mg of the powdered sample was placed in the crucible and analysed under a nitrogen atmosphere at a heating rate of 10 °C/min, from room temperature up to 1000 °C. The thermal decomposition ranges were interpreted in terms of bound water content, associated with the dehydration of hydration products; portlandite content, associated with Ca(OH)_2 dehydroxylation; and calcium carbonate content, associated with decarbonation at high temperature. These results were used to assess the degree of hydration, clinker dilution effects, and the possible secondary reactivity of the slags.

The use of TG analysis to estimate portlandite and calcium carbonate contents in hydrated cementitious systems has been extensively discussed in the literature and is considered a suitable approach for the interpretation of phase evolution in blended binders [14].

2.2.4. X-Ray Diffraction of Hydrated Pastes

X-ray diffraction (XRD) analyses were conducted on selected hydrated pastes in order to identify the main crystalline phases and evaluate their evolution with curing time and slag content. The measurements were performed using a D8 Advance diffractometer (Bruker AXS, Madrid, Spain). The diffractograms were recorded over a 2θ range of 5–70°, using a step size of 0.02° and a counting time of 1s per step, under $\text{Cu K}\alpha$ radiation. The diffraction patterns were used to identify hydration-related phases such as portlandite, calcite, gypsum, and other crystalline compounds, as well as to assess changes in phase assemblage caused by SAW slag incorporation.

3. Results

3.1. Setting Time and Water Demand

The setting time results for the reference paste (R-0) and the SAW-containing paste mixtures are presented in Figure 3. R-0 exhibited an initial setting time of 213 min and a final setting time of 301 min. For both SAW slags, the initial and final setting times increased with increasing slag replacement level.

For the PT series, the initial setting time increased from 260 min for PT-5 to 375 min for PT-15 and reached 463 min for PT-30. The final setting time increased from 344 min for PT-5 to 579 min for PT-30. In the PN series, a comparable but slightly less pronounced increase was observed. The initial setting time increased from 243 min for PN-5 to 320 min for PN-15 and 389 min for PN-30, while the final setting time increased from 333 min for PN-5 to 405 min for PN-15 and 481 min for PN-30. In all cases, both initial and final setting times increased with higher replacement levels of SAW slag.

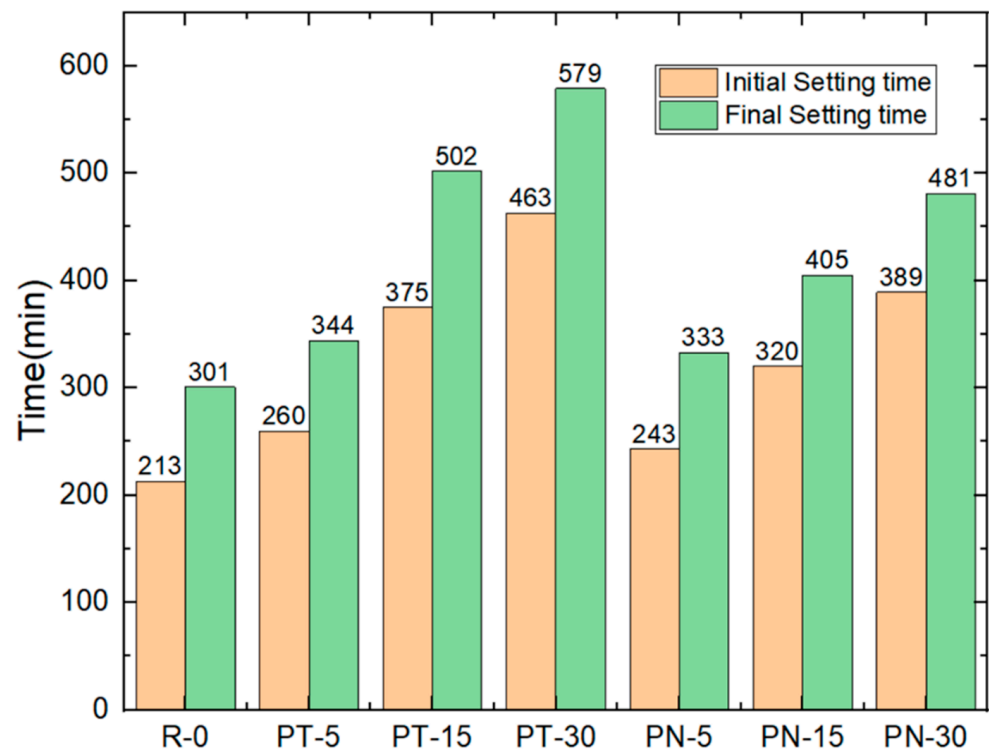


Figure 3. Setting time test of pastes with SAW slags.

The water demand values of the developed pastes are shown in Table 4. The reference paste required 140 mm. PT-5, PN-5, PT-15, and PN-15 showed the same water demand value of 140 mm, whereas PT-30 and PN-30 exhibited a slight increase to 142 mm.

Table 4. Water demands for developed pastes.

Mixture	R-0	PT-5	PT-15	PT-30	PN-5	PN-15	PN-30
Water Demand (mm)	140	140	140	142	140	140	142

3.2. Pore Structure Characterization by MIP

The total porosity results obtained by mercury intrusion porosimetry are presented in Figure 4. At all curing ages, the pastes prepared with $w/b = 0.3$ exhibited lower porosity than those prepared with $w/b = 0.4$. In most mixtures, porosity decreased with time. For the $w/b = 0.3$ pastes, the incorporation of 5% slag did not produce major changes in total porosity, whereas at $w/b = 0.4$ a slight increase in porosity was observed even at low replacement levels. No consistent effect of slag type on total porosity was identified. This suggests that, under the investigated conditions, the effect of slag chemistry on total porosity was secondary compared with the influence of water-to-binder ratio and replacement level.

The cumulative mercury retention results are shown in Figure 5. In general, the $w/b = 0.3$ pastes exhibited slightly higher mercury retention than the $w/b = 0.4$ mixtures, particularly after 28 and 90 days. Slag incorporation generally increased mercury retention, although no clear and systematic differences were observed between T slag and N slag.

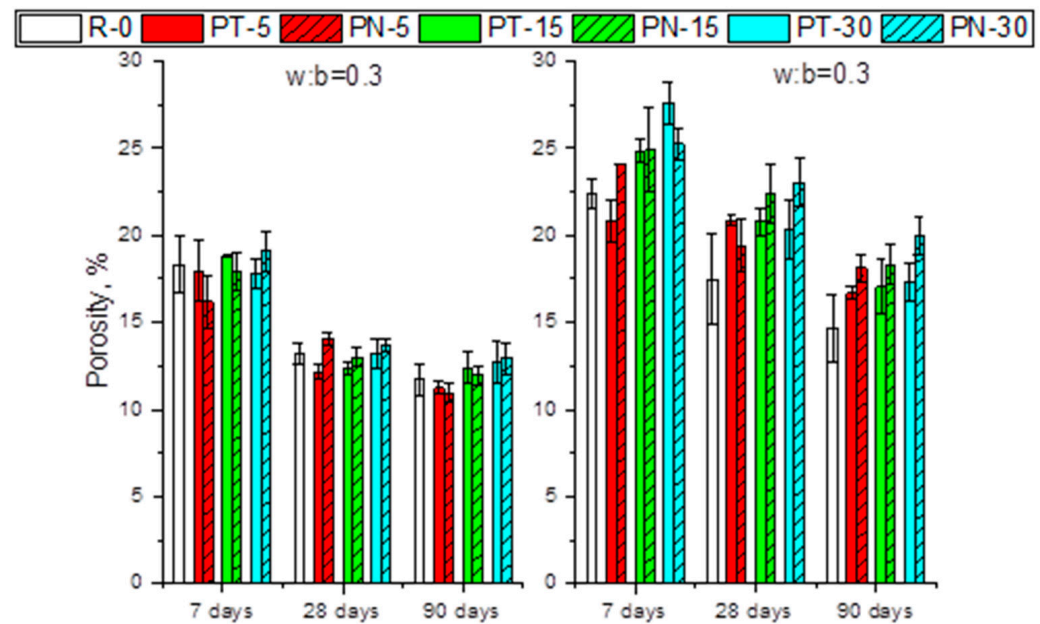


Figure 4. Porosity of the samples measured at different ages, as a function of age, percentage of slag, and type of slag.

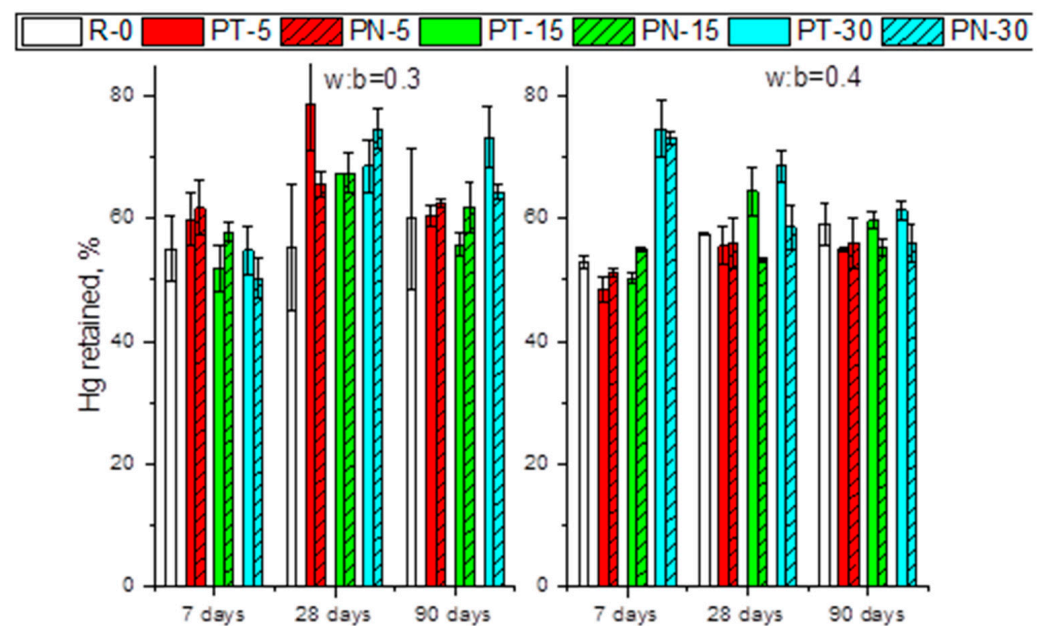


Figure 5. Mercury retained in the samples measured at different ages, as a function of age, percentage of slag, and type of slag.

The pore size distribution results are presented in Figure 6. With the exception of the mixtures containing 5% and 15% T slag at 7 days, the fraction of pores smaller than $10^{-2} \mu\text{m}$ was generally higher in the $w/b = 0.3$ pastes. This difference became less pronounced with curing time, and after 28 days, the $w/b = 0.4$ mixtures also showed a substantial proportion of fine pores. By contrast, pores in the range of 0.1 to $100 \mu\text{m}$ followed the opposite trend. For $w/b = 0.3$, the pastes containing N slag generally showed a similar or slightly higher proportion of fine pores than those containing T slag, except for the 5% replacement level at 90 days. A similar trend was observed at $w/b = 0.4$, with the main exception being the mixture containing 30% slag at 28 days.

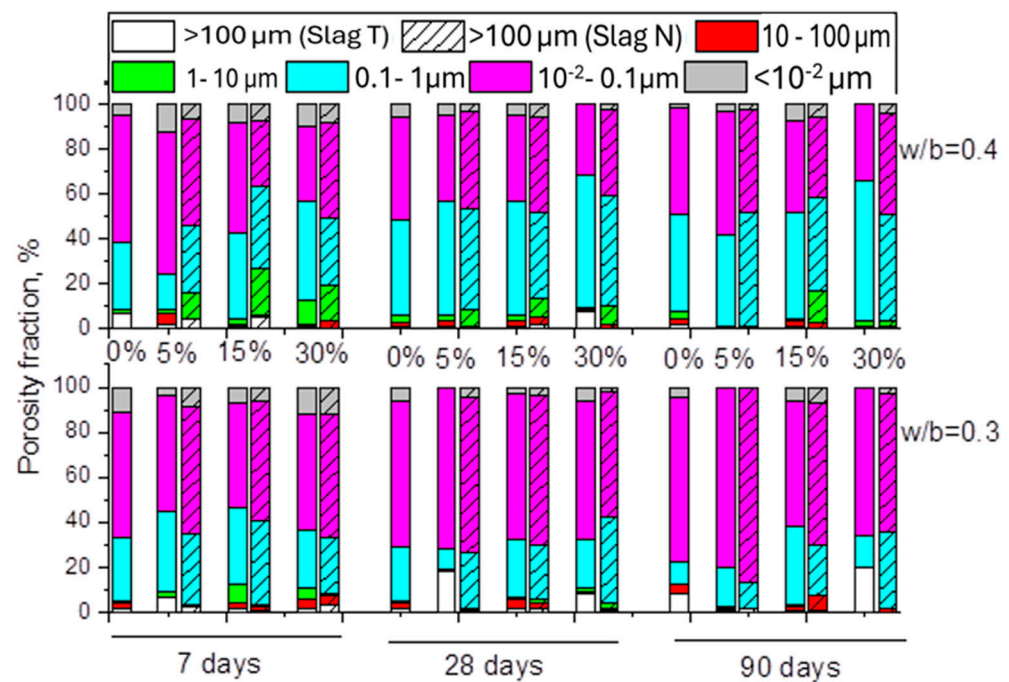


Figure 6. Pore size distribution, in percentage, of the samples measured at 7, 28, and 90 days as a function of percentage (0, 5, 15, and 30%) and type of slag. Bars with no pattern correspond to the reference (R-0) or samples prepared with TS, while the bars with a pattern are used for the results of slag type NS.

3.3. Thermal Analysis (TGA)

The thermogravimetric results are presented in Figure 7. In general, all hydrated pastes exhibited total mass losses of around 20% at 800 °C, which were substantially higher than those measured for the raw slags up to 1000 °C. This indicates that the observed mass losses are mainly associated with the hydration products and carbonate phases formed in the cementitious system rather than with thermal decomposition of the slags themselves. The complete TG curves for all mixtures, curing ages, and water-to-binder ratios are provided in Figures S1–S6 of the Supplementary Materials.

Following the approach proposed by Monteagudo et al. [17], three main temperature intervals were considered in the interpretation of the TGA curves. The first interval, from room temperature to 140 °C, corresponds to the dehydration of hydration products and was used to estimate the bound water content (dh). The second interval, between approximately 430 and 540 °C, is associated with the dehydroxylation of portlandite and was used to determine the CH-related mass loss (dx). The third interval, from 540 °C to the end of the test, corresponds to the decarbonation of carbonate-bearing phases and was used to quantify the carbonate-related mass loss (dc). The results derived from this analysis are shown in Figure 8.

For the reference paste, the dh values showed only limited variation with curing time. The pastes prepared with $w/b = 0.4$ generally exhibited higher bound water contents than those with $w/b = 0.3$. The incorporation of SAW slag slightly reduced the bound water content at early ages, particularly at high replacement levels.

A similar tendency was observed for the portlandite-related mass loss (dx). The reference paste exhibited the highest CH contents, while the slag-containing pastes showed progressively lower values as the replacement level increased. In some mixtures, slight additional reductions in CH were observed at later ages.

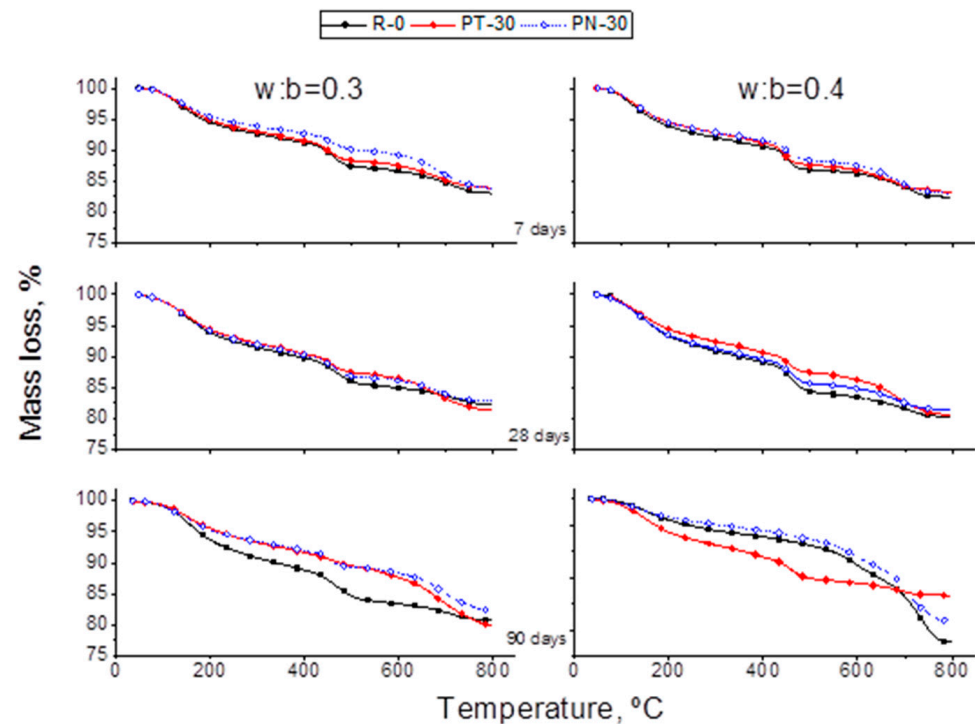


Figure 7. TGA curves of the selected hydrated pastes as a function of slag type and curing age.

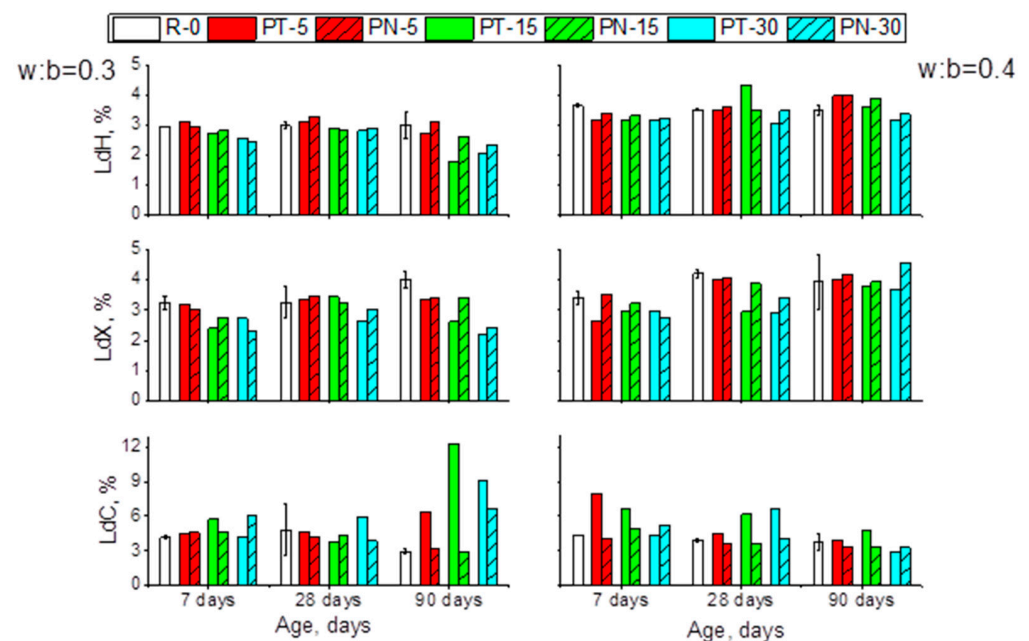


Figure 8. Bound water (dh), portlandite-related mass loss (dx), and carbonate-related mass loss (dc) derived from the TGA, as a function of slag type, replacement level, and curing age.

The carbonate-related mass loss (dc) was generally higher in the slag-containing pastes than in the reference mixture. In some mixtures, particularly selected samples at 90 days, a marked increase in decarbonation-related mass loss was observed. However, this behaviour was not consistently reproduced across the full experimental series and did not follow the general trends observed in the rest of the mixtures.

3.4. XRD of Hydrated Pastes

The XRD diffractograms obtained are shown in Figures 9–12, each corresponding to a different slag replacement level. In general, only limited differences were observed in the dominant crystalline phases among the different mixtures. Some isolated patterns showed atypical behaviour and were therefore interpreted with caution. The gypsum peak remained essentially unchanged with curing time and slag replacement level.

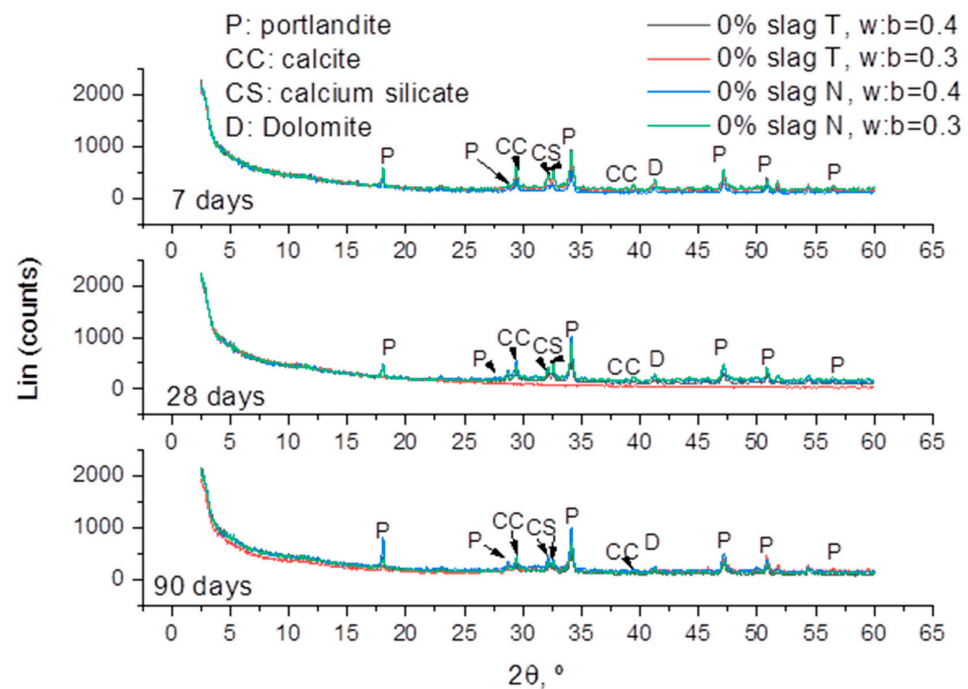


Figure 9. XRD patterns, with the main peaks identified for the samples with no slag as a function of age.

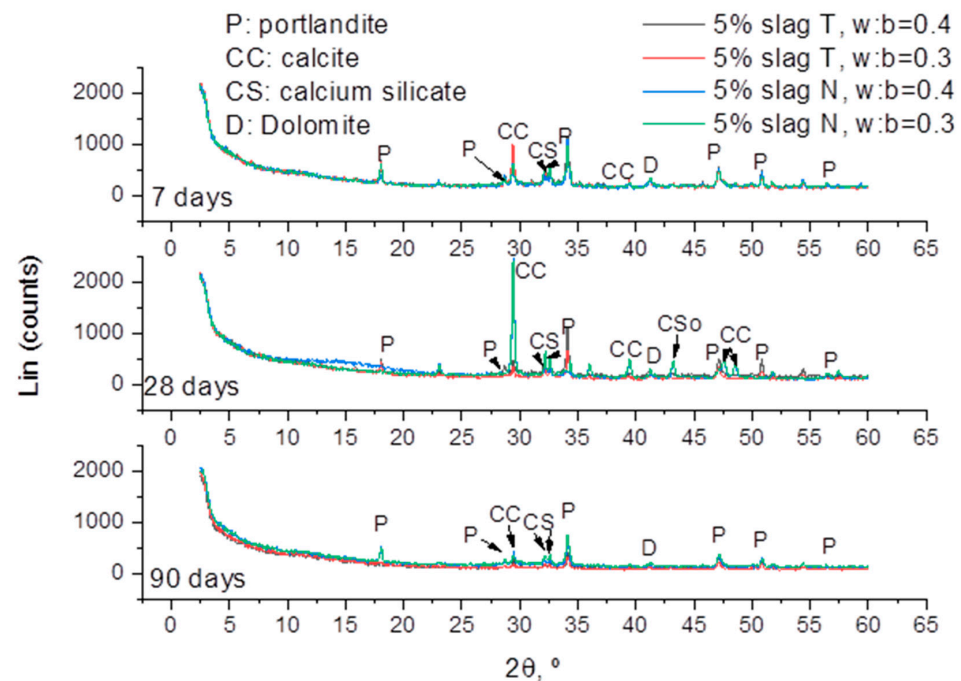


Figure 10. XRD patterns, with the main peaks identified for the samples with 5% slag as a function of age.

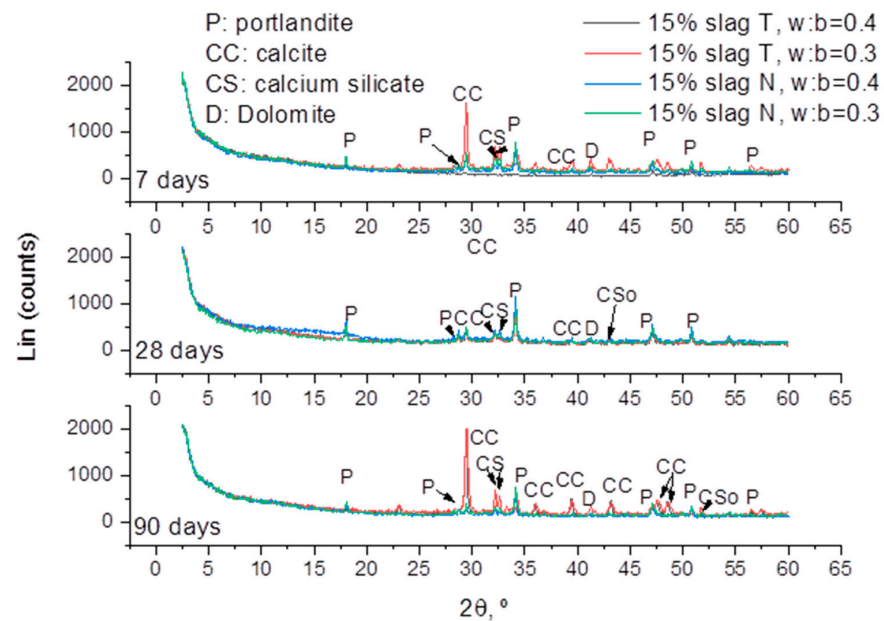


Figure 11. XRD patterns, with the main peaks identified for the samples with 15% slag as a function of age.

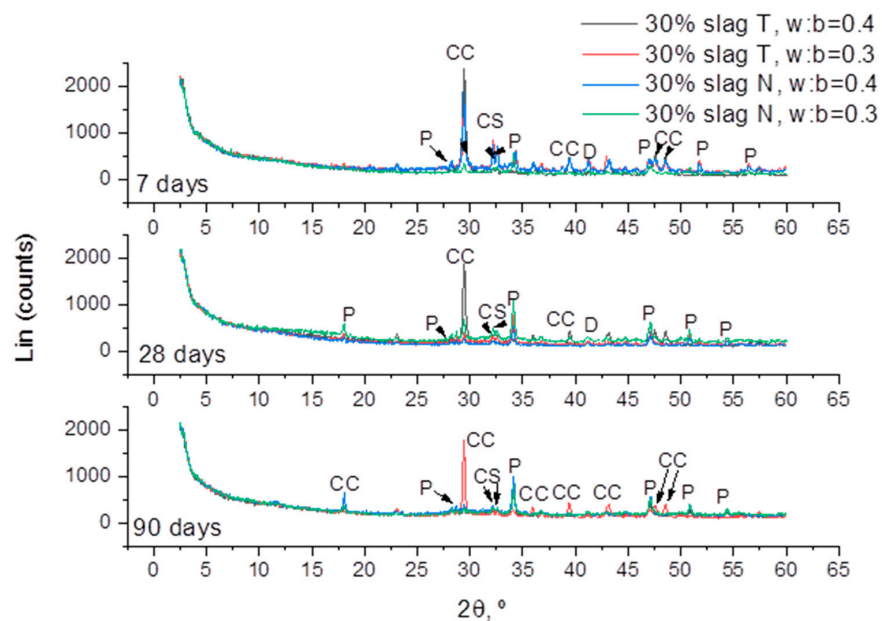


Figure 12. XRD patterns, with the main peaks identified for the samples with 30% slag as a function of age.

For the reference paste, the intensity of the portlandite peaks increased with curing time, particularly at around 18° and 34° 2θ , whereas the dolomite peak tended to decrease and calcite remained approximately stable. In the slag-containing pastes, lower portlandite intensity was generally observed, especially at higher replacement levels and later ages. However, no additional dominant crystalline phases were identified in the SAW-containing systems compared with the reference paste.

4. Discussion

4.1. Effect of SAW Slag on Setting Behaviour and Early Paste Structuration

The setting time results indicate that the incorporation of SAW slag delays both the initial and final setting times of the cement pastes. This effect becomes more pronounced

as the replacement level increases. Since the water demand remained unchanged up to 15% replacement and only increased slightly at 30%, the observed retardation cannot be attributed to major changes in paste consistency alone.

Under the fixed mix conditions adopted in this study, this behaviour is interpreted as the combined effect of clinker dilution and modified fresh-state conditions, rather than as a direct indication of hydration kinetics alone. The partial replacement of OPC reduces the amount of reactive clinker phases available for the formation of early hydration products, which likely contributes to the delayed development of a rigid structure. However, clinker dilution is unlikely to be the only mechanism involved. The higher fineness of the slags may also have introduced physical effects such as heterogeneous nucleation and particle packing, while possible surface-chemistry effects cannot be excluded [18–20].

The unusually high F and MnO contents of the SAW slags may also have contributed to the observed hydration behaviour. Although this possible chemical influence was not directly isolated in the present study, it should not be excluded and deserves further investigation.

Therefore, the setting time results provide comparative evidence that SAW slag delays the early structuration of the paste systems, although the relative contribution of dilution, physical effects, and possible weak secondary chemical interactions cannot be rigorously separated under the present experimental conditions.

4.2. Influence of SAW Slag on Pore Structure Development

The MIP results show that pore structure evolution was governed primarily by the water-to-binder ratio and, to a lesser extent, by the slag replacement level. As it was stated on Section 3.2 it seems to be no influence of the slag type on the total porosity. This fact could be due that in spite of the differences on composition, the filling or reactivity of the samples is similar. If Table 2 is observed, the value of silicon dioxide is very similar for both slag type and the percentages of CaO and Al₂O₃ are inverse, and one could compensate the other oxide, having a similar effect on terms of porosity.

As expected, the lower w/b ratio (0.3) favoured the development of a denser pore network, as reflected by lower total porosity and generally higher mercury retention values. This behaviour indicates a more refined and less accessible pore structure compared with the mixtures prepared at w/b = 0.4.

SAW slag incorporation did not produce major changes in porosity at low replacement levels for w/b = 0.3, but at w/b = 0.4 it led to a slight increase in porosity even at 5% replacement. In addition, higher slag contents tended to delay pore refinement, particularly at early ages. The pore size distribution results support this interpretation, showing that the proportion of fine pores depended strongly on curing age and water availability. Overall, the microstructural results suggest that the effect of SAW slag on pore structure is secondary to the effect of water-to-binder ratio, but becomes more noticeable at high replacement levels and early ages.

The relevance of pore size distribution extends beyond microstructural description, since pore connectivity and the proportion of fine pores are also closely related to transport-related properties and durability performance [21,22].

4.3. Hydration Products and Phase Evolution from TGA and XRD

The TGA results indicate that the incorporation of SAW slag mainly affected the evolution of the hydrated system through clinker dilution. The lower bound water contents observed in the slag-containing pastes at early ages, particularly at high replacement levels, are consistent with a reduced amount of reactive clinker and, consequently, with a slower development of hydration products. A similar trend was observed for the CH-related mass

loss, which progressively decreased as the slag replacement level increased. This behaviour is primarily attributed to the lower amount of OPC available to generate portlandite during hydration.

Although some mixtures showed slight additional reductions in CH at later ages, these differences remained limited and do not provide strong evidence of pronounced supplementary reactivity under the conditions investigated. Therefore, the present results suggest that clinker dilution was the most evident effect of SAW slag incorporation, although limited supplementary reactivity cannot be ruled out. However, small differences in mercury retention and water demand indicate that fineness-related physical effects and possibly weak secondary interactions cannot be completely excluded.

The carbonate-related mass loss was generally higher in some slag-containing pastes, suggesting a tendency toward increased carbonate formation under the investigated conditions. However, some isolated mixtures exhibited unusually high dc values at 90 days, and this behaviour was not consistently reproduced across the full experimental series. For this reason, these values were interpreted with caution and were not considered sufficient, on their own, to support a broader mechanistic conclusion. In addition, since no direct carbonation test was performed, the TG-derived carbonate mass loss should not be interpreted as direct proof of carbonation susceptibility. Superficial carbonation during sample grinding, storage or preparation may also have contributed to some of the measured dc values.

The XRD results provide qualitative support for this interpretation. The diffractograms did not reveal the formation of new dominant crystalline phases in the SAW-containing pastes compared with the reference system. Instead, the main differences were associated with changes in the relative intensity of hydration-related phases, particularly portlandite and calcite. These observations are consistent with the thermal analysis results and support a predominantly dilution-controlled behaviour, although they do not rule out weak secondary contributions [6,22].

Taken together, the TGA and XRD results indicate that the main effect of SAW slag in the investigated pastes was to modify the extent and evolution of hydration products through clinker dilution, while only limited evidence of strong secondary reactivity was observed. A direct assessment of carbonation performance would be necessary to confirm whether the observed microstructural trends result in greater carbonation susceptibility [13,23].

5. Conclusions

This study investigated the effect of submerged arc welding (SAW) slag as a partial replacement of ordinary Portland cement on the hydration behaviour and microstructural evolution of cement pastes. Based on the experimental results, the following conclusions can be drawn:

- SAW slag delayed both the initial and final setting times, and this effect became more pronounced as the replacement level increased. Compared with the reference paste, the initial setting time increased from 213 min to 243–463 min and the final setting time from 301 min to 333–579 min, depending on slag type and dosage. Under the fixed mix conditions adopted in this study, this retardation is interpreted as the combined effect of clinker dilution and modified fresh-state conditions, while fineness-related physical effects and possible weak secondary chemical interactions cannot be completely excluded.
- Water demand was only marginally affected by SAW slag incorporation. The reference paste showed a water demand of 140 mm, which remained unchanged up to 15% replacement and increased only slightly to 142 mm at 30% slag. This limited variation indicates that the observed delay in setting cannot be explained by major consistency changes alone.

- The incorporation of SAW slag increased early-age porosity, particularly at high replacement levels and at $w/b = 0.4$, whereas mixtures with up to 15% slag at $w/b = 0.3$ approached the reference pore structure at later ages. This indicates that moderate replacement levels did not severely impair long-term pore refinement, while the effect became more noticeable at higher slag contents and under higher water availability.
- Thermal analysis and XRD indicate that SAW slag mainly affected the evolution of hydration products through clinker dilution. Slag-containing pastes showed lower bound water and portlandite contents at early ages than the reference paste, with the effect becoming more pronounced as the replacement level increased. However, under the investigated conditions, the results did not provide strong evidence of pronounced supplementary reactivity at paste scale.
- Higher SAW replacement levels were associated with a tendency toward increased carbonate formation in some mixtures at later ages. However, since some dc values at 90 days were not consistently reproduced and no direct carbonation test was performed, these results should be interpreted with caution and not as direct evidence of carbonation susceptibility.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/infrastructures11080268/s1>. Figure S1. TG curves for samples with a $w/b = 0.3$ at 7 days of age. Figure S2. TG curves for samples with a $w/b = 0.4$ at 7 days of age. Figure S3. TG curves for samples with a $w/b = 0.3$ at 28 days of age. Figure S4. TG curves for samples with a $w/b = 0.4$ at 28 days of age. Figure S5. TG curves for samples with a $w/b = 0.3$ at 90 days of age. Figure S6. TG curves for samples with a $w/b = 0.4$ at 90 days of age.

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Abbreviations

The following abbreviations are used in this manuscript:

CH	Portlandite
DSC	Differential Scanning Calorimetry
MIP	Mercury Intrusion Porosimetry
NS	N slag
TS	T slag
OPC	Ordinary Portland Cement
R-0	Reference paste without slag incorporation
SAW	Submerged Arc Welding
SCMs	Supplementary Cementitious Materials

TGA	Thermogravimetric Analysis
w/b	Water-to-binder ratio
XRD	X-ray Diffraction
dx	CH-related mass loss associated with portlandite dehydroxylation
dh	Bound water content associated with dehydration of hydration products
dc	Carbonate-related mass loss associated with decarbonation

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