

INFLUENCE OF QUARTZITE WASTE FROM INDUCTION FURNACES ON THE HYDRATION AND HARDENING PROCESSES OF PORTLAND CEMENT

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Abstract

This study investigates the influence of quartzite waste from induction furnaces on the hydration, hardening, and phase formation processes of Portland cement. Composite cements were produced by partial replacement of clinker with quartzite waste in an amount of 15–20 wt.%. X-ray diffraction analysis was used to examine changes in the mineralogical composition and microstructure of cement stone at curing ages of 3, 7, 14, and 28 days. It was established that the incorporation of quartzite waste intensifies pozzolanic reactions, reduces the content of portlandite, and promotes the formation of a well-developed amorphous C–S–H gel phase, which leads to densification of the cement stone structure and enhancement of its strength characteristics.

Keywords. Portland cement, quartzite waste, hydration, X-ray diffraction analysis, C–S–H gel, pozzolanic activity.

Introduction

The modern development of the cement industry is accompanied by the need to reduce energy costs, reduce CO₂ emissions, and rationally utilize man-made waste. One of the promising areas is the use of silica-containing waste as mineral additives for Portland cement.

Quartzite waste from induction furnaces is characterized by a high content of silicon dioxide and a fine-grained structure, which determines its potential pozzolan activity. However, the mechanism of their influence on the hydration, solidification, and phase formation processes of Portland cement requires detailed study. The purpose of this work is to investigate the influence of quartzite waste from induction furnaces on the hydration and hardening processes of Portland cement and to establish the correlation between “composition - structure – properties”.

Literature Analysis

Analysis of scientific publications shows that in recent years, significant attention has been paid to the use of mineral and technogenic additives in cement systems to enhance their operational characteristics and reduce the environmental impact of the cement industry. In the monograph by I. P. Morozov and V. A. Petrov, the theoretical foundations of mineral additives' action, their influence on clinker mineral hydration, and the formation of cement stone structure are examined in detail, serving as a methodological basis for this study.

The works of A. V. Kuznetsov and S. D. Ivanov are dedicated to the study of putzolan materials in the cement industry. The authors demonstrated that silica-containing additives facilitate the binding of calcium hydroxide and the formation of secondary calcium hydrosilicates, leading to the compaction of the cement stone structure and an increase in strength. These provisions are directly correlated with the results obtained in this work.

Foreign researchers have made significant contributions to the study of puzzolan activity in industrial waste. In the works of J. Smith and R. Taylor, it is shown that waste with high content of active SiO₂ is capable of intensifying hydration processes and reducing the content of portlandite in cement systems. Similar conclusions are provided in the studies of L. Zhang and Y. Chen, where it was established that the addition of quartz-containing waste improves the microstructure of cement stone by forming a developed amorphous phase of C–S–H-gel. The publication by X. Chen, Q. Liu, and S. Wu examines the influence of fine-dispersed silica additives on the hydration kinetics of Portland cement. The authors note an acceleration of the initial stages of hydration and a decrease in the crystallite sizes of hydrate neoplasms, which aligns with the X-ray phase analysis results obtained in this work.

The methodological foundations of X-ray phase analysis of cement systems are detailed in the work of A. E. Gromov and Yu. N. Lebedev, where the effectiveness of RFA for assessing the phase composition, crystallinity degree, and amorphous component of cement stone is demonstrated. These approaches were utilized in the interpretation of diffractograms in this study.

Fundamental patterns in cement chemistry and the hydration mechanisms of clinker minerals are presented in the classic monograph by H. F. W. Taylor, as well as in the review by K. L. Scrivener and co-authors, where the evolution of cement stone microstructure and the role of C–S–H-gel in the formation of strength characteristics are examined in detail.

Methodology.

Normal-hardening Portland cement was used as the primary binder. Quartzite waste from induction furnaces was introduced into the cement composition in amounts of 15 and 20% by weight instead of a portion of clinker. Cement stone samples were molded and hardened under normal conditions for 3, 7, 14, and 28 days. The phase and mineralogical composition were investigated using X-ray phase analysis (XRA) in the angle range of $2\theta = 10\text{--}80^\circ$ using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). Based on the diffractograms, the main crystalline phases, crystallinity degree, presence of amorphous component (C-S-H-gel), and average crystallite size were determined.

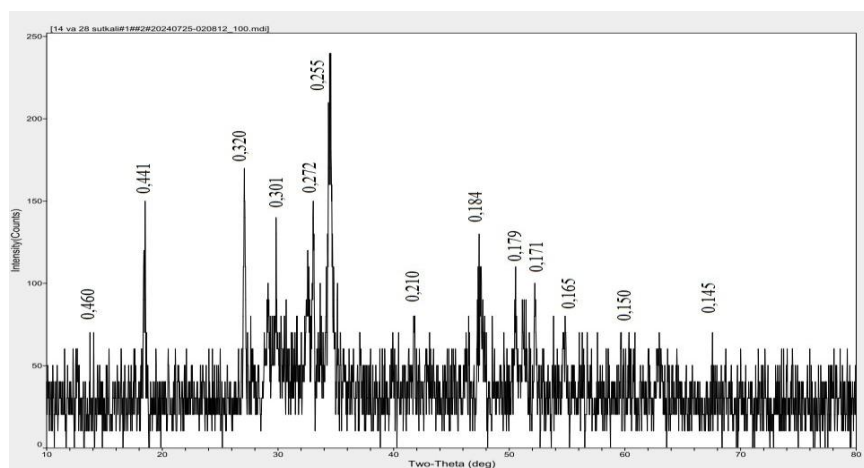
Discussions and Results

In the PC-D20 sample containing quartzite waste, studied 3 days later, intensive peaks at $\sim 30.1^\circ$ and 34.9° 2θ (CuK α) characteristic of alite (C3S), an intensity line at $\sim 18.7^\circ$ for belite (C2S), and less pronounced peaks in the $\sim 45\text{--}52^\circ$ region corresponding to three-calcium aluminate (C3A) or four-calcium aluminoferrite (C4AF) are identified. The dominance of C3S explains the expected early strength of the cement, where C3S hydrates quickly, ensuring strength gain in the first days. The presence of C2S in a proportion of $\sim 10\%$ is typical for clinker mixtures, while the presence of belite in it hydrates more slowly and affects later strength. C3A and C4AF participate in the formation of hydroxide-aluminate and ferrite matrices; their ratio affects the color and heat of hydration. Visual estimation errors are caused by: the absence of digital data, peak overlap, sample texture, and the possible presence of an amorphous phase. The average size of the crystals is 45-55 nm, which is typical for the early stage of cement stone solidification, when primary hydrate formations predominate, and the addition of quartzite waste contributes to the formation of the first products of the pozzolan reaction.

The X-ray of the 7 day-old sample shows a decrease in the intensity of clinker phase peaks and the appearance of pronounced Ca (OH) 2 portlandite reflexes at $2\theta \approx 18.1^\circ$ and 34.2° , as well as weak SiO₂ reflections at $2\theta \approx 26.6^\circ$. This indicates the development of pozzolan reactions between calcium hydroxide and the activated silica of the quartzite waste. The diffuse densification of the background in the $2\theta = 20\text{--}25^\circ$ region confirms the increase in the amount of amorphous C-S-H-gel involved in the densification of the structure.

The average size of the crystals decreases to 35-45 nm, reflecting the active phase of hydration and the formation of secondary silicate compounds.

After 28 days of solidification, a significant restructuring of the phase composition is observed. The sample's X-ray was obtained in the angle range of $2\theta = 10\text{--}80^\circ$. Presumably, CuK α radiation was used as the anode ($\lambda = 1.5406 \text{ \AA}$). Diffraction maxima corresponding to the main crystalline compounds of cement stone after solidification were recorded. After 28 days of composite Portland cement hardening, the diffractogram shows pronounced peaks of Portlandite (Ca (OH) 2) and calcium hydrosilicates (CSH-I and CSH-II), indicating a high level of hydration in the clinker minerals.



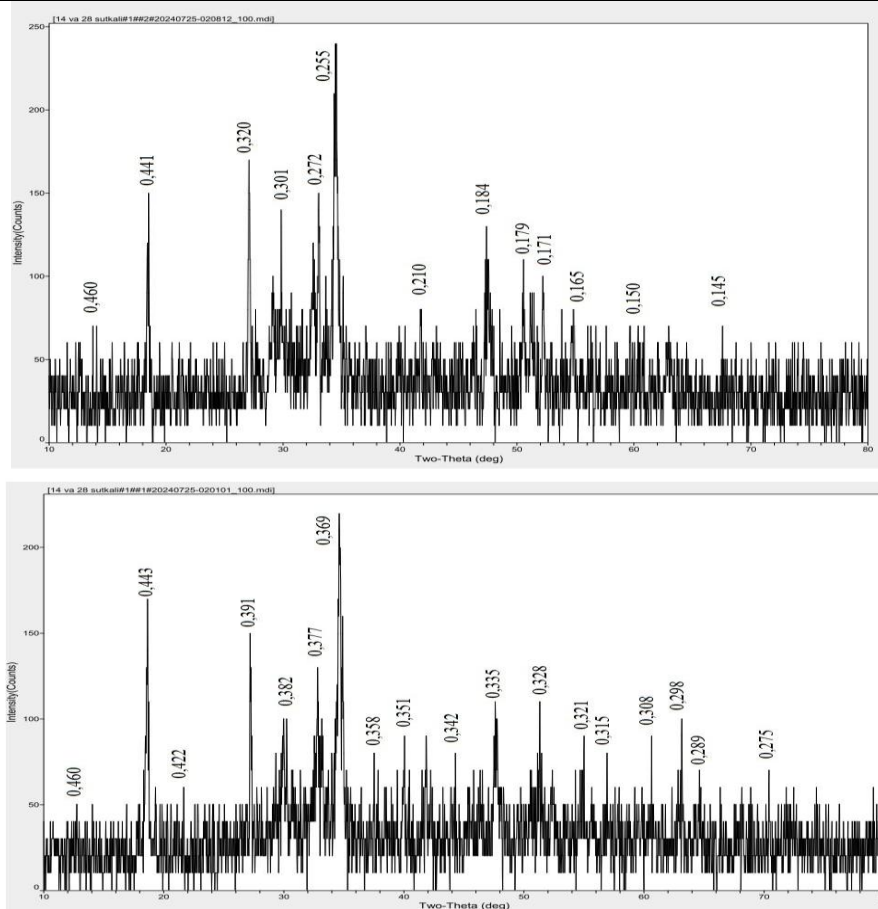


Figure 1 Diffractogram of PC-D20 containing quartzite waste that has hardened for 3 (a), 7 (b), and 28 (c) days under normal conditions

According to the visual analysis of the diffractogram, the most pronounced reflexes are recorded at $2\theta \approx$: portlandite, a hydration product of C3S and C2S formed during the interaction of calcium silicates with water at $\sim 18^\circ$; the main phase of cement stone—calcium hydrosilicates at $\sim 29\text{--}30^\circ$; weak peaks of unhydrated C3S and C2S particles at $\sim 32\text{--}34^\circ$; carbonized C4AF and C3A products at $\sim 41\text{--}48^\circ$, which is natural for 28-day-old age—the hydration process of these minerals proceeds gradually and does not complete completely; the presence of a weak reflex near $\sim 50\text{--}52^\circ$ of traces of free calcium (CaO) and calcium carbonates may be associated with minor surface carbonization and formation (CaCO₃); in this range, quartz and inactive impurities, Mg-containing compounds at $\sim 60\text{--}63^\circ$ are characteristic of cement stone hydration products such as calcium hydrosilicates, portlandite, and trace amounts of residual clinker. The predominance of a wide amorphous background in the $2\theta = 20\text{--}25^\circ$ range indicates the dominance of C-S-H-gel, which forms a dense spatial network. The average size of the crystals is estimated at 30-40 nm, which is characteristic of mature cement stone with a high degree of hydration.

As the solidification period increases, a regular decrease in the intensity of clinker phase peaks and an increase in the amorphous component are observed. The addition of quartzite waste accelerates the binding of calcium hydroxide and the formation of secondary silicate phases, contributing to the compaction of the microstructure and an increase in the material's strength

characteristics. The average crystalline size varies from 55 nm (3 days) to 30 nm (28 days), which confirms the development of nanostructured hydrate products and the active occurrence of pozzolan reactions. The results obtained indicate that the quartzite waste actively participates in hydration and pozzolan processes. Active silica interacts with calcium hydroxide formed during the hydration of alite and belite, forming secondary low-base calcium hydrosilicates.

The decrease in portlandite content reduces the probability of weak contact formation and internal stresses, while the development of the amorphous phase of C-S-H-gel contributes to the compaction of the cement stone microstructure. The reduction in crystallite sizes indicates the development of nanostructured hydrate phases, which has a positive impact on the strength and performance characteristics of the material. The optimal content of quartzite waste is approximately 15%, which achieves a balance between additive activity and the preservation of the required amount of clinker phases.

Conclusion

As a result of the conducted research, it has been established that quartzite waste from induction furnaces possesses pronounced pozzolan activity and can be effectively utilized as a mineral additive for Portland cement. The introduction of quartzite waste in an amount of 15-20% by mass contributes to the intensification of Portland cement hydration processes and the accelerated binding of calcium hydroxide formed during the hydration of clinker minerals. The formation of a developed amorphous phase of calcium hydrosilicates (C-S-H-gel) and the reduction of crystallite sizes to 30-40 nm lead to the compaction of cement stone microstructure, a decrease in porosity, and an increase in its strength characteristics. The results obtained confirm that the use of quartzite residues from induction furnaces is a promising and effective direction for obtaining composite cements with improved physical and mechanical properties and additional environmental advantages related to the disposal of man-made waste and the reduction of resource and carbon load in cement production.

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