12^{th} International Conference on Fracture Mechanics of Concrete and Concrete Structures
FraMCoS-12
B.L.A. Pichler, Ch. Hellmich, P. Preinstorfer (Eds)

https://doi.org/10.21012/FC12.1259
MS02-1:4

ENHANCING MATRIX-FIBER BOND AND MECHANICAL PERFORMANCE WITH HIGH-PERFORMANCE PLASTICIZERS

JAIME D. RUÍZ-MARTÍNEZ[1], JOSÉ D. RÍOS[2], EVA M. PÉREZ-SORIANO[3], HÉCTOR CIFUENTES[2] AND CARLOS LEIVA[1]

[1] Universidad de Sevilla, ETS de Ingeniería, Dept. of Chemical and Environmental Engineering
Caminos de los Descubrimientos s/n, 41092 Seville, Spain
e-mail: cleiva@us.es

[2] Universidad de Sevilla, ETS de Ingeniería, Dept. of Continuum Mechanics and Structural Analysis
Caminos de los Descubrimientos s/n, 41092 Seville, Spain
e-mail: bulte@us.es

[3] Universidad de Sevilla, Escuela Politécnica Superior, Dept. of Materials Science and Engineering and Transport
Virgen de África 7, 41011 Seville, Spain

Key words: ultra-high-performance fiber-reinforced concrete; high performance plasticizer

Abstract. This study explores the influence of sodium gluconate (SG), an organic electrolyte, on the rheology and mechanical properties of ultra-high-performance fiber-reinforced concrete (UHPFRC). SG was incorporated at varying dosages (0.03%-0.15%) to assess its effects on workability, hydration, porosity, and fracture behavior. Key findings demonstrate that SG effectively retards hydration by inhibiting gypsum dissolution and AFt formation, resulting in significant delays in setting time—up to 295% with higher SG content. Furthermore, increased SG dosages improved workability, with a slump diameter increase of up to 56%, facilitating better fiber distribution and bonding. No major chemical changes were observed in the concrete matrix; however, SG decreased macropores ($> 10\mu m$) and increased micropores ($< 0.1\mu m$), which contributed to enhanced mechanical performance. Compressive strength rose by 9.5%, and flexural cracking initiation improved by 38% for Mix-0.15. Residual flexural strengths also showed substantial increases (up to 38%), attributed to improved fiber-matrix adhesion. These findings highlight SG's potential to improve UHPFRC's mechanical properties and durability, making it a promising additive for high-strength construction applications.

1 INTRODUCTION

In the field of construction, concrete is a widely used material due to its remarkable characteristics, such as its exceptional compressive strength, durability, cost-effectiveness, abundant availability of constituent materials, and adaptability to various shapes through casting molds. However, one of its main drawbacks is the high CO_2 emissions in clinker production. Given these characteristics, the exploration of recycled materials in concrete production has garnered considerable attention from researchers in recent decades [1].

Ultra-high-performance fiber-reinforced concrete (UHPFRC) is an innovative cement-based composite material known for its extremely high strength, exceptional durability, and remarkable toughness. The components used in the formulation of UHPFRC predominantly include cementitious materials, quartz sand, chemical additives, and water, among others. Additionally, the integration of high-strength steel fibers into UHPFRC serves to substantially enhance the toughness and tensile strength of the concrete. The demand for UHPFRC continues to grow due to its use in large structures. One application of this material is its use in structures designed for the storage or production of thermal energy, such as steam storage tanks in solar thermal power plants or salt storage tanks. Compared to conventional concrete, UHPFRC is known to have higher viscosity and pumping losses. Therefore, admixtures, including retarders and additional plasticizers, must be incorporated.

The integration of steel fibers is widely recognized for potentially decreasing the flowability of ultra-high-performance concrete (UHPC), resulting in increased air content in its fresh state and, consequently, higher porosity in the hardened state. Research has indicated that UHPC mixtures incorporating fibers with a smaller aspect ratio are more workable, even at higher fiber dosages, compared to mixtures with fibers possessing a larger aspect ratio. However, it is noted that fibers with a smaller ratio tend to lower strength [2].

As a consequence, a high-performance superplasticizer is a crucial element in the preparation of UHPFRC, improving its rheology. Recently, the development of polycarboxylate superplasticizers has offered crucial technological support for the advancement and realization of such concretes. Nonetheless, solely utilizing these superplasticizers often fails to meet UHPFRC's combined fluidity loss standards [3].

sodium gluconate (SG) is an organic electrolyte known for its high water solubility. SG also acts as a high-performance plasticizer. While SG alone has a relatively low water reduction rate, it can make a significant difference in improving the water reduction rate or enhancing the concrete's flowability and reducing slump loss when paired with other superplasticizers. The addition of SG can delay cement hydration, reduce adsorption, and increase the concentration of other superplasticizers in solution, leading to increased concrete fluidity and reduced slump loss [3].

Several hypotheses describe the setting retarding mechanism of sodium gluconate. Firstly, it is proposed that SG impedes the hydration process of tricalcium silicate (C_3S) by adsorbing onto specific dissolution sites on the surface of the silicate phase. This leads to diminished hydration heat and rate, thereby extending the induction period and delaying the setting. Another perspective suggests that the adsorption or complexation of SG with Ca^{2+} hinders the formation of ettringite (AFt) [4]. Furthermore, it is suggested that SG delays AFt formation by impeding the dissolution of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$), which is crucial for AFt production [4]. Additionally, a theory revolves around the control of calcium hydroxide (CH) crystals, indicating that SG suppresses the typical precipitation of CH by restricting the growth of CH nuclei. However, the predominant role among these four mechanisms and their interrelation remains unclear at present.

Recent studies have identified the optimal dosage of superplasticizers, ranging from 0.03% to 0.07% concerning cement content. Notably, varying quantities of superplasticizers, coupled with different superplasticizer dosages, led to diverse degrees of enhancement in concrete strength. Each superplasticizer amount corresponded to an optimum dosage for achieving peak concrete strength. Furthermore, different cement varieties showcased distinct optimal dosages, highlighting concerns regarding superplasticizer-cement compatibility. However, the mechanism underlying superplasticizers' enhancement of cement compressive strength remains elusive, since the amount of superplasticizer, as well as its aspect ratio, has varied in previous investigations.

2 MATERIALS AND METHODS

In this study, three different materials were used as binders. Type I cement of 52.5 R/SR, according to EN 197-1 [5], was produced by Portland Valderrivas. The S-92-D silica fume was provided by the SIKA company, while the ground-granulated blast-furnace slag (GGBS) was obtained from the Arcelor-Mittal company. Regarding the aggregates used, two types of quartz sand were utilized: the finest sand (Quartz sand 1) with a maximum particle size of 0.315 mm, and the coarse sand (Quartz sand 2) with a particle size below 0.800 mm. Steel fibers measuring 13 mm in length and 0.2 mm in diameter, sourced from Beckaert, were also employed. The superplasticizer (20HE) was supplied by SIKA, while SG with a purity of 99.8% was obtained from Scharlab.

Table 1: Design for plain concrete

Constituent/mix	(kg/m³)
Cement	540
Quartz sand 1	470
Quartz sand 2	470
GGBS	310
Silica fume	210
Water	199
Steel fibers	196
Superplasticizer	43

Four different formulations of ultra-high-performance steel fiber-reinforced concrete were produced, each differing in the quantity of SG incorporated. The matrix dosage remained consistent across all mixtures (see Table 1), while varying proportions of SG additions were added (0.00%, 0.05%, 0.10%, and 0.15% of the cement content). These four formulations are denoted as Mix-0.00 (representing the reference concrete), Mix-0.05, Mix-0.10, and Mix-0.15, respectively.

2.1 Slump Flow Assessment

A modified mini-slump test was developed to evaluate the workability of fresh concrete, adhering to the guidelines of EN 12350-2 [6]. The setup for this test used a smaller version of the geometric Abrams cone with dimensions: 50 mm diameter at the top, 100 mm diameter at the base, and 150 mm height. The test was performed on a flat surface made of the same material. Following the standard procedure, measurements were taken with a gauge accurate to one millimeter, and the results were averaged from four readings.

The Abrams cone was quickly filled with fresh concrete and then slowly lifted to reduce inertial effects. Five seconds after removing the cone, the slump of the concrete was measured, which is the vertical distance between the original height of the concrete and the height of the slumped concrete. This method provides information on the concrete's consistency and ease of placement.

Additionally, two measurements were taken directly above the resulting specimen in orthogonal directions, producing two similar diameters. The average of these measurements gives the slump flow rate. The self-compacting ability of the concrete was evaluated using the mean value of the flow extension. If the diameter of the spread concrete exceeds 28 cm in a test with a 30 cm cone, the mix is classified as self-compacting [7].

2.2 Porosity Assessment

A porosimetry analysis was conducted using a Micromeritics Autopore IV mercury intrusion porosimeter (Norcross, U.S.A.). The study encompassed a pore size range from 0.007 to 150 μm. For sample preparation, they were formed into 5 mm pellets and then dried in an oven at 105°C. Important parameters included a surface tension of 480 mN/m, a contact angle of 140°, and a maximum pressure of 413 MPa. These factors were essential for achieving precise and dependable porosity measurements.

2.3 Mechanical Properties

The compressive strength evaluation was performed on three cubic specimens, each with a side length of 40 mm, for every concrete type, adhering to the EN 12390-3 standard [8]. These tests were conducted using a servo-hydraulic testing machine with a 3000 kN load capacity.

Three-point bending tests were conducted on each type of manufactured concrete using prismatic specimens measuring 40 mm by 40 mm by 160 mm. These tests followed the EN 14651 standard [9]. Prior to testing, a precise notch, equal to one-sixth of the specimen's depth [9], was made at the center of each sample. The tests were performed with hydraulic equipment capable of a maximum load of 50 kN, using crack mouth opening displacement (CMOD) control. In addition to recording the 5 mm CMOD, the deflection at the specimen's center was measured with a 10 mm vertical transducer.

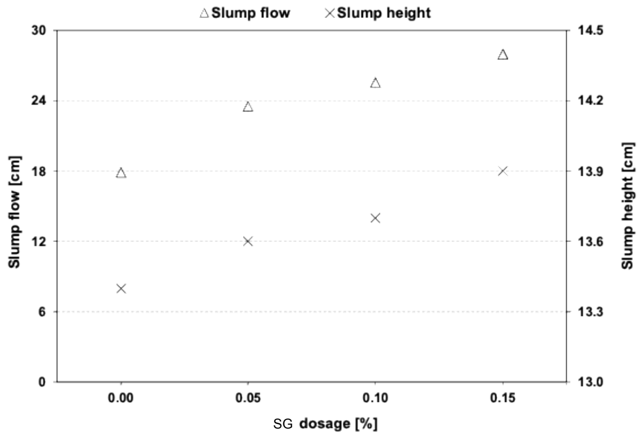

Figure 1: Slump flow and height results of mixes with different SG content.

3 RESULTS AND DISCUSSION

This section presents the findings from the conducted tests, including slump tests, porosimetry analyses, and compressive and flexural tensile strength evaluations. These results offer a detailed overview of the concrete's workability, pore structure, and mechanical performance, providing a basis for in-depth discussion and analysis.

3.1 Slump Test Analysis

The outcomes of the Abrams slump tests for each mixture are illustrated in Figure 1. These figures clearly show a consistent pattern: as the SG content increases, the spread values also rise. For example, at an SG/binder ratio of 0.15, there is a notable 55% increase compared to the UHPFRC without the high-performance plasticizer. Additionally, it is important to note that all mixtures demonstrate self-compacting properties. This means that the concrete can flow and fill formwork solely under the influence of gravity, even with dense reinforcement, without the need for vibration, while maintaining uniform consistency throughout the process [10]. Conversely, regarding the concrete slump, a consistent positive trend is observed, reflecting the slump flow relationship, which consistently indicates the fluidizing effect of SG on concrete. Moreover, none of the pastes showed significant deformation or segregation during the mini-slump test.

3.2 Pore Structure Analysis

Porosity is a critical factor in assessing the compressive strength of concrete. The presence of pores within the concrete matrix reduces the solid surface area available for stress transmission, thereby compromising the material's load-bearing capacity. It is essential to consider not only the total porosity but also the size, distribution, and interconnectivity of the pores, as these aspects significantly influence the mechanical behavior [11]. Specifically, macropores, which are pores larger than 0.1 μm, weaken the concrete matrix by creating stress concentration points and facilitating crack propagation.

Conversely, micropores, which are smaller than 0.1 μm, do not significantly impact compressive strength. In fact, a small amount of micropores can be beneficial by enhancing the workability of concrete and reducing shrinkage.

The porosimetry results (Figure 2) indicate that as the SG percentage increases, the number of pores larger than 50 μm decreases, while the number of pores smaller than 0.1 μm increases in all samples with added SG. Pores in the 0.5 to 5 μm range decrease due to the formation of ettringite from the addition of SG. This reduction in large pores is expected to increase compressive strength. However, it is important to consider other factors that may affect porosity, such as an excess of superplasticizers, which could increase pore size and total porosity in pastes, mortars, and concretes.

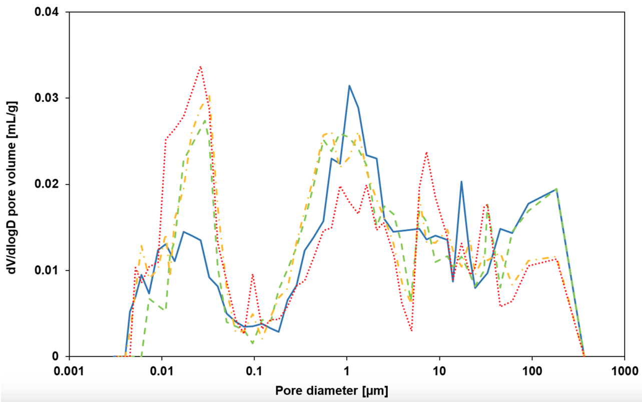

Figure 2: Pore size distribution of Mix-0.00 (solid line), Mix-0.05 (dashed line), Mix-0.10 (dash-dot line and Mix-0.15 (dotted line).

3.3 Compressive Strength

The mean compressive strength values derived from four repetitions are shown. As illustrated in Figure 3, the average compressive strength of the concrete increased with higher SG concentrations. For the Mix-0.05 concentration, there was a negligible 0.4% increase in compressive strength compared to plain concrete. However, for the Mix-0.10 concentration, the increase was 4.5%, and for Mix-0.15, it was 9.5% higher than plain concrete.

These results are closely related to porosity. For Mix-0.05, the increase in compressive strength was minimal because the porosity for pores larger than 1 μm was similar to that of Mix-0.00, as shown in Figure 2. In contrast, for Mix-0.10 and Mix-0.15, a more significant reduction in porosity was observed for pores larger than 1 μm, particularly in the range of pores larger than 90 μm. This demonstrates the consistency and correlation between compressive strength and the internal porosity of the matrix.

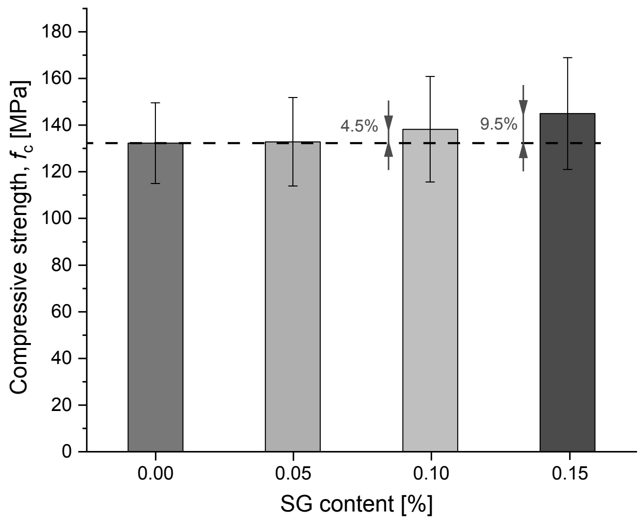

Figure 3: Compressive strength of mixes with different SG content.

3.4 Residual Flexural Tensile Strength

After understanding the residual behavior of this ultra-high-performance fiber-reinforced concrete, we will examine the impact of SG addition on residual strength.

At all SG concentrations, there is an observed increase in the initiation of flexural cracking (black squares in Figure 4): 10% for Mix-0.05, 31% for Mix-0.10, and 38% for Mix-0.15. This improvement is linked to the reduction of macropores, as indicated by the porosimetry results (Figure 2), due to the inclusion of SG.

For the Mix-0.05 concentration, f_L (black square in Figure 4) is enhanced by 10%, f_{R1} improves by 9%, while f_{R2} remains negligible, and f_{R3} and f_{R4} decrease by 7% and 9%, respectively. This slight improvement in fiber adhesion results in f_{R1} for Mix-0.05 being 9% higher than f_{R1} for Mix-0.00.

Increasing the SG concentration to 0.10% further improves adhesion, affecting more fibers and enhancing their effectiveness. f_{R1} increases by 30%, f_{R2} by 23%, and the residual strengths f_{R3} and f_{R4} each increase by 12% compared to Mix-0.00.

As anticipated, the same pattern is observed for the Mix-0.15 concentration, with f_{R1} increasing by 38%, f_{R2} by 33%, f_{R3} by 23%, and f_{R4} by 27%. In summary, it has been noted that adding SG has a dual effect on enhancing both the initial crack resistance and the residual strength of fiber-reinforced concrete. The first improvement is that the matrix becomes more robust as the SG concentration rises, due to the reduction of macropores within the matrix. Secondly, the inclusion of SG enhances the encapsulation of fibers by the cementitious material, thereby improving fiber adhesion, which directly impacts the residual strength. This results in better performance, especially for Mix-0.15.

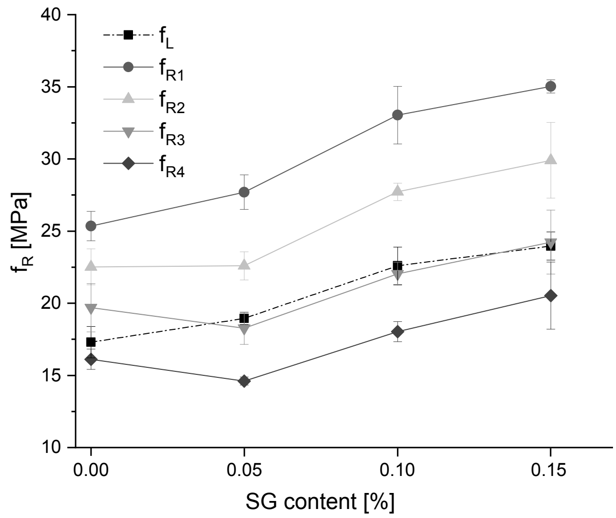

Figure 4: Residual flexural strength of mixes with different SG content.

4 CONCLUSIONS

This study investigates the impact of sodium gluconate on the UHPFRC matrix, keeping the steel fiber content constant across all samples while varying the dosage of the acid sodium salt to evaluate its effects. The specimens were subjected to compressive and flexural loading tests, leading to several conclusions.

The evaluation of the matrix in its fresh phase showed a significant increase in workability with higher SG content. Using SG dosages of 0.10% and 0.15% resulted in a nearly 43% and 56% increase in slump diameter compared to plain concrete. This suggests that the fluidization of the cementitious mix may enhance steel fiber bonding. Furthermore, it is inferred that in UHPFRC with approximately 10% steel fibers, the fluidization of the cementitious matrix contributes to a more uniform structure.

No significant chemical changes were observed in the matrix at the dosages investigated. Additionally, the addition of SG reduced pores larger than 10 μm while increasing those smaller than 0.1 μm. This confirms the beneficial impact of SG on ensuring fiber distribution, effectively halting the propagation of microcracks and delaying the development of macrocracks, thereby significantly enhancing the mechanical properties of UHPFRC, including flexural and compressive strength.

The compressive strength and the initiation of flexural cracking of the concrete matrix increased by 9.5% and 38%, respectively, for Mix-0.15, due to the reduction of macropores larger than 50 μm. Residual strengths have been improved by the enhancement of fiber-matrix adhesion due to better concrete workability in the fresh state, resulting in better fiber coverage by the matrix. For Mix-1.5, the greatest improvement was observed, with f_{R1} increasing by 38%, f_{R2} by 33%, f_{R3} by 23%, and f_{R4} by 27%, compared to concrete without SG.

REFERENCES

[1] H. Abdolpour, P. Niewiadomski, Ł. Sadowski, and A. Chowaniec, Self-compacting ultra-high performance mortars produced with waste catalysts from petrochemical industry: Rheological, mechanical and microstructural properties, *Journal of Cleaner Production*, vol. 369, p. 133225, (Oct. 2022), doi: 10.1016/j.jclepro.2022.133225.

[2] R. Yu, P. Spiesz, H.J.H. Brouwers, Mix design and properties assessment of Ultra-High Performance Fibre Reinforced Concrete (UHPFRC), *Cement and Concrete Research* 56 (2014) 29–39. https://doi.org/10.1016/j.cemconres.2013.11.002

[3] Y. Wu, Y. Yuan, M. Niu, Y. Kuang, Effect of Sodium Gluconate on

Properties and Microstructure of Ultra-High-Performance Concrete (UHPC), *Materials* 16 (2023) 3581. https://doi.org/10.3390/ma16093581

[4] B. Li, X. Lv, Y. Dong, S. Zhou, J. Zhang, Comparison of the retarding mechanisms of sodium gluconate and amino trimethylene phosphonic acid on cement hydration and the influence on cement performance, *Construction and Building Materials* 168 (2018) 958–965. doi: 10.1016/j.conbuildmat.2018.03.022.

[5] UNE-EN 197-1:2011, Cement - Part 1: Composition, specifications and conformity criteria for common cements. (n.d.).

[6] UNE-EN 12350-2:2020, Ensayos de hormigón fresco. Parte 2: Ensayo de asentamiento, AEN/CTN 83.

[7] UNE-EN 196-3:2017 Methods of testing cement - Part 3: Determination of setting times and soundness.

[8] UNE-EN 12390-3:2020. Testing hardened concrete - Part 3: Compressive strength of test specimens.

[9] UNE-EN 14651:2007+A1:2008. Test method for metallic fibre concrete - Measuring the flexural tensile strength (limit of proportionality (LOP), residual).

[10] G. Azeredo, M. Diniz, Self-compacting concrete obtained by the use of kaolin wastes, *Construction and Building Materials*, 38 (2013) 515–523. ISSN 0950-0618. https://doi.org/10.1016/j.conbuildmat.2012.08.027.

[11] J.D. Ríos, C. Leiva, M.P. Ariza, S. Seitl, H. Cifuentes, Analysis of the tensile fracture properties of ultra-high-strength fiber-reinforced concrete with different types of steel fibers by X-ray tomography, *Mater. Des.* 165 (2019) 107582. https://doi.org/10.1016/j.matdes.2019.107582