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Final report from 15 December 2024

CREATE

Carbon Reforming to Economic Additives for Transitioning into Emission-less era

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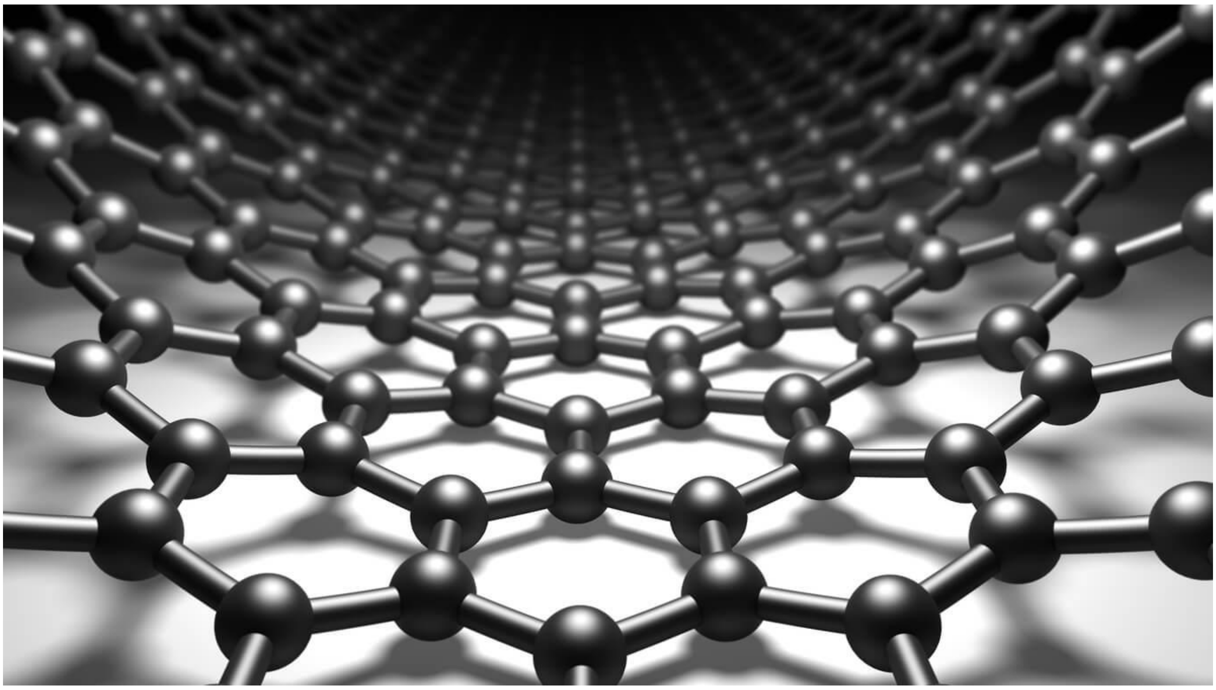

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The authors bear the entire responsibility for the content of this report and for the conclusions drawn therefrom.

Summary

The CREATE ACT3 project was based on an innovative patented technology of Carbonova which converts GHG (namely CO2 and CH4) into carbon nanofibers (CNF). As part of this consortium, Sika technology AG (STAG) had the task to evaluate the implementation of those CNF into various technologies and product lines covering its core activities in specialty chemicals towards systems and products for bonding, sealing, damping, reinforcing, and protecting in the building sector and motor vehicle industry.

STAG's primary focus in the CREATE project was on reintegrating CNFs, produced from the CO2 emissions during cement production, into cement as part of a circular economy concept. This led to the development of a robust strategy that utilizes the high shear forces in cement mills to efficiently disperse CNFs into the cement matrix. Various sources and types of CNFs were evaluated, some of which showed promising strength improvements. Key characteristics that enable effective dispersion and integration into cement matrices have been identified and understood. Additionally, attempts were made to use CNFs to enhance the electrical conductivity of cement matrices, using a custom-designed experimental setup. However, the results so far have been disappointing, as the high quantities of CNFs required to reach the percolation threshold, further exacerbated by poor dispersion, have hindered success.

Zusammenfassung

Das Projekt CREATE ACT3 basierte auf einer innovativen, patentierten Technologie von Carbonova, die Treibhausgase (insbesondere CO2 und CH4) in Kohlenstoff-Nanofasern (CNF) umwandelt. Als Teil dieses Konsortiums hatte die Sika Technology AG (STAG) die Aufgabe, den Einsatz dieser CNF in verschiedenen Technologien und Produktlinien zu evaluieren, die ihre Kernaktivitäten in der Spezialitätenchemie abdecken, hin zu Systemen und Produkten zum Kleben, Dichten, Dämpfen, Verstärken und Schützen im Bausektor und in der Automobilindustrie.

Der Hauptfokus von STAG im CREATE-Projekt lag auf der Reintegration von CNFs, die aus den CO2-Emissionen während der Zementproduktion erzeugt werden, in den Zement im Rahmen eines Kreislaufwirtschaftskonzepts. Dies führte zur Entwicklung einer robusten Strategie, die die hohen Scherkräfte in Zementmühlen nutzt, um CNFs effizient in die Zementmatrix zu dispergieren. Verschiedene Quellen und Typen von CNFs wurden evaluiert, von denen einige vielversprechende Verbesserungen der Festigkeit zeigten. Wichtige Merkmale, die eine effektive Dispersion und Integration in Zementmatrizen ermöglichen, wurden identifiziert und verstanden. Zusätzlich wurden Versuche unternommen, CNFs zur Verbesserung der elektrischen Leitfähigkeit von Zementmatrizen einzusetzen, wobei ein eigens entwickeltes experimentelles Setup verwendet wurde. Die bisherigen Ergebnisse waren jedoch enttäuschend, da die hohen Mengen an CNFs, die benötigt werden, um den Perkolationsschwellenwert zu erreichen, und dies noch verstärkt durch eine unzureichende Dispersion, den Erfolg behinderten.

Résumé

Le projet ACT3 CREATE était basé sur une technologie innovante brevetée de Carbonova qui convertit les gaz à effet de serre (notamment le CO2 et le CH4) en nanofibres de carbone (CNF). En tant que membre de ce consortium, Sika technology AG (STAG) avait pour mission d'évaluer la mise en œuvre de ces CNF dans diverses technologies et lignes de produits couvrant ses activités principales dans le domaine des produits chimiques spécialisés vers des systèmes et des produits de collage, d'étanchéité, d'amortissement, de renforcement et de protection dans les secteurs industriels de la construction et de l'automobile.

L’objectif premier de STAG dans le cadre du projet CREATE était de réintégrer des CNFs, produites à partir des émissions de CO2 générées lors de la production de ciment, dans le ciment fini en vue d’atteindre un concept d'économie circulaire. Cela a conduit au développement d'une stratégie robuste qui utilise les forces de cisaillement élevées dans les broyeurs de ciment pour disperser efficacement les CNFs dans les matrices cimentaires. Plusieurs sources et types de CNOs ont été évalués, certains montrant des améliorations prometteuses de la résistance. Les caractéristiques clés permettant une dispersion et une intégration efficaces dans les matrices de ciment ont été identifiées et comprises. De plus, des tentatives ont été réalisées pour utiliser les CNOs afin d'améliorer la conductivité électrique des matrices de ciment, à l'aide d'un dispositif expérimental conçu sur mesure. Les résultats préliminaires obtenus n'ont pas été concluants, en raison des grandes quantités de CNOs nécessaires pour atteindre le seuil de percolation, et ce particulièrement dans le cas de dispersion insuffisante.

Main findings («Take-Home Messages»)

- A highly efficient, low-energy strategy has been developed to disperse carbon nanomaterials in cement matrices, making use of the high shear forces present in cement mills.
- Key properties of carbon nanomaterials (CNOs) have been identified, showing their potential to significantly enhance the strength of cement-based materials. Once optimized, these improvements could help reducing the clinker factor in cement and concrete, thereby lowering the associated CO2 emissions from cement production.
- However, due to the very low concentrations of CNOs that can be incorporated into cement compared to the vast CO2 emissions from cement production, this recycling of carbon should not be considered a form of circular economy and has a negligible impact on the decarbonization of the construction sector.

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List of abbreviations

SFOE	Swiss Federal Office of Energy
NG	natural gas
GHG	greenhouse gas
CCUS	carbon capture, utilisation and storage
CAGR	compound annual growth rate
STAG	Sika Technology AG
CNO	carbon nano objects
CNT	carbon nano tubes
CNF	carbon nano fibers
GTC	global technological center
PSD	particle size distribution
FT	field test
W/C	water to cement ratio
bwob	by weight of binder

1 Introduction

1.1 Context and motivation

The cement industry is responsible for 8% of global CO2 emissions, and as pressure mounts to reduce these emissions, the development of carbon capture and storage/utilization (CCS/CCU) technologies is accelerating. Currently, most captured CO2 is stored underground at high costs, losing its value. To address this, companies and startups are working to convert CO2 into useful products, such as basic chemicals or solid carbon in the form of nano-objects like CNTs, CNFs, graphene, carbon black, or macro carbon materials.

Graphene is a single layer of carbon atoms arranged in a hexagonal lattice. It is a 2D material that can be rolled into carbon nanotubes (CNTs), tubular structures with diameters ranging from 1 to 100 nm. These tubes can be either single-walled (SWCNTs) or multi-walled (MWCNTs). Carbon nanofibers (CNFs) are similar cylindrical structures but with larger diameters (2–100 nm) and can be arranged randomly or aligned. All these carbon nanomaterials exhibit exceptional properties, including high mechanical strength, electrical conductivity, and thermal stability.

Over the past decade, carbon nano-objects have gained high attention for their unique combination of properties. CNFs, in particular, have mechanical strength comparable to steel, electrical conductivity like copper, and thermal conductivity similar to graphite, making them suitable for a variety of applications. These include sectors such as plastics, rubber, tires, batteries, inks, and coatings. However, their high production cost (due to high energy requirements of the various production processes, coupled with low product yields) has been a barrier to widespread use across industries.

Carbonova Corp, a spin-off from the University of Calgary, has developed a method for producing CNFs using a novel chemical process with custom catalysts and equipment. This technology, proven at a small scale (TRL 5), converts CO2 and natural gas (or biogas) with high C1 content into solid CNFs using a patented catalyst and moderate heat.

Carbonova’s process could potentially cut the cost of CNF production by more than an order of magnitude due to its novel synthesis method relying on critical differentiating features of production: the approach is based on a readily scalable energy efficient process (thermodynamically favored) using a proprietary catalyst made from cheap and non-scarce resources (abundant in the earth crust) and inexpensive gas feedstocks (CO2 and NH4),

The carbon nanofiber market is rapidly growing, with a compound annual growth rate (CAGR) of 14.4% (Research and Markets, 2021), but demand is currently only in the thousands of tons. However, thanks to its disruptive cost structure, Carbonova's approach targets a larger market, including alternative carbon products such as carbon black, carbon fibers, and graphene, which have a combined demand of 16 million tons (Das, Warren, & West, 2016; Graphene Council, 2020; Televisory, 2018).

The primary goal of the CREATE project was to explore the potential of establishing a circular economy model by integrating this technology into a cement plant. The idea is to produce carbon nanofibers from waste energy and captured CO2 from industrial flue gases during cement production. The resulting CNFs would then be incorporated into the finished cement, effectively sequestering carbon and adding valuable properties to the cement and concrete.

1.2 Project objectives

This project primarily aimed at evaluating the economic viability and greenhouse gas (GHG) reduction benefits of integrating Carbonova’s technology into a cement plant. It also focuses on developing an economically feasible process for producing carbon nanofiber (CNF)-based additives for use in composites within construction and transportation materials. The project took take place as a multinational consortium across several international laboratories in Canada, the USA, France, and Switzerland, spanning CO2 emitters, natural gas suppliers, chemical manufacturers, and technology developers, to bring this innovative carbon capture, utilization, and storage (CCUS) technology to market.

The key objectives of the CREATE project for the entire consortium were to:

- Demonstrate the scalability and consistent production of this new CCUS technology.
- Assess the economic and GHG benefits of integrating the CCUS technology into a cement plant.
- Validate the performance of Carbonova’s solid products in field tests for composite applications (cement and thermoplastics) compared to benchmark materials.
- Identify and promote business opportunities for large-scale carbon sequestration by converting CO2 into solid carbon reinforcement additives and develop a targeted market strategy for Europe and North America.

Sika Technology AG, the Swiss entity of the CREATE consortium funded by DETEC / SFOE was involved in a single work package focused on developing methods and technologies to enable the value-added implementation of the CNFs produced by the Carbonova process.

The primary objective was to explore their use in cement-based application, particularly how to incorporate CNFs back into cement during production, aligning with the circular economy vision of Carbonova, essentially, reintroducing CO2 to the source. To achieve this, a specific strategy has been developed to leverage the high shear forces involved during the cement grinding process, allowing dispersing CNFs without the need of additional high energy mixers. This strategy forms the core of the work and is the focus of this report.

Given that the amount of carbon reintroduced into cement using this strategy is relatively low compared to the emissions generated during cement production, a secondary concept was explored, which aimed to enhance the electrical conductivity of cement and concrete by incorporating higher amounts of CNFs, though it was given less priority.

Additionally, as Sika is a global leader in adhesive, polymer materials and coatings where CNFs could add value, one secondary task concerned exploring additional applications for the CNF technology in other technological sectors. While these applications are related to the construction industry, they extend beyond traditional concrete uses and thus fall outside the scope of the circular economy concept.

This report focuses solely on the activities led by STAG. For comprehensive details about the entire project, please refer to the reports submitted to the other funding agencies in Canada and France, where the other consortium partners report their respective activities.

2 Approach, method, results and discussion

2.1 Approach

At project start, Carbonova was unable to provide any carbon nanofiber (CNF) material for internal testing in significant quantities. This was primarily due to the company's reliance on a small-scale research reactor, and to the fact that upscaling the production was one of the main objectives of the CREATE project, which the aim to enable the supply of larger quantities of materials for testing by the other project's partners, in particular Sika France SA and Sika Technology AG.

To ensure progress and prevent delays in the project, these two partner entities have sourced carbon nanotubes (CNTs), CNFs, graphene, and other carbon nanomaterials from commercial suppliers.

Sika Technology AG, in particular, has acquired several types of graphene and CNTs, which have been evaluated for their potential use in cement production, specifically during the grinding of finished cement. The rationale for this approach is that carbon nanomaterials tend to agglomerate easily and are difficult to disperse uniformly in any matrix—whether inorganic (like cement) or organic (like adhesives). The high shear forces generated in industrial cement mills are expected to effectively disperse these materials, preventing the formation of large aggregates that would negate their beneficial properties. Initial trials have shown that cement mills are capable of dispersing individual graphene platelets onto cement particles. Additionally, graphene has been found to act as a grinding aid, improving the fineness of the cement and enhancing its strength when combined with other common cement additives.

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Sika's corporate R&D division, STAG, is coordinating these global efforts to ensure consistency and alignment across all testing and development activities.

2.2 Methods and experimental strategy

The experimental strategy adopted for the evaluation of carbon nano objects (CNO) in cement production has been systemized as followed:

- Sourcing of Materials: Commercially available products from established suppliers were sourced, alongside Carbonova CNFs, when accessible, as detailed in Table 1.

Table 1: List and characteristics of all CNO types sourced and investigated in laboratory grinding trials.

Supplier/source	Material type	State	Label
Graphene producer A	Graphene 50 microns	20% slurry	GRP A - 50
Graphene producer A	Graphene 70 microns	20% slurry	GRP A - 70
Chemical supplier	Graphene oxide	Powder	GRO B
Chemical supplier	Graphite	Powder	GRA C
Graphene producer A	Graphene 50 microns	10% slurry	GRP D - FT
Graphene producer B	Graphene 10 microns	Powder	GRP E - 10
Graphene producer B	Graphene 20 microns	Powder	GRP E - 20
Graphene producer B	Graphene 40 microns	Powder	GRP E - 40

Carbonova	CNF	Powder	CNF F
Graphene producer C	Graphene	Powder	GRP G
Graphene producer D	Graphene	Powder	GRP H
Graphene producer E	Graphene oxide	20% slurry	GRO I - 200
Graphene producer E	Graphene oxide	1.5% slurry	GRO I - 15
Graphene producer E	Graphene oxide	0.5% slurry	GRO I - 5
Graphene producer F	Graphene	Powder	GRP J
Graphene producer G	Graphene	Powder	GRP K
Graphene producer H	Graphene	Powder	GRP L
CNT Producer A	CNT	Powder	CNT M

- Pilot Grinding Trials: Grinding experiments were conducted in a pilot-scale ball mill with 10 kg of clinker and the other raw materials so as to produce a blended CEM II/B-LL cement with 30% limestone, using varying dosages of CNOs. These trials also included combinations with typical cement grinding chemicals to identify potential synergies. Laboratory batch grinding differs significantly from industrial cement milling, where a separator classifies finer particles that have reached the target size. In laboratory trials, fines remain in the drum, reducing friction and hindering further grinding of coarser particles. Based on proprietary experience from Sika, the batch grinding trials were conducted under carefully controlled conditions (temperature, time, and energy), ensuring that the cement fineness achieved closely mimicked the quality and performance of industrial-grade cement.
- Mechanical Performance Evaluation: Mechanical performance was assessed according to the EU cement standard EN 196-2, typically used for testing cement additives. The procedure involved mixing 450g of cement, 1350g of standard quartz sand, and 225g of water (water-to-cement ratio, W/C = 0.5) in a Hobart mixer for 3 minutes, following the prescribed methodology in the standard. Fresh properties, including density, spread flow, and air content, were measured immediately after mixing. The mortar was then cast into 4x4x16 cm^3 molds and cured for 24 hours. The hardened prisms were demolded and further cured in water at a constant temperature for 28 days. At 1, 2, and 28 days, the prisms were tested for density, flexural strength, and compressive strength.
- Analytical Characterization: The produced cement was characterized analytically by particle size distribution (PSD) using a Sympatec Helos laser granulometer in wet mode with isopropanol, to assess the effect of CNOs on cement fineness (physical impact). Additionally, isothermal calorimetry was performed with TAM AIR and ICAL isothermal calorimeters over a 24-hour period on fresh cement pastes (W/C = 0.4), mixed at 1200 rpm for 2 minutes, to evaluate the impact on hydration kinetics (chemical effect and reactivity)..

The evaluation of electrical conductivity was carried out based on an experimental setup and protocol developed as part of the Create project. The goal was to determine whether cement matrices loaded with CNF or graphene can conduct electricity for purposes such as energy storage, charge dissipation, or the creation of heating blocks for mortar/concrete through the Joule effect.

To achieve the Joule effect via conductivity, a minimum concentration of graphene or CNF must be added to reach the percolation threshold. This threshold ensures that the nanocarbon particles are sufficiently close to transfer electrical charges. Below this threshold, the particles are too distant, resulting in an insulating material.

As a result, various dosages of CNF- or graphene-loaded cement mixes were prepared and tested in 4cm x 4cm x 16cm mortar prisms. Metallic grids were embedded in the prisms, as shown in the Figure 1 below, to enable the measurement of electrical properties according to the circuit in Figure 2.

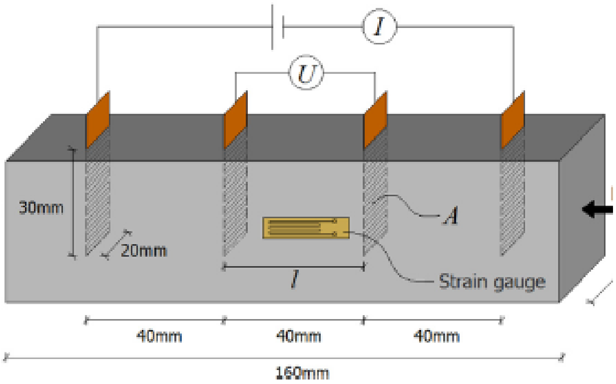

Figure 1: Scheme of a 4x4x16 cm3 prism loaded with grid electrode for courant input and conductivity measurement

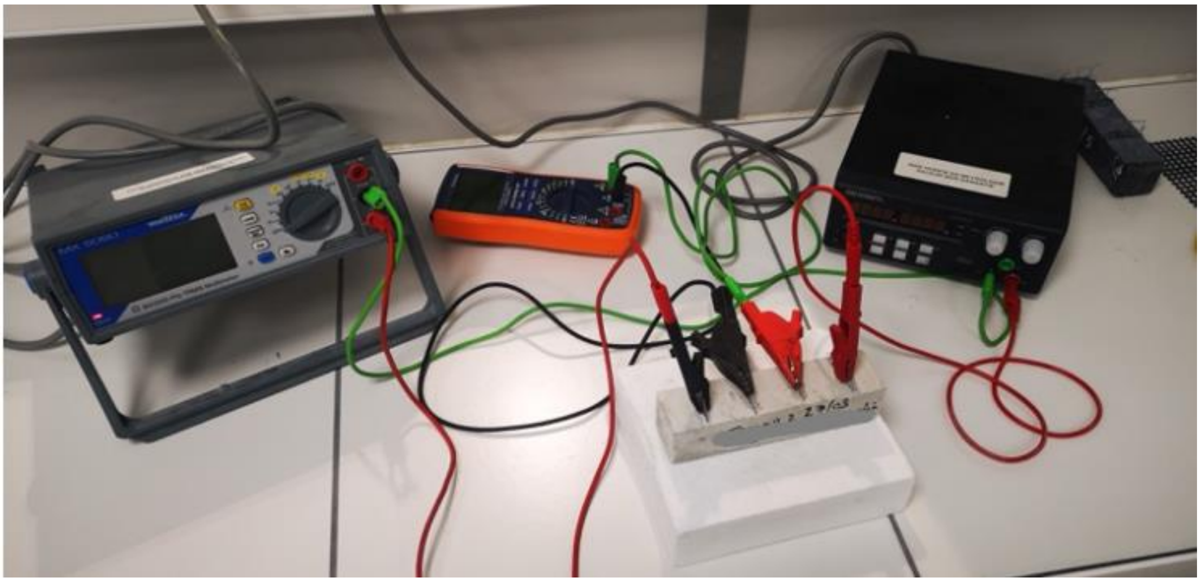

Figure 2: Electrical setup developed to measure electrical conductivity of CNF-loaded cement matrices.

3 Results and discussion

3.1 Cement strength enhancement thanks to CNOs

To evaluate the potential of CNOs to enhance the mechanical strength of cement and understand its underlying effects, one of the graphene sources that showed significant performance in preliminary screening tests was selected. This source was then tested under various conditions and dosages until optimal performance was achieved. The results presented below were obtained using this specific graphene source, under the conditions that provided the greatest strength improvement.

The performance of CNOs was consistently evaluated by comparing them to a reference blank cement of the same type produced under identical conditions without any chemicals nor CNOs. The performance of this blank cement at key curing ages (1, 2, and 28 days, as per EN 196-2) was used as a baseline (referred to as baseline 1 or blank hereafter). Given that CNOs are expected to be used in combination with other chemicals commonly found in the cement grinding industry, the sensitivity of the clinkers and cements used in this project to some of these chemicals was also assessed as a second baseline. The graph below shows the 28-day response of a clinker to a pure activating substance commonly often used in cement additives. When combined with such substances, any additional performance gains achieved by CNOs have been evaluated relative to this baseline. Similar baseline assessments were conducted with other chemicals, particularly those involving combinations of multiple chemicals, as cement additives are typically multicomponent formulations (referred to as baseline 2 or Chemical xxx hereafter). For confidentiality and proprietary reasons, these chemicals will be labeled as Chemical 1, 2, 3, etc., with no further details provided in this report outside section **Fehler! Verweisquelle konnte nicht gefunden werden.**.

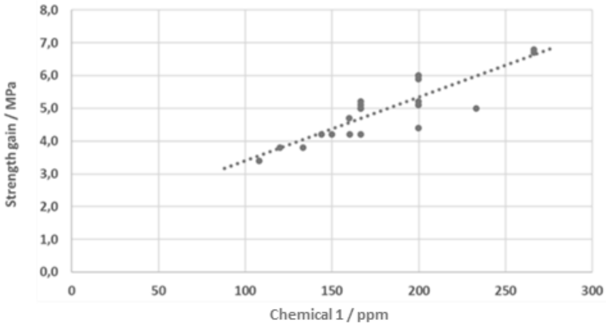

Figure 3: 28-days dosage response of an investigated CEM II/B-LL to one common pure chemical (Chemical 1) used in cement grinding.

Trials were systematically conducted as described in §2.2, that is by grinding a CEM II/B-LL 42.5 cement blend consisting of 70% clinker, 26% limestone, and 4% gypsum. For each trial, the mill was loaded with approximately 10 kg of materials and various additives at specified dosages. The mill ran for 1 hour, after which the finished cement was unloaded, and mechanical performance tested in standard mortar at 1, 2, and 28 days, following the EN-196-2 norm. The results, shown in Figure 4, indicate that graphene, when used alone with no other chemicals, provides an extra performance boost of 3-4 MPa at all tested ages. Moreover, this effect adds up on top of the strength increase observed with conventional cement additive chemicals. At 28 days, the strength of the blended cement increases by nearly 10 MPa, from 38 MPa to 47 MPa. This performance gain could either qualify the cement for a higher performance class or allow the cement producer to reduce clinker content further by increasing limestone replacement, maintaining the same performance while achieving nearly a 10% reduction in CO2 footprint.

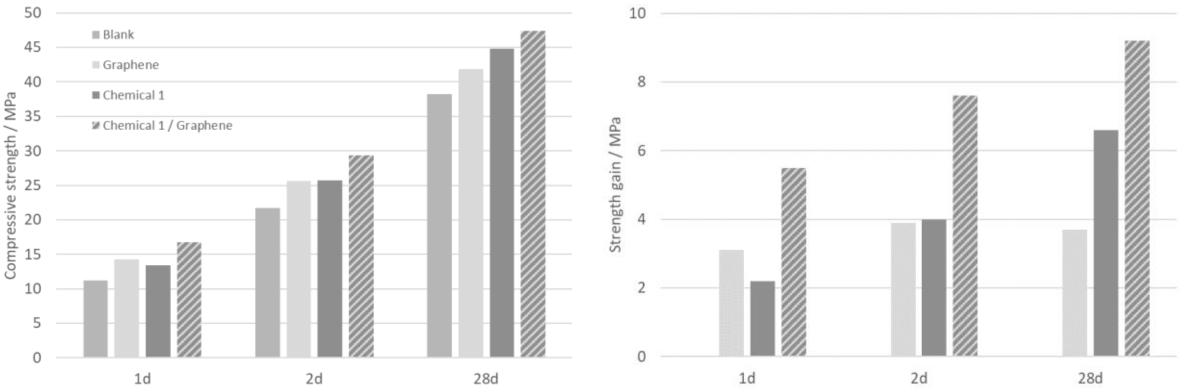

Figure 4: Absolute strength (left) and strength gain compared to blank (right) of CEM II/B-LL grinded with graphene, Chemical 1 and combination thereof.

The fineness analysis of the produced cement suggests that graphene acts as a grinding aid, preventing the re-agglomeration of fine cement particles during grinding, which in turn enhances its reactivity. However, isothermal calorimetry measurements of cement pastes indicate an acceleration of nearly 1 hour early on, which cannot be solely attributed to the improved fineness. The reasons for this accelerated behavior are not yet fully understood but certainly partially explain the strength gain observed at 1 day. However, this does not account for the strength improvements seen at later ages. Therefore, the beneficial impact of graphene on cement performance is likely a combination of enhanced fineness, increased reactivity, and potential microstructural benefits that have yet to be investigated.

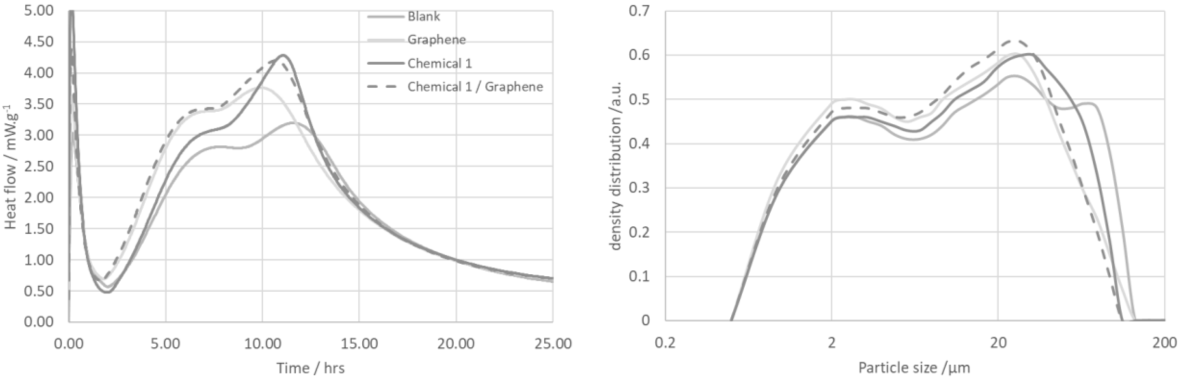

Figure 5: Isothermal calorimetry (left) and particle size distribution (right) of CEM II/B-LL grinded with graphene, Chemical 1 and combination. Graphene enables a strong refinement of the PSD, in particular coarse particles in the range of 100 microns are de-agglomerated which could explain part of the enhanced hydration kinetics at early age.

Subsequent screening series were conducted to evaluate the consistency of graphene-mediated strength enhancement across different clinker sources and at various graphene dosages. The same grinding procedure as previously described was applied. The results revealed a strong dependence of performance on the graphene dosage. Specifically, at 20% of the optimal dosage used earlier, the effect was completely lost, and the performance was almost identical to the control. The highest dosage tested (100%) still demonstrated a positive impact, similar to the results presented in Figure 4, where this dosage was used, showing nearly the same absolute strength increase of approximately +3-4 MPa at all ages.

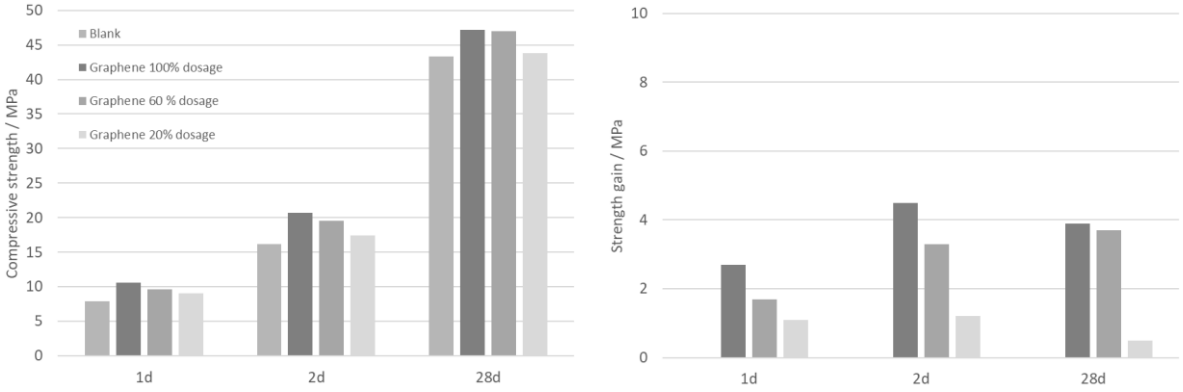

Figure 6: Absolute strength (left) and strength gain compared to blank (right) of CEM II/B-LL grinded with graphene @ various dosages and without any chemicals.

However, a comparison between Figure 4 & Figure 6 reveals a significant decrease in the absolute strengths measured in the latter, which can be attributed to the inherently lower reactivity of the clinker used in this series. This suggests that, regardless of the clinker reactivity, graphene consistently contributes to strength enhancement. This effect appears to be partly due to its role in improving fineness (PSDs in Figure 5 & Figure 7) and partly due to an additional, possibly non-chemical influence that may be independent of the clinker characteristics.

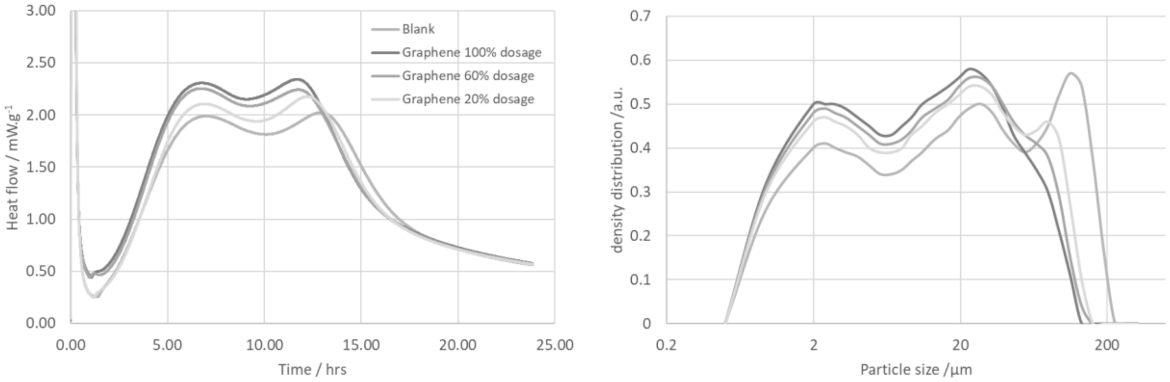

Figure 7: Isothermal calorimetry (left) and particle size distribution (right) of CEM II/B-LL grinded with graphene @ various dosages.

However, a similar approach using graphene at various dosages in combination with Chemical 1 (Figure 8) shows that graphene only provides a modest performance boost (1-2 MPa) compared to Chemical 1 alone, with no additional gain observed at 28 days. This can be attributed to the fact that this particular clinker is highly sensitive to the chemical activation provided by Chemical 1, beyond which the contribution of graphene becomes negligible. In other words, graphene can be considered an additive to conventional chemical activators when these activators are insufficient to fully activate a given clinker, but it may offer no significant benefit when the full reactivity of the clinker is already triggered by the chemicals.

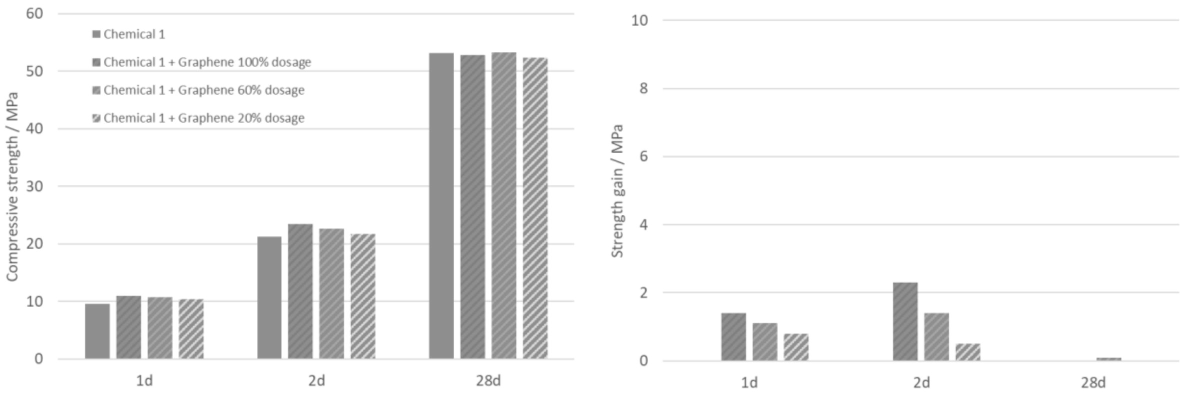

Figure 8: Absolute strength (left) and strength gain (right) compared to blank in combination with Chemical 1 of CEM II/B-LL grinded with graphene @ various dosages.

3.2 Impact of CNO type and source on cement performance

Based on the promising results obtained above and given the robustness of the approach & experimental procedure, an extensive matrix testing has been conducted to evaluate the impact of the CNOs properties on their performance, considering their nature, fineness, degree of agglomeration, physical state and concentration, etc.

A selection of the most significant and representative results accumulated over the project is summarized inTable 2. The main findings and learnings extracted from those are summarized thereafter.

Table 2: Selected performance gains obtained with various sources, types and characteristics of CNOs.

Performance gains compare to the blank cement (baseline 1) when CNOs are used alone (without chemicals) and to blank cement + Chemical (baseline 2) when used with chemicals. Dosage ‘1’ refer to 100% of the optimum dosage used in § 3.1. Chemical dosage kept constant all the way long at a dosage ensuring given pre-determined grinding power. Intensity of colours reflect extent of positive (green) and negative (red) impact on strength.

			Strength gains			Fresh properties	
CNO	Chemical	CNO dosage	1 day MPa	2 days MPa	28 days MPa	Flow mm	Density Kg.l^{-1}
GRP A - 50		1	3.1	3.9	3.7	108	2.185
GRP A - 50	1	1	3.3	3.6	2.6	109	2.193
GRA C		1	0.4	1	1.9	106	2.258
GRA C	1	1	0.1	0.3	-0.4	105	2.197
GRP A - 70		1	1.8	3.3	3.9	102	2.239
GRO A - 70	1	1	1.6	1.6	0.8	103	2.196
GRO B		1	1.1	0.7	2.6		
GRO B	1	1	2.2	5.2	-2.2		
GRP A - 50		0.5	1.6	1.3	1.8		
GRP A - 50	2	1	0.3	1.4	4.4	117	2.234
GRP H	2	1	-1.2	-1.6	1.9	117	2.230
GRP G	2	1	-1.0	-1.1	2.1	120	2.224
GRP A - 50	2	1	1.7	2.1	3.5	122	2.226
CNF F	2	1	1.2	0.3	0.2	121	2.216
CNF F	2	2	-0.2	-0.4	0.2	116	2.200
GRP J	2	0.1	1.4	1.4	1.0	118	2.200
GRP J	2	0.2	-1.0	2.2	0.9	118	2.221
GRP J	2	0.4	-1.0	0.0	1.8	115	2.215
GRO I - 200	2	1	1.6	2.8	0.8	114	2.198
GRO I - 200	2	0.075	0.9	1.6	1.6	115	2.210
GRO I - 15	2	0.075	2.0	2.7	2.3	116	2.200
GRO I - 5	2	0.025	0.9	1.6	-0.1	117	2.202
GRP E - 10	1	1	1.1	1.3	1.3	105	2.204
GRP E - 20	1	1	1.0	1.7	1.7	107	2.201

GRP E - 40	1	1	-1.6	-1.6	1.3	109	2.196
GRP D - FT	1	1	-2.5	-1.4	0.4	118	2.218
CNT M		0.004	1.2	2.3	4.0		
CNT M	4	0.004	-0.1	3.0	3.5		
GRP K	2	1	1.4	1.9	1.4	122	2.225
GRP L	2	1	-0.3	0.6	0.7	122	2.233

Physical nature of the CNO:

Five different types of CNOs (including graphite which is by nature not a nanomaterial) have been investigated, some being single sourced only.

Based on the accumulated results, graphene, graphene oxide and CNTs have all exhibited varying degrees of enhanced strength performance, suggesting that the physical characteristics of the CNOs likely play a minor role in the observed improvements.

Only as expected, trials with graphite yielded minimal or negligible strength increase either when used pure or in combination with chemicals, confirming the fact that shear forces involved in a ball mill are not high enough to slice graphite into graphene sheets.

On the other hand, better performance was expected from the Carbonova CNFs (the original focus of the CREATE project). As shown in further details in (§ 3.4), these CNFs exhibited a high segregation behavior due to their strong hydrophobicity. This led to two main issues: 1/ their tendency to agglomerate and 2/ their inability to be integrated in the cementitious matrix where they did not contribute to strength. This issue has been communicated to Carbonova but to date they have not planned any surface treatment to increase their miscibility with water and would only eventually consider mixing them with surfactants, although this remains an on-going task. As such, it was not possible to successfully implement those CNFs in cement-based matrices within the scope of this project.

Native dispersion state:

The CNO samples used in this study were sourced in powders with varying particle size distributions (PSDs), representing different agglomerated states, as well as in slurries at several concentrations.

Graphite and coarse powdered graphene sources consistently showed limited, if any, strength improvements. In general, when powders were available in multiple sizes, the finest PSDs always demonstrated better performance than the coarser ones.

Thicker slurries (i.e., those with higher solid content) consistently performed worse than the same materials in a more diluted, native state.

These findings suggest that subjecting CNOs to the high shear forces of a ball mill to enhance dispersion is only effective when the particles are sufficiently de-agglomerated in their native form or as provided.

Across all tests, slurries yielded better results than powdered samples. This indicates that in their dry state, the primary particles, due to their high specific surface area, tend to agglomerate strongly and irreversibly under the processing conditions used here. In contrast, maintaining CNOs in more or less stable suspensions, with or without surfactants, appears to prevent, or at least significantly slow, their agglomeration.

In all cases, none of the materials tested showed any strength improvement when simply added to the mixing water. It was only when exposed to high shear forces that some of the materials demonstrated performance improvements.

In conclusion, achieving both proper dispersion and a fine suspension of CNOs, combined with ball mill processing, is essential for realizing CNO-mediated strength improvements in cement-based materials.

3.3 Upscaling and real scale cement production field testing

Building on the promising results obtained from lab-scale grinding of cement with graphene slurries, a decision was made to assess whether similar performance could be achieved at an industrial scale using a standard ball mill with a separator. Sika convinced one of its customers to pause regular operations for a trial on a small industrial mill with a capacity of 20 tons per hour. For this trial, Sika sourced 300 kg of the original 20% graphene slurry used in § 3.1, which was then diluted to 10% to be pumped using the standard pumps typically found in cement plants. The 20% slurry was too viscous, requiring more powerful pumps, which could not be installed on short notice. However, the 10% slurry exhibited instability, with separation and sedimentation of the graphene particles occurring within a few hours. This necessitated the implementation of a complex circuit for continuous pumping and recirculation within the IBC. The total cost of the materials, including raw materials, transport, and dilution, amounted to nearly CHF 15,000.

One day before the test, a lengthy mill operation was run using the same mill parameters to be used the day after during the trial. The mill operated at a consistent productivity of 18.5-19 t/h throughout the entire run. A reference cement sample was taken during steady-state mill operation. On the trial day, the mill was started at 02:00 am and operated until steady-state conditions were reached, maintaining the same productivity (18.5-19 t/h) and achieving a Blaine fineness of 4300. The admixture, Chemical 3, was dosed at dosage dos.a throughout the trial.

The industrial setup, including the dosing and recirculation lines for the graphene slurry, was established early in the morning (Figure 9). The slurry in the IBC showed slight separation in the upper part, with the measured density 5 cm from the upper liquid layer at 1.000 g/ml, compared to the theoretical value of 1.040 g/ml. To address this, the slurry was remixed in the IBC with an electric stirrer for 10 seconds until the correct density was achieved.

Figure 9: IBC (left) and pumping/recirculating system (right) of the graphene slurry during the trial.

The trial began at 08:15 when the slurry dosage was set to 0.8 l/min, corresponding to a dosage in solid graphene of “0.5”. The mill operating parameters (mill feed and elevator power absorption) remained unchanged, and productivity stayed at 18.5 t/h for the next three hours. The Blaine value slightly increased from the baseline to 4400, based on measurements taken at 10:30.

The dosage was manually checked every hour and remained consistent with the initial setup. The density of the dosed slurry was within specifications, ranging between 1.037 and 1.039 g/ml. At 11:00, a separation was observed again at the top of the IBC (density 1.025 g/ml, measured 5 cm from the upper liquid layer), which was remixed with the electric stirrer for 5 minutes until the slurry reached homogeneity.

At 11:45, after 3 hours of steady operation, cement samples were collected for quality control and mechanical testing, and the dosage was increased to 1.7 l/min, corresponding to a dosage of “1”. To maintain the correct dosing, recirculation had to be reduced, but mill operating parameters remained stable. At 12:30, the dosage was checked again and found to be 0.9 l/min. It was noted that at higher dosages, the pumping system's efficiency significantly decreased. To address this, the recirculating loop line was connected to the dosing point to increase the dosage to 0.45% on cement, but it was no longer possible to reach the planned dosage “1”. As a result, the dosage was manually checked every 30 minutes and remained steady at dosage “0.9” for the remainder of the trial.

After 2 hours of attempting to stabilize the mill and maintain consistent slurry dosing, an increase in productivity of 0.8 t/h (a 4% increase) was observed, and the Blaine value rose to 4600. Meanwhile, the separator speed was reduced from 1360 rpm to 1300 rpm, indicating a slight improvement in fineness.

By 16:00, the Blaine value and sieve residue of the produced cement were in line with the target specifications, and new samples were taken at 16:30 for the higher slurry dosage. The trial was concluded at 17:00 when the IBC was nearly empty, with only a small amount of sticky residual slurry remaining on the IBC walls.

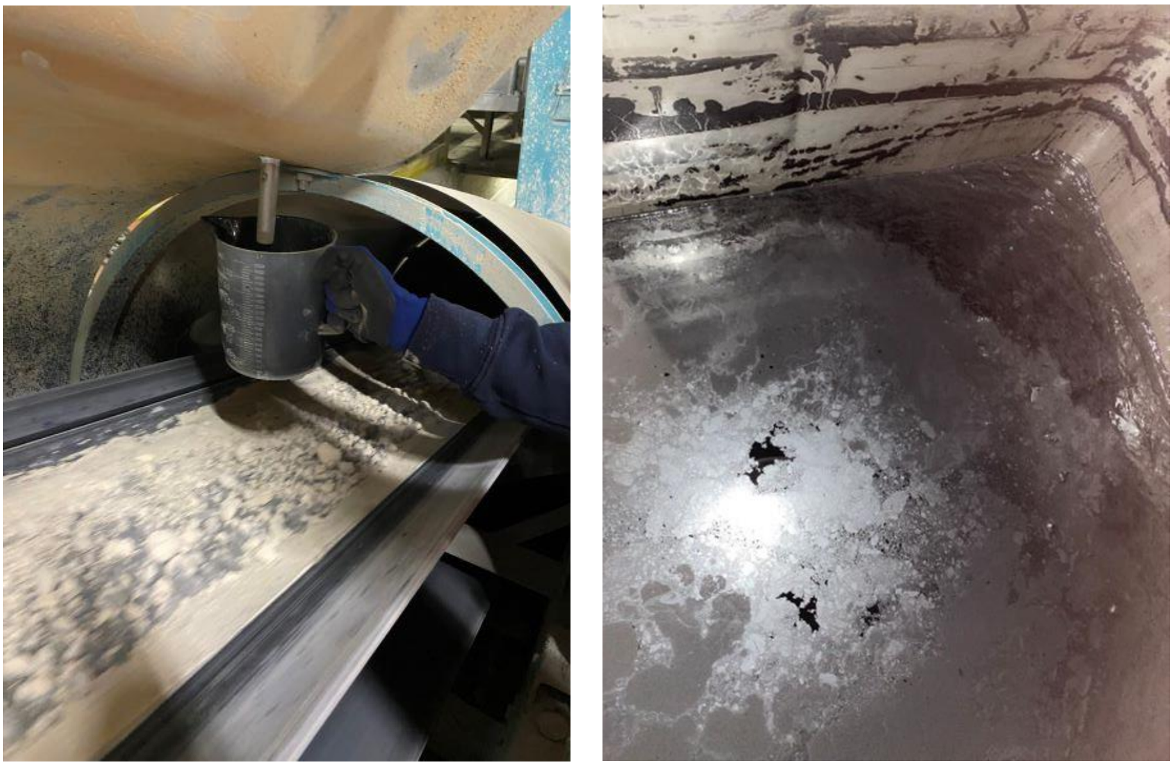

Figure 10: Automatic dosage checked every hour (left) and empty IBC at the end of the trial (right).

All cements, with and without graphene, produced during the trial were stored in different silos for a few weeks after which both Sika and the cement producer sampled a few tens of kilograms of each for independent testing. The remaining cement parts were diluted in bigger silos with regular cement by the cement producer and used for regular applications,

The PSD showed a slight refinement of the fineness as already observed during preliminary lab trials, highlighting the enhanced grindability of graphene loaded cement.

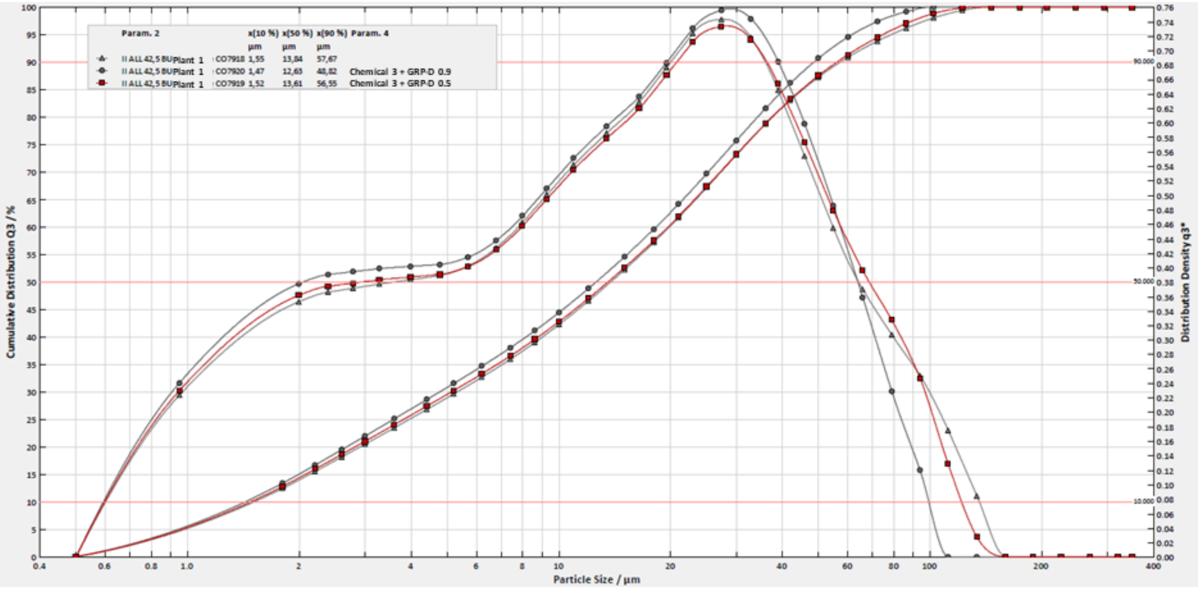

Figure 11: PSD analysis of the three cements sampled with 0, dosage “0.5” and dosage “1” of graphene slurry. As observed during lab trials, graphene helps refining the fineness of the cement with a significant decrease of agglomerates in the 100-200 micron range.

However, the compressive strength results obtained from standard mortar testing according to EN 196-2 (Table 3), showed no noticeable impact from the graphene, regardless of the dosage, when compared to the benchmark cement additives currently used in the field (Chemical 3 in this case). This outcome was far below expectations, especially given the strong synergistic effects observed between the chemicals and graphene in preliminary laboratory results. A very limited 5% increase in mill production was measured at the full dosage of “0.9” dry, which still fell short of expectations based on the significant impact graphene had on the fineness of the cement milled at the lab scale.

Table 3: Mortar strength results obtained from cements produced during real scale field test.

		Compressive strength			Fresh properties	
Additive	Dosage	1 day	2 days	28 days	Fresh density	flow
	%	MPa	MPa	MPa	Kg.l^{-1}	mm
Chemical 3	dos.a	15.0	31.2	53.0	2.222	123
Chemical 3 + GRP D - FT	dos.a / 0.5	15.1	31.7	53.9	2.233	122
Chemical 3 + GRP D - FT	dos.a / 0.9	14.4	30.8	54.6	2.232	122

Subsequent laboratory evaluation of the same graphene dispersion as used in the field trial showed significantly lower efficiency in enhancing cement strength compared to earlier trials with the non-diluted graphene source. The most probable explanation is that the quality of the 300 kg batch used for the trial may not have been as high as the smaller quantities used in previous tests, as the producer encountered difficulties in supplying the larger volume. Another potential factor is the dilution effect; the large volumes of water introduced during the milling process could have caused pre-hydration of the cement, potentially reducing its reactivity and hindering strength development.

To date, no other industrial trials have been performed yet. Since higher performing sources of graphene have been identified, this should happen in the coming months as soon as all logistic, supply chain and cost structure aspects have been fixed.

3.4 Potential of CNOs to increase the electrical conductivity of cement-based material

A few tens of grams of Carbonova CNFs were available for testing in 2023. Since the CNFs-loaded cement produced were to be used both for strength enhancement and electrical conductivity, dosages were increased compared to the average levels applied in § 3.1 & 3.2 Starting at the same optimal nominal dosage of ‘1’ (100% of the dosage of GRP A-50 used in § 3.1), the concentration of CNF in the mill was doubled to test sensitivity on strength improvement and multiplied by 4 as a proxy towards electrical percolation threshold (anticipated @ x 2-3 based on internal preliminary testing).

Similarly to all tests done with the other CNOs, the same baselines were applied. The three dosages of CNF were systematically combined with the blend of chemicals and tested in strength in 2 mix designs, a regular one according to EN-196-2 and one at lower W/C to try promoting CNF percolation.

In all cases, whatever the dosage, Carbonova CNFs were systematically showing strong segregation during mortar mixing. This is attributed to their strong hydrophobic nature while dispersion was visualy acceptable after grinding. This is shown in the pictures below taken respectively in the mixing pot right after mixing where some black CNF aggregates start being visible at the surface of the mortar and becomes more pronounced over time as seen at the surface of the cake formed during flow measurements and finally in the 4x4x16 cm3 prism molds during casting of the specimens for strength testing.

Figure 12: bleeding of Carbonova CNF in freshly mixed mortar (left) and slump flow cake (right).

Figure 13: Bleeding of Carbonova CNF in prism molds right after casting.

Despite this problem (which was not observed with any other CNO source), the strength levels achieved @ dosage ‘2’ in both mix designs (tables below), although lower than those reached with the benchmark in § 3.1 at half dosage, showed some slight strength increase compared to the chemical baseline. This suggests that CNF may have a similar beneficial impact on strength beyond any grinding aid effect as graphene. Performance was even slightly better at doubled concentration but decreased thereafter with further increased dosages.

Table 4: Performance gains obtained Carbonova CNF loaded cements @ various dosages in two mix designs.

			Strength gains			Fresh properties	
CNO	Chemical	CNO dosage	1 day MPa	2 days MPa	28 days MPa	Flow mm	Density Kg.l^{-1}
Mix 1 - Baseline 2	2		*16.4*	*31.2*	*52.8*	*122*	*2.225*
GRP A-50	2	1	2.4	0.9	3	106	2.258
CNF F	2	1	0.4	-1	-0.1	105	2.197
CNF F	2	2	0.4	-0.7	1.5	102	2.239
CNF F	2	4	-0.5	-0.3	-1.6	103	2.196
Mix 2 - Baseline 2	*2*		*32.1*	*54.9*	*75.7*	*156*	*2.213*
GRP A-50	2	1	3	1	1.8	150	2.311
CNF F	2	1	0.8	-2.3	0.2	150	2.312
CNF F	2	2	1.8	-2.2	1.6	147	2.307
CNF F	2	4	1	-1.1	1.4	149	2.320

Potential increased electrical conductivity thanks to CNF percolation was investigated with the three CNFs-loaded cement produced (@ ‘1’, ‘2’ & ‘4’ dosages) according to the experimental setup developed by Sika France in the frame of the CREATE project and described in § 2.2. Selected representative results obtained under various maturity and conditioning levels are produced in Table 5. Those include two curing times of 5 and 14 days during which the maturity of the sample increases (i.e. there is less internal liquid water available inside the prims and a more tortuous porous network to transfer electrical charges) and two drying stages (one mild and one harsh) to remove free water and humidity and measure the sole conductivity of CNOs if they percolate.

In the wet state (no drying at all and short curing time) all results obtained with CNFs at the various dosages mentioned above and with GRP A-50 showed an electrical conductivity of around 1 S.m^{-1}, exactly in the range of the control specimen without any CNO in the same conditions. For comparison, this is 60 million times that of copper, while drinking and sea water would be at 0.05 and 5 respectively. This means that the conductivity measured is solely due to the ions present in the liquid water migrating through the internal pore network of the mortar.

After a soft drying of 7 days at 55°C (aiming at mimicking higher degrees of maturity with reduce internal water but still humidity), the conductivity decreased by 80 around % for all specimens, with no difference between the blank and the CNO loaded cements, confirming that conductivity is not driven by the CNOs but by the ions available in the internal porosity which charge transfer is strongly reduced in the absence of water.

This is further strengthened in the case of the harsh drying conditions, only evaluated with GRP A-50 where humidity has been also removed at high temperature: there the conductivity is null due to an infinite a resistivity) no current could be measured at all but was approximated to 1E-07 for the resistance calculation) : the mortar behaves like a pure insulator and percolation of the CNOs has not been achieved.

This result is fully understandable in the case of GRP A-50 which dosage was way below the theoretical percolation threshold while highlighting the poor dispersion of CNF F even at dosages above that required to reach percolation.

For comparison, Figure 14show some conductive mini slabs produced by Sika France loaded with 20 times the dosage required for percolation and conductivity which black color evidences the over dosing of CNO needed to overcome poor dispersion and ensure conductivity.

Table 5: Electrical conductivity measurements of Carbonova CNF loaded cement under various conditioning.

Conditioning: curing age (in days) / mild drying @ 55°C (in days) / harsch drying @ 105°C (in days)

CNO	dosage	conditioning days	tension U / V	intensity I / A	resistance R / Ω	resistivity ρ / Ω.m	conductivity σ / S.m^{-1}
blank		5 / 0	2.37	1.26	1.88	0.94	1.06
GRP A-50	1	5 / 0	2.76	1.34	2.06	1.03	0.97
CNF F	1	5 / 0	2.80	1.4	2.00	1.00	1.00
CNF F	2	5 / 0	2.80	1.34	2.09	1.04	0.96
CNF F	4	5 / 0	3.00	1.38	2.17	1.09	0.92
blank		14 / 7	2.87	0.33	8.70	4.35	0.23
GRP A-50	1	14 / 7	2.92	0.32	9.13	4.56	0.22
CNF F	1	14 / 7	2.53	0.28	9.04	4.52	0.22
CNF F	2	14 / 7	2.79	0.28	9.96	4.98	0.20
CNF F	4	14 / 7	2.77	0.26	10.65	5.33	0.19
blank		14 / 7 / 7	0.019	0.00	1.89E06	9.45E05	1.06E-06
GRP A-50	1	14 / 7 / 7	0.029	0.00	2.86E06	1.43E06	6.99E-07

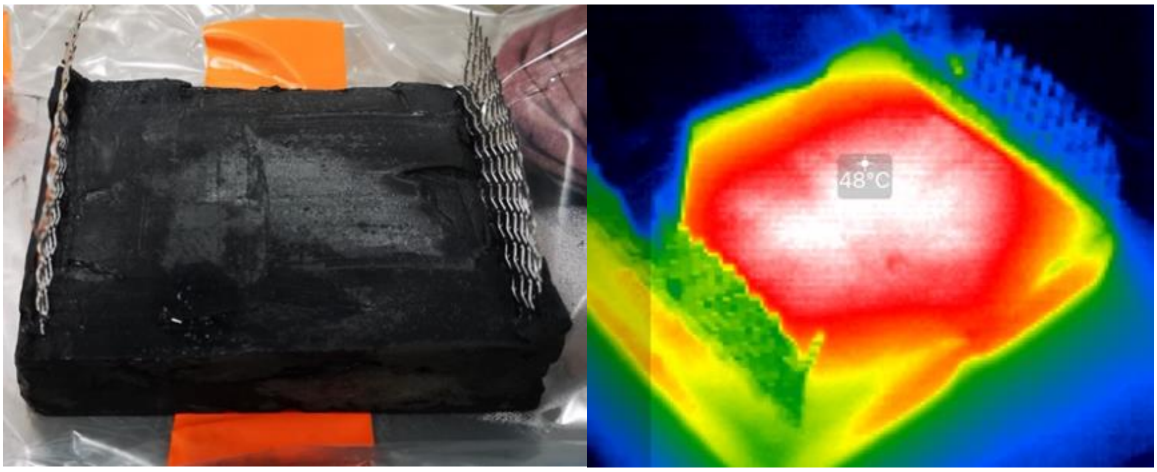

Figure 14: Minislab (15-20cm2) loaded with 2% CNF for heating trial (left) & thermal imaging after 90 minute under 40V tension (48°C increase).

4 Conclusions and outlook

The primary objective and focus of this part of the CREATE project focused on the use of the CNF in cement-based material. It resulted in the development of a robust strategy that leverages the high shear forces in cement mills to efficiently disperse CNOs into cement. Several sources and types of CNOs were evaluated, some of which showed promising improvement in strength. Key characteristics of CNOs that enable effective dispersion and integration into cement matrices have been identified and understood. Following a failed industrial-scale test, STAG has identified alternative CNO sources of higher quality and greater robustness. Plans are in place to conduct another field test with a cement partner in the coming months. This approach is promising and holds strategic importance for Sika which will continue working on this topic beyond the CREATE project conclusion.

However, the amounts of carbon in the form of CNO needed to significantly enhance the mechanical performance of cement are extremely low, several orders of magnitude smaller than the CO2 emissions produced during cement production. This presents a significant challenge to the circular economy concept at the heart of the CREATE project.

Moreover, Carbonova has been unable to provide CNFs in sufficient quantities or of the required quality to enable proper investigation or compatibility with water-based systems like cement and concrete. As a result, 95% of the work reported here was conducted using alternative CNF sources, primarily graphene, from other suppliers. This limitation has significantly hindered the exploration of CNF potential for both strength enhancement and increased electrical conductivity of cement matrices, with initial disappointing results.

Also, due to the limited availability of CNFs, efforts to explore their use in non-water-based systems have yet to begin and remain pending. However, the interaction with Carbonova will continue after the project’s completion, and there are expectations of gaining access to additional material to further investigate the three scenarios outlined above in the future.

5 National and international cooperation

No cooperation with any third party in Switzerland was initiated as side activity of the CREATE project or the approach described above.

Sika Technology AG has interacted with many NCO producers/dealers across the world, always in the frame of bilateral Non-Disclosure-Agreements (NDA) protecting the exchange of materials and results. Those interaction were disconnected from the CREATE core and ran independently from the ACT 3 frame.

6 Publications and other communications

No public communication (articles, conferences) was made to any third parties outside the bilateral NDAs mentioned above. The results presented in this report and the general scope of this research are of strategic importance for Sika. This is the reason why dosages and CNO sources used in this work are not made public and categorized as strictly confidential.

7 References

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