# American Journal of Civil Engineering and Constructions (AJCEC)

VOLUME 1 ISSUE 2 (2025)

PUBLISHED BY
E-PALLI PUBLISHERS, DELAWARE, USA

American Journal of Civil Engineering and Constructions (AJCEC)
Volume 1 Issue 2, Year 2025
https://journals.e-palli.com/home/index.php/ajcec

# Macro-Chemical Bonding as an Alternative Binding System: Beyond Asphalt and Conventional Cement

Mohammad Abdullah Ahmed Saad[1*]

**Article Information**

**Received:** September 20, 2025

**Accepted:** October 24, 2025

**Published:** November 20, 2025

**Keywords**

*Alternative Binders, Crystalline Admixtures, C–S–H, C–A–S–H; N–A–S–H, Macro-Chemical Bonding, Pozzolanic Feedstock*

## ABSTRACT

Traditional road construction depends on asphalt as a physical binder and ordinary Portland cement (OPC) as a chemical binder forming calcium–silicate–hydrate (C–S–H) gels. Yet the exploration of macro-chemical bonding as a distinct binding paradigm remains limited. This framework establishes Macro-Chemical Bonding as a new research paradigm and intellectual school within construction material science. This study theorizes a new scientific framework that re-examines binding mechanisms beyond asphalt and cement by focusing on chemical glues capable of generating robust gel and crystalline networks at the macro scale. Beyond conventional systems, the review also examines non-traditional chemical glues- calcium sulfoaluminate/aluminate, magnesium-phosphate, phosphate-bonded, carbonation-bonded, and bio-mineral (MICP) systems - that form rapid crystalline or biomineral networks with lower $CO_2$ footprints and niche suitability for hot-arid environments. All chemically bonded systems are organized into five mechanistic categories forming a unified macro-chemical bonding spectrum: (1) cement hydration forming C–S–H gels as the baseline glue; (2) lime/slag systems forming C–A–S–H; (3) alkali-activated binders forming N–A–S–H; (4) crystalline or nano-engineered enhancers that densify or self-seal gel networks; and (5) pozzolanic feedstock supplying reactive Si and Al as precursors. This five-fold framework defines the chemical continuum from conventional cement to next-generation macro-chemical glues. Recent literature confirms the high technical potential of these systems but also highlights institutional gaps: despite their strength, durability, and sustainability, alkali-activated and geopolymeric binders remain hindered by the absence of harmonized standards particularly in hot-arid regions where asphalt still dominates. The study argues that barriers are regulatory and investment-based rather than scientific. The conclusion raises an open question: if cement hydration already demonstrates chemical bonding at the macro scale, what other activated materials could evolve into a resilient, standardized macro-chemical bonding system for future pavements?

## INTRODUCTION

This study introduces Macro-Chemical Bonding (MCB) as a new scientific paradigm in construction materials engineering. Rather than examining isolated material types, MCB establishes a unified theoretical framework that explains how different chemistries gel-based, crystal-based, and hybrid systems create macro-scale cohesion and structural integrity. This paradigm defines a new school of thought in material science, integrating chemistry, mechanics, and sustainability under one conceptual language. As such, Macro-Chemical Bonding (MCB) constitutes not only a classification framework but a scientific school of thought that bridges chemistry, structural mechanics, and climate-responsive design.

Modern pavement engineering is governed by two binding paradigms: a physical one (asphalt), where a viscoelastic bitumen film provides cohesion without forming a mineral-bridging chemical network, and a chemical one (OPC), where hydration produces calcium–silicate–hydrate (C–S–H) gels that act as a macro-scale glue. This paper reframes the problem around macro-chemical bonding-i.e., engineered reactions that generate continuous gel or crystalline networks at the structural scale-and evaluates both mainstream and non-conventional chemistries under hot-arid constraints.

Alongside alkali-activated (N–A–S–H) and lime/slag (C–A–S–H) systems, we consider crystalline self-sealing pathways, nano-engineered amplification, and rapid or low-carbon routes (CSA/CAC, magnesium-phosphate (MPC), phosphate- and carbonation-bonded, and bio-mineral MICP).

The goal is to shift from composition labels (cementitious, bituminous, geopolymeric) shifting to mechanism-based design of the glue itself and laying a clear pathway toward a climate-aligned macro-chemical binder concept, independent of any proprietary formulation. Within this framework, the paper classifies macro-chemical bonding systems into five interrelated categories representing a continuum of chemical adhesion. The first is the classical C–S–H system of cement hydration - the benchmark macro-chemical glue.

The second and third are C–A–S–H and N–A–S–H gels, generated respectively in lime/slag and alkali-activated systems. The fourth encompasses crystalline and nano-

---

[1] Roads & Transport Specialist, Professional in Urban Infrastructure Development, Independent Researcher in Civil Engineering and Urban Planning, Muscat, Oman

[*] Corresponding author's e-mail: eng.mohammad.pa@gmail.com

engineered enhancers, which intensify or extend existing bonding networks through in-situ crystal growth and microstructural densification. Finally, the fifth category includes pozzolanic feedstock materials that supply reactive Si and Al essential for gel or crystal formation, functioning as enablers rather than independent binders. Together, these five classes define the operational taxonomy adopted throughout this study. Amidst growing pressure for sustainable infrastructure, research has expanded into alternative binders, including alkali-activated materials (AAMs), geopolymers, crystalline admixtures, and nano-engineered additives (Provis, 2022; Juenger *et al.*, 2025). These studies demonstrate that chemical reactions beyond cement hydration can yield binding gels or crystalline networks with comparable or superior mechanical and durability properties. Alkali silicates, for example, generate sodium–alumino–silicate hydrate (N–A–S–H) gels; lime/slag systems can produce calcium–alumino–silicate hydrates (C–A–S–H); crystalline admixtures form insoluble crystals within pores and microcracks; and nano-silica accelerates hydration while refining the interfacial microstructure (Kashani *et al.*, 2024; Zhang *et al.*, 2023). Supplementary pozzolanic precursors such as fly ash and metakaolin enrich these reactions, but they act as feedstock rather than independent glues (Bernal & Provis, 2014).

Despite these advances, the concept of macro-chemical bonding-deliberately engineered reactions that act as a glue at the macro scale-remains underdeveloped in pavement research. Existing literature often frames these binders as substitutes for cement or asphalt rather than as a broader binding paradigm. This gap is pronounced in Gulf contexts, where specifications remain asphalt-centric and regulatory acceptance of chemical alternatives is limited (Provis, 2022). Accordingly, we also survey non-conventional chemical binders-calcium sulfoaluminate/aluminate cements (CSA/CAC), magnesium-phosphate cements (MPC), phosphate-bonded matrices, carbonation-bonded materials cured in $CO_2$, and bio-mineral systems via microbially induced calcite precipitation (MICP)-to position them within a unified macro-chemical bonding framework relevant to hot-arid pavements.

The objective is twofold: (i) to establish the chemistry of cement hydration-specifically the formation of C–S–H gels-as the baseline model of a macro-chemical glue; and (ii) to systematically analyze and compare the full spectrum of emerging chemical systems that can function as macro-chemical bonding agents, including C–A–S–H (lime/slag-based), N–A–S–H (alkali-activated), crystalline and nano-engineered enhancers, and the supporting pozzolanic feedstock that enables their gel or crystal formation. We emphasize that the primary barrier to adoption is institutional rather than technical, rooted in the lack of standards and the inertia of asphalt-based procurement.

The following sections develop the proposed macro-chemical bonding framework through a progressive analysis of traditional and alternative binders, linking their chemical mechanisms, material classifications, and performance implications under hot-arid conditions.

## LITERATURE REVIEW

### From Physical to Chemical Binding: Asphalt vs. Cement

The dichotomy between asphalt and cement defines the conceptual baseline for binding systems in pavement engineering. Asphalt provides adhesion through physical coating and viscoelastic behavior, while cement offers chemical cohesion through hydration and the formation of calcium–silicate–hydrate (C–S–H) gels (Scrivener *et al.*, 2018). These C–S–H gels act as a macro-scale glue, binding aggregates into a rigid network. The reliance on asphalt persists due to cost and constructability, but its limitations under high temperature, oxidation, and environmental scrutiny underscore the need for chemically driven alternatives (IEA, 2023).

### Cement Hydration as the Baseline Macro-Chemical Glue (C–S–H System)

The hydration of ordinary Portland cement (OPC) provides the fundamental reference for all macro-chemical bonding systems. Through the hydration of tricalcium and dicalcium silicates ($C_3S$ and $C_2S$), calcium–silicate–hydrate (C–S–H) gels are formed, establishing the prototype of a chemical "glue" that binds aggregates into a rigid continuum.

Early research on cement chemistry (e.g., Taylor, 1997; Scrivener *et al.*, 2018) established that C–S–H is a poorly crystalline, tobermorite-like phase with variable Ca/Si ratios, capable of sustaining both strength and self-healing under moisture cycling. Subsequent studies confirmed that the heterogeneous morphology of C–S–H-composed of layered silicate chains and interlayer calcium hydroxide-allows stress redistribution and crack bridging, which collectively define its macro-scale cohesion (Gartner & Quillin, 2007; Juenger *et al.*, 2025).

From a macro-chemical perspective, cement hydration represents the first successful example of a self-organized gel network that performs the three essential functions of a chemical binder: forming a continuous load-bearing matrix, sealing voids, and maintaining long-term stability through secondary reactions. The by-product calcium hydroxide (CH), once considered a weakness, has since been recognized as a reactive feedstock that enables further gel growth in pozzolanic and blended systems. Thus, the C–S–H system provides both a chemical and conceptual benchmark against which all emerging alternative binders-such as C–A–S–H and N–A–S–H gels-can be evaluated.

### Lime/Slag Systems (C-A-S-H Development)

Lime and slag systems form another cornerstone of research into alternative chemical binders. When ground granulated blast furnace slag (GGBFS) is activated in the presence of lime (CaO or $Ca(OH)_2$) and moderate alkaline environments, the main reaction products are calcium–alumino–silicate hydrates (C-A-S-H) with structural similarities to the C-S-H of ordinary Portland cement (OPC) (Bernal & Provis, 2014). These hydrates exhibit a higher degree of polymerization and incorporate aluminum into the silicate chains, which enhances durability under sulfate and chloride exposure (Shi *et al.*, 2022). Compared to alkali silicate systems, lime/slag activation offers several practical advantages. First, slag is widely available as an industrial by-product, making it an attractive candidate for circular economy applications. Second, the presence of calcium accelerates early strength development, addressing one of the key limitations of purely sodium silicate–based systems (Aydın *et al.*, 2022). Third, lime/slag binders are more chemically compatible with existing concrete standards, facilitating partial substitution of OPC in blended systems. However, challenges remain. Carbonation shrinkage and microcracking are frequently reported, particularly in high-calcium AAS (alkali-activated slag) systems exposed to dry or hot climates (Zhang *et al.*, 2021). Dimensional instability under accelerated carbonation raises questions about long-term durability, and there is evidence of variability in performance depending on slag composition and fineness (Fernández-Jiménez *et al.*, 2020).

The adoption of "one-part" activation methods, where dry slag is mixed with powdered activators such as sodium sulfate or gypsum, has recently emerged as a safer and more field-compatible approach, but requires further validation under pavement conditions (Kastiukas *et al.*, 2024). From the perspective of macro-chemical bonding, lime/slag systems highlight the possibility of engineering binders that replicate cement-like gel structures (C-A-S-H) while reducing reliance on clinker. Yet they are still framed within the language of "supplementary cementitious materials" rather than as independent chemical glues. This reflects a conceptual gap: although C-A-S-H gels can act as robust macro-scale adhesives, the lack of recognition as a distinct binding paradigm limits their wider application in road engineering.

### Alkali-Activated Materials (AAMs) and the Formation of N–A–S–H Networks

Alkali-activated materials (AAMs) and alkali silicates represent one of the most advanced research trajectories in alternative binders. When precursors rich in silica and alumina (e.g., fly ash, metakaolin, slag) are dissolved in alkaline solutions such as sodium silicate ($Na_2SiO_3$) or sodium hydroxide (NaOH), they form three-dimensional sodium–alumino–silicate hydrate (N–A–S–H) gels.

These gels exhibit high compressive strength, low permeability, and chemical resistance (Provis, 2022). Recent studies have refined understanding of the Na/Al ratio and Si/Al ratio as critical parameters controlling gel polymerization and microstructure densification (Juenger *et al.*, 2025; Zhang *et al.*, 2022).

Emerging trends focus on "one-part" AAM systems, where dry precursors are blended with solid activators, thereby eliminating the handling risks of concentrated alkaline solutions. This approach significantly improves constructability and aligns better with industrial practice (Kastiukas *et al.*, 2024). However, carbonation shrinkage and long-term dimensional stability remain concerns, especially under hot-arid climates where moisture loss accelerates (Shi *et al.*, 2023). While AAMs have been tested extensively in structural concretes, their framing as macro-chemical bonding systems remains underexplored in pavement applications.

### Crystalline and Nano-Engineered Enhancers

### Crystalline Admixtures (CA): In-Situ Crystal Growth and Self-Sealing

Crystalline admixtures (CA) constitute a specialized category of chemical additives that function by promoting the in-situ growth of insoluble crystals within the pore network of cementitious systems. Unlike conventional supplementary cementitious materials, their role is not to contribute reactive silica or alumina, but rather to initiate nucleation and crystal formation that progressively fill capillary voids and microcracks (Tiwari *et al.*, 2022). These crystals, typically calcium silicate hydrates with modified morphology or complex insoluble salts, enhance impermeability and act as a form of internal "self-sealing" glue at the macro scale. Empirical evidence shows that CA can substantially reduce permeability, water absorption, and chloride ingress in concrete structures (Snoeck & De Belie, 2021).

Several studies report improvements in compressive strength and long-term durability, though the magnitude of improvement is highly dependent on dosage and mix design (Mohammed *et al.*, 2023). Crystalline admixtures are also synergistic with conventional hydration, as they utilize free calcium hydroxide to generate additional crystalline deposits within voids, thereby densifying the interfacial transition zone (ITZ). Despite these benefits, inconsistencies in performance remain a concern. Over-dosage can lead to heterogeneity and delayed hydration, while under-dosage results in negligible improvements (Snoeck & De Belie, 2021). Furthermore, the proprietary nature of many commercial crystalline admixtures limits transparency regarding their exact chemical mechanisms, creating challenges for scientific standardization and reproducibility (Tiwari *et al.*, 2022).

From a macro-chemical bonding perspective, crystalline admixtures are significant because they operate differently from gel-based systems such as C-S-H or N-A-S-H. Instead of relying on continuous gel formation, CA enhance binding by growing crystalline networks that interlock and seal voids at the macro scale. This suggests a complementary pathway for designing macro-chemical glues-one that relies on controlled crystal propagation rather than gel polymerization. Yet, similar to alkali-activated systems, the lack of codified standards has prevented crystalline admixtures from being fully recognized as a distinct binding system in pavement engineering.

### Nano-Silica and Nano-Additives: Nucleation Acceleration and Gel Densification

Nano-silica (NS) and related nano-engineered additives (e.g., nano-alumina, nano-clays, functionalized nanoparticles) operate as microstructural catalysts that accelerate gel formation and densify the pore network, thereby strengthening the macro-scale "chemical glue" in cementitious systems. Mechanistically, NS provides abundant high-energy nucleation sites, consumes portlandite through secondary pozzolanic reactions, and refines the interfacial transition zone (ITZ), which collectively promote the precipitation of additional C–S–H with lower Ca/Si and a denser packing (Kashani *et al.*, 2024; Zhang *et al.*, 2023). In the macro-chemical bonding lens, NS does not replace the binder with a new gel family; rather, it amplifies the formation and connectivity of gel/crystalline networks that already act as the adhesive phase. Recent reviews report consistent gains in compressive and tensile strength, reduced permeability and chloride diffusivity, and improved freeze–thaw and sulfate resistance when NS is used at optimized dosages-typically in the range of ~0.5–3% by binder mass, with performance plateaus or reversals at higher contents due to agglomeration and rheological penalties (Kashani *et al.*, 2024). Dispersion quality is a decisive factor: poorly dispersed NS can increase viscosity and entrap air, offsetting durability benefits, while well-dispersed sols or surface-modified particles enhance early-age kinetics without compromising workability (Zhang *et al.*, 2023).

At the micro- to nano-scale, NS narrows capillary pores, converts large gel voids to finer distributions, and strengthens the ITZ by bridging microcracks and improving aggregate–paste adhesion-effects that directly translate to macro-scale glue continuity.

For pavement-oriented systems, NS shows promise in accelerating early strength gain (facilitating earlier trafficking) and in mitigating moisture- and ion-driven degradation pathways. However, three caveats emerge from the literature. First, dose–response nonlinearity requires careful optimization; benefits can invert beyond a critical dosage because of particle clustering and water demand (Kashani *et al.*, 2024). Second, interaction effects with other admixtures (superplasticizers, shrinkage-reducers, crystalline admixtures) are non-trivial; synergistic or antagonistic behaviors depend on polymer chemistry and ionic strength of the pore solution (Zhang *et al.*, 2023).

Third, scalability and quality control-ensuring consistent dispersion at plant scale and across varying cement chemistries-remain practical barriers to standardization, keeping NS framed as a performance modifier rather ified binding system in its own right. From a macro-chemical bonding perspective, NS is best interpreted as a force-multiplier that strengthens and knits together the chemical glue produced by hydration (C–S–H) or activation (C-A-S-H/N-A-S-H), narrowing the gap between laboratory potential and field durability. When positioned alongside alkali-activated and crystalline pathways, NS helps define a design space where gel formation (C–S–H/C-A-S-H/N-A-S-H) and crystal growth (CA) are both intensified and better connected, pointing toward integrated binding strategies for next-generation pavements rather than single-additive solutions. Within the five-class taxonomy, nano-silica operates as an enhancer rather than a standalone binder.

### Emerging and Non-Conventional Chemical Glues (CSA/CAC, MPC, Phosphate- and Carbonation-Bonded, and Bio-Mineral MICP)

While the five core categories define the main continuum of macro-chemical bonding-from gel-based to crystalline and feedstock-driven mechanisms-several non-conventional or hybrid systems extend this spectrum. These materials do not constitute a sixth category; rather, they sit within the crystal-growth and mineralization domain and complement the primary framework. Calcium sulfoaluminate/aluminate (CSA/CAC) cements develop strength primarily through ettringite-rich or aluminate hydrates, enabling fast setting and a lower embodied $CO_2$ footprint-typically 30–40% less than OPC, depending on clinker design (Gartner & Quillin, 2007). Magnesium phosphate cements (MPC) cure via acid–base reactions forming struvite-type phases, achieving very high early strength and strong substrate bonding for rapid repair, although moisture sensitivity and cost limit broader use. Phosphate-bonded cements (Ca/Mg/Al-phosphates) form acid-resistant M–O–P frameworks, while carbonation-bonded systems rely on controlled $CO_2$ curing to precipitate carbonate networks ($CaCO_3$/$MgCO_3$), simultaneously achieving densification and $CO_2$ uptake during early curing. At the biological end of the spectrum, microbial-induced calcite precipitation (MICP) shows how living processes can induce macro-scale cohesion via calcite formation, sealing voids and microcracks with minimal carbon impact. Collectively, these systems broaden the macro-chemical lens to crystalline, acid–base, carbonation, and bio-mineral pathways, reinforcing that macro-scale chemical adhesion can arise from diverse chemistries. Their performance in hot-arid pavements remains largely unstandardized, but they provide critical insight for developing performance-based codification of next-generation binders.

### Pozzolanic Feedstock as Reactive Precursors

Pozzolanic precursors-fly ash, metakaolin, and ground granulated blast-furnace slag (GGBFS)-supply reactive Si and Al that are mobilized under alkaline or lime-rich conditions to form gel phases (C–S–H, C–A–S–H, or N–A–S–H). Functionally, they act as reactive feedstock that nourishes macro-chemical glue formation rather than serving as independent binders. In OPC systems, pozzolans consume portlandite to generate secondary C–S–H of lower Ca/Si, densifying the matrix and the interfacial transition zone (ITZ). In alkali-activated systems (AAMs), aluminosilicate dissolution followed by polycondensation produces three-dimensional N–A–

S–H or mixed C–A–S–H networks with demonstrated strength and durability gains when mix chemistry is properly tuned (precursor glass content, fineness, and activator modulus).

Recent comparative and state-of-the-art reviews confirm that precursor chemistry and Na/Al–Si/Al ratios govern gel topology, kinetics, and permeability, but also highlight variability across industrial ashes and slags that complicates standardization. In short, pozzolans enable the chemistry of the glue; they are not the glue per se.

Implications for macro-chemical bonding. Treating pozzolans as feedstock clarifies design priorities: (i)Select and pre-process the precursor for consistent reactivity; (ii) Engineer activator chemistry to target the desired gel family (C–S–H/C–A–S–H vs. N–A–S–H); (iii) Manage moisture/$CO_2$ exposure to limit carbonation-shrinkage and preserve gel continuity-especially under hot-arid conditions relevant to Gulf pavements. These decisions position pozzolans as enablers of macro-scale chemical adhesion rather than as a third "class" of binders competing with asphalt or cement. Note that certain materials (e.g., GGBFS) can appear either as primary constituents in C–A–S–H binders or as reactive feedstock in blended systems; the role is determined by activation chemistry and mix design.

## Institutional & Standards Gap

Despite robust lab-scale evidence for alkali-activated and geopolymer binders-and growing data for crystalline admixtures and nano-silica-codified standards remain fragmentary, slowing adoption in structural and pavement applications. RILEM's technical letters (2022) identify three intertwined barriers: (1) limited, non-harmonized standards tailored to AAM chemistry; (2) variability of industrial precursors (slag/ash) across sources; and (3) durability datasets that are promising yet still uneven for code writing. This keeps many agencies anchored to asphalt or OPC-centric specifications and legacy test methods that are not fully diagnostic for AAMs (e.g., chloride/$CO_2$ protocols not calibrated to N–A–S–H/C–A–S–H chemistries).

Contemporary reviews echo the same institutional friction: calls for performance-based durability metrics aligned to AAM chemistry; guidance on "one-part" (dry) activation to improve constructability and safety; and standardized production/bond testing for reinforced geopolymer concretes-prerequisites to mainstream codes and procurement. In parallel, crystalline-admixture research shows permeability reductions and self-healing potential, but proprietary chemistries and dosage sensitivity complicate method harmonization, again delaying specification-level acceptance. Collectively, the literature frames the primary bottleneck as regulatory and investment-related, not purely scientific-precisely the barrier this paper foregrounds for hot-arid, asphalt-centric markets.

## Synthesis and Gap Statement

The reviewed literature reveals a clear evolution from physical binders (asphalt) to a structured framework of five interrelated categories of chemical binders-namely:

(1) C–S–H (cement hydration),
(2) C–A–S–H (lime/slag-based),
(3) N–A–S–H (alkali-activated),
(4) Crystalline and nano-engineered enhancers, and
(5) Pozzolanic feedstock serving as reactive precursors.

Together, these categories define the conceptual spectrum of macro-chemical bonding, demonstrating that macro-scale cohesion can be engineered through chemical reactions forming continuous gel or crystalline networks. In addition, several emerging non-conventional systems-including CSA/CAC, MPC, phosphate-, carbonation-, and bio-mineral (MICP) binders-extend this framework into hybrid crystalline and biomineral pathways that remain underexplored in codified pavement research. Collectively, these five principal families and their hybrid extensions establish the foundation for a mechanism-based understanding of chemical adhesion at the structural scale.

### Cement hydration (C–S–H)

Cement hydration (C–S–H) represents the baseline macro-chemical glue, where silicate and aluminate hydration products create a cohesive gel matrix that defines the benchmark for subsequent systems.

### Lime/Slag Systems

Lime/slag systems generate calcium–alumino–silicate hydrates (C–A–S–H) that mimic OPC-like glue, offering early strength and industrial feasibility but showing variability tied to slag composition and fineness.

### Alkali-Activated Systems (AAMs)

Alkali-activated systems (AAMs) confirm the feasibility of designing sodium–alumino–silicate hydrates (N–A–S–H) with high strength and durability, though carbonation and dimensional instability remain challenges.

### Crystalline and Nano-Engineered Enhancers

Crystalline and nano-engineered enhancers act as internal self-sealing and densifying agents, reducing permeability and refining the interfacial transition zone (ITZ), yet their proprietary formulations and dosage sensitivity hinder standardization.

### Pozzolanic Pecursors

Pozzolanic Precursors act as reactive feedstock, enabling gel growth without serving as independent binders, underscoring their supporting rather than central role.

Despite this technical maturity, a common thread emerges: none of these systems are explicitly conceptualized as macro-chemical bonding paradigms. Instead, they continue to be treated as supplementary materials, modifiers, or cement replacements. This framing obscures their potential role as independent binding systems that-like cement hydration-can function as macro-scale chemical glues. The second and more critical gap is institutional. As identified by RILEM and other reviews, the lack of harmonized standards, variability of industrial feedstock, and entrenched reliance on asphalt-centered procurement prevent these materials from being recognized beyond the laboratory (RILEM TC Rossi *et al.*, 2022; Provis, 2022).

Thus, the barrier to adoption is not purely scientific but regulatory and investment-related. This paper addresses that gap by reframing these materials through the lens of macro-chemical bonding. Cement hydration is presented as the baseline case of a successful macro-chemical glue, against which emerging binders are systematically compared. By analyzing their reaction mechanisms, gel/crystal products, and macro-scale adhesive performance, this paper seeks to articulate a coherent paradigm for alternative chemical binding systems in pavement engineering.

## MATERIALS AND METHODS

This study adopts a conceptual–analytical methodology rather than an experimental program, aimed at reframing alternative binders through the lens of macro-chemical bonding. The methods are structured in four layers: (i) establishing the hydration chemistry of ordinary Portland cement (OPC) as the reference macro-chemical glue; (ii) introducing bitumen and asphalt as the physical (non-chemical) baseline, summarizing binder composition (SARA) and mixture-level performance indices (PG/M 320; MSCR per M 332; DSR/BBR, Hamburg, TSR) to delimit what "physical adhesion" means in practice; (iii) identifying and describing the reaction pathways of emerging chemical binders (e.g., N–A–S–H, C–A–S–H, crystalline self-sealing networks, nano-engineered amplification, and next-generation phosphate/CSA/CAC/carbonation/bio-mineral systems); and (iv) developing a seven-parameter comparative matrix linking microstructural mechanisms to macro-scale adhesion, durability, constructability/safety, and adoption readiness under hot-arid exposure and performance-based specifications.

### Literature Scope & Inclusion

We prioritized peer-reviewed articles, standards, and technical letters (2010–2025), with emphasis on studies reporting strength, permeability, and durability under high-temperature/low-humidity conditions; when multiple results existed, we favored performance-based and standards-aligned datasets.

### Baseline: Cement Hydration as a Macro-Chemical Glue

Cement hydration provides the reference case for a chemical system that generates macro-scale adhesion. The hydration of the four principal clinker phases produces a spectrum of gels and crystalline products that act as the macro-chemical glue. The fundamental reactions can be summarized as follows:

**Tricalcium Silicate ($C_3S$ – Alite)**

Dominant source of early strength through rapid C–S–H gel formation.

$3CH+(H\text{-}S\text{-}C_3S_2H_3)C \rightarrow 6H+2C_3S$

**Dicalcium Silicate ($C_2S$ – Belite)**

Slower reaction, contributing to long-term strength and durability.

$CH+(H\text{-}S\text{-}C_3S_2H_3)C \rightarrow 4H+2C_2S$

**Tricalcium Aluminate ($C_3A$) with Gypsum**

Governs setting behavior and early-age dimensional stability.

$C_6\bar{A}S_3H_{32}(\text{Ettringite}) \rightarrow 26H + (CaSO_4\,2H_2O)3+C_3A$

**Tetracalcium Aluminoferrite ($C_4AF$) with Gypsum**

Produces ettringite-like phases incorporating Fe, with secondary influence on durability and color.

$${}_{32}C_6(A,F)\bar{S}_3H \rightarrow 30H + (CaSO_4\cdot 2H_2O)3 + C_4AF$$

Together, these reactions produce a continuous network of C–S–H gel and associated hydrates, which collectively act as a macro-chemical glue that binds the granular skeleton of the composite. This system serves as the baseline reference against which emerging alternative binders (alkali silicates, lime/slag systems, crystalline admixtures, and nano-silica) are evaluated in this study. This interplay among the silicate, aluminate, and ferrite phases defines the chemical foundation of Portland cement as the benchmark macro-chemical glue. The dominance of $C_3S$ drives rapid C–S–H gel formation, ensuring early strength, while $C_2S$ continues the process at a slower rate, sustaining long-term performance. Gypsum moderates the reactivity of $C_3A$, preventing flash setting and promoting stable ettringite formation. The by-product calcium hydroxide (CH), often regarded as a weakness, subsequently becomes a reactive feedstock in blended or pozzolanic systems, contributing to secondary C–S–H formation.

Together, these coupled reactions generate a cohesive, self-reinforcing chemical network that exemplifies macro-scale adhesion through hydration. To clarify the individual contributions of each phase, Table 1 summarizes the principal hydration reactions of the four clinker constituents and their respective roles in macro-chemical bonding.

**Table 1:** Hydration of Portland Cement Clinker Phases and Their Function in Macro-Chemical Bonding

| Clinker Phase | Simplified Hydration Reaction | Primary Product(s) | Role in Macro-Chemical Glue |
|---|---|---|---|
| Tricalcium Silicate ($C_3S$ – Alite) | $–S–C_3S_2H_3$ (C →6H + $2C_3S3CH$ +H) | C–S–H gel + CH | Rapid formation of C–S–H; provides early strength and main adhesive phase. |

| | | | |
|---|---|---|---|
| Dicalcium Silicate ($C_2S$ – Belite) | –S–$C_3S_2H_3$ (C →4H + 2$C_2S$ CH +H) | C–S–H gel + CH | Slower hydration; contributes to long-term strength and durability. |
| Tricalcium Aluminate ($C_3A$ + Gypsum) | +($CaSO_4.2H_2O$)3 + $C_3A_{(Ettringite)}$ $_{32}C_6\bar{A}S_3H$ → 26H | Ettringite (AFt) | Controls setting time, prevents flash setting, contributes to early stability. |
| Tetracalcium Aluminoferrite ($C_4AF$ + Gypsum) | +($CaSO_4.2H_2O$)3 + $C_4AF$ $_{32}C_6(A, F)^{-}S_3H$ →30H | Ettringite-like phases with Fe | Secondary influence on durability and microstructure; minor adhesive role. |

### Microstructural Characteristics of Cement Hydration Products

The C–S–H gel formed from $C_3S$ and $C_2S$ hydration is poorly crystalline, often described as tobermorite-like chains with variable Ca/Si ratios. Its disordered morphology contributes to flexibility in accommodating shrinkage stresses while maintaining macro-scale cohesion. Ettringite (AFt phase), produced primarily through $C_3A$–gypsum reactions, plays a critical role at early ages by stabilizing the system and preventing flash setting.

Although calcium hydroxide (CH) is often considered a weakness due to its solubility and susceptibility to leaching, it simultaneously serves as reactive feedstock in blended or pozzolanic systems, enabling secondary gel growth that densifies the matrix. Collectively, these hydration products establish a multi-phase adhesive network that exemplifies successful macro-chemical bonding.

### Baseline: Bitumen and Asphalt as Physical (Non-Chemical) Binders

Bitumen-the binder in asphalt mixtures-provides physical adhesion and viscoelastic cohesion, rather than a macro-scale chemical glue. At the molecular scale, it is a multicomponent petroleum residue typically described by the SARA fractions (saturates, aromatics, resins, asphaltenes; separable per ASTM D4124). In the prevailing colloidal view, asphaltenes are dispersed as nano-aggregates within a maltene phase (aromatics + resins), producing a temperature- and rate-dependent viscoelastic film that coats aggregate and occupies voids. This yields composite-level cohesion but does not form a continuous chemical gel or crystalline network across the mineral skeleton-unlike C–S–H/C–A–S–H/N–A–S–H in cementitious or alkali-activated systems (e.g., Lesueur, 2009; Shell Bitumen Handbook, 2015). Because asphalt bonding is physical, durability is governed by processes that alter binder rheology and interfacial adhesion: (i) oxidative aging during production and service increases polarity and apparent asphaltene content (Petersen, 2009); (ii) volatilization/structural rearrangement changes film thickness and ductility; and (iii) moisture damage (stripping) weakens binder–aggregate interactions, especially with silica-rich aggregates (Little & Bhasin, 2007). To align the physical baseline with the macro-chemical analysis, Tables 2–3 consolidate the bitumen/asphalt baseline (composition → mechanism → performance indices) used for later comparisons in §§1.13–1.16.

**Table 2:** Bitumen (Binder): Composition, Microstructure, and Physical Bonding Pathways

| Attribute | Bitumen (Binder) – Physical Baseline |
|---|---|
| Chemical family (SARA) | Saturates · Aromatics · Resins · Asphaltenes; separable per ASTM D4124 (fractions vary by source/grade). |
| Microstructure | Colloidal model: asphaltene nano-aggregates dispersed in maltenes; viscoelastic film coats aggregate-no macro-chemical gel. |
| Adhesion/Cohesion | Wetting & surface-energy interactions at mineral surfaces; cohesion from temperature-/rate-dependent film viscoelasticity. |
| Aging & damage | Oxidation (short/long term) stiffens binder; volatilization; stripping at the binder–aggregate interface under moisture. |
| Modifiers (examples) | SBS/EVA polymers, crumb rubber, PPA, anti-strip amines/silanes, WMA additives, rejuvenators. |
| Hot-arid response | Elevated temperatures → rutting/oxidation; mitigated via PG upgrades, polymer modification, aggregate structure, anti-strip. |
| Key binder indices | DSR: ($G^*/\sin \delta$); MSCR: nrJ, %recovery; BBR: (S, m) (low-temp). |
| Position on spectrum | Physical binder (non-chemical); baseline for comparison to macro-chemical glues. |

**Table 3:** Asphalt Mixture (Composite): Macro Performance & Failure Modes

| Attribute | Asphalt Mixture |
|---|---|
| Nature | Composite of mineral aggregate + bitumen film (typically ~4–6% by mass for dense mixes); physical cohesion + volumetric interlock. |
| Structure/Film | Film thickness, gradation, air-voids (VMA/VA), and aggregate texture govern durability and deformation. |

| | |
|---|---|
| Failure modes | Rutting; fatigue/thermal cracking; moisture damage (stripping). |
| Design levers | PG grade & polymer modification; aggregate type/texture; compaction quality; anti-strip treatments (hydrated lime/amine); WMA/rejuvenators. |
| Key mixture tests | Hamburg wheel-track (AASHTO T 324); TSR (AASHTO T 283); optional cracking metrics: SCB-IFIT (AASHTO T 393/TP 124) and/or IDEAL-CT (ASTM D8225( |
| Position | Physical composite-performance emerges from rheology + structure; no macro-chemical gel/crystal network. |

*Table note. PG per AASHTO M 320; MSCR per AASHTO M 332; DSR/BBR per standard AASHTO protocols; Hamburg wheel-track AASHTO T 324; TSR AASHTO T 283; optional cracking metrics: SCB-IFIT (AASHTO T 393/TP 124) and/or IDEAL-CT (ASTM D8225). Adhesion is interpreted via Young–Dupré and van Oss–Chaudhury–Good surface-energy frameworks, and oxidative aging via Arrhenius-type temperature dependence*

### Expanded Analytical Matrix for Comparative Evaluation

The comparative framework is operationalized through a seven-parameter matrix that evaluates both micro- and macro-scale performance of binding systems:

**Reaction Pathway**
Hydration, dissolution–polycondensation, or nucleation–growth.

**Primary Binding Phase**
C–S–H, C–A–S–H, N–A–S–H, or crystalline deposits.

**Gel/Crystal Topology**
Continuity, crystallinity, and Ca/Si or Na/Al ratios.

**Microstructural Effects**
Pore refinement, ITZ densification, crack sealing.

**Macro-Scale Bonding**
Strength evolution, durability (sulfate, carbonation, chloride), permeability.

**Constructability and Safety**
Practicality of mixing/curing, handling of activators, compatibility with field conditions.

**Institutional Readiness**
Codification in standards, acceptance in procurement frameworks.

This matrix allows direct benchmarking of emerging systems against the OPC hydration baseline and clarifies their roles as primary gel-forming families, network enhancers, or reactive precursors within a unified macro-chemical perspective.

### Environmental and Contextual Considerations

Because this study is situated within the broader challenge of pavement materials in hot-arid regions, the analytical framework explicitly incorporates climatic constraints. Elevated temperatures accelerate hydration kinetics for OPC but also intensify shrinkage and evaporation-driven cracking, while alkali-activated slag binders are prone to accelerated carbonation under low humidity.

Crystalline admixtures may benefit from moisture cycling to trigger self-sealing, whereas nano-silica systems require careful water management to avoid rheological penalties. These contextual parameters are integrated into the evaluation matrix to ensure relevance for Gulf-region pavements, where asphalt remains dominant but vulnerable under thermal loading.

### Candidate Systems for Macro-Chemical Bonding

Building on the five-class taxonomy adopted in this study, we organize candidates as follows:

**Category 1 - C–S–H (OPC hydration baseline)**
Established in §1.10 as the benchmark macro-chemical glue.

**Categories 2–3 - Full Binders**
Lime/slag-based systems (C–A–S–H) and alkali-activated systems (N–A–S–H), each forming continuous gel networks via different chemistries.

**Category 4 - Enhancers**
Crystalline admixtures and nano-engineered additives that intensify self-sealing and gel densification rather than forming an independent binder.

**Category 5 - Pozzolanic Feedstock**
Reactive precursors (e.g., fly ash, metakaolin, natural pozzolans, slag) supplying Si–Al for gel/crystal growth.

Non-conventional systems-CSA/CAC, MPC, phosphate- and carbonation-bonded, and bio-mineral (MICP)-are discussed within the crystalline/hybrid lens in 1.6. To clarify the conceptual hierarchy of macro-chemical bonding systems, we distinguish core gel families that act as full binders from auxiliary systems that reinforce or extend their performance. Ordinary Portland cement (OPC) hydration produces the classical calcium–silicate–hydrate (C–S–H) gel, which serves as the baseline macro-chemical glue against which all emerging systems are evaluated. When calcium is partially replaced by alumina or sodium through alternative activation routes, the same macro-scale bonding principle persists but manifests as different gel families-namely calcium–alumino–silicate hydrate (C–A–S–H) in lime/slag systems and sodium–alumino–silicate hydrate (N–A–S–H) in alkali-activated materials (AAMs). Beyond these gel-forming systems, crystalline admixtures (CA) and nano-engineered additives (e.g., nano-$SiO_2$) function as secondary bonding enhancers, promoting in-situ crystal growth and microstructural densification that strengthen the existing macro-chemical network rather than forming an independent binder. Table 4 summarizes the five principal categories of macro-chemical bonding materials and clarifies their mechanisms, binding phases, and functional

**Table 4:** Comprehensive Classification of Macro-Chemical Bonding Systems and Their Functional Roles

| **Category** | **Representative Compounds / Systems** | **Dominant Reaction Mechanism** | **Primary Binding Phase / Product** | **Typical Constituents & Activators** | **Functional Role in Macro-Chemical Bonding** | **Distinctive Features / Challenges** |
|---|---|---|---|---|---|---|
| 1. C–S–H (Cement Hydration Baseline) | Ordinary Portland Cement (OPC) hydration system | Hydration of $C_3S$, $C_2S$, $C_3A$, $C_4AF$ | Calcium–silicate–hydrate (C–S–H) gel + Ettringite (AFt) | Clinker phases ($C_3S$ = alite, $C_2S$ = belite, $C_3A$, $C_4AF$) + Gypsum ($CaSO_4 \cdot 2H_2O$) + Water | Baseline macro-chemical glue; forms continuous semi-crystalline C–S–H network providing load-bearing adhesion and durability | High mechanical performance; fully standardized (ASTM, EN); high $CO_2$ emissions from clinker production |
| 2. Lime / Slag-Based Systems (C–A–S–H) | Ground Granulated Blast Furnace Slag (GGBFS) activated with lime ($CaO/Ca(OH)_2$) or mild alkali | Hydration / Activation → Cross-linked C–A–S–H formation | Calcium–alumino–silicate hydrate (C–A–S–H) gel | Slag ($SiO_2–Al_2O_3–CaO–MgO$) + $Ca(OH)_2$ or $Na_2SO_4/Na_2CO_3$ as moderate activators | Full chemical binder similar to cement; lower $CO_2$ footprint; fast early strength | Carbonation shrinkage in dry climates; performance sensitive to slag composition and curing |
| 3. Alkali-Activated Systems (AAMs = N–A–S–H) | Fly ash, Metakaolin, Slag activated by $Na_2SiO_3$ (sodium silicate) + NaOH / KOH | Dissolution–polycondensation of aluminosilicates | Sodium–alumino–silicate hydrate (N–A–S–H) gel ± C–A–S–H hybrids | Si-, Al-rich precursors + alkaline activators ($Na_2SiO_3$, NaOH, KOH, $Na_2CO_3$) | Complete macro-chemical binder forming 3-D polymeric gel network with high strength and chemical resistance | Excellent mechanical performance; safety issues with liquid alkalis; "one-part" dry mix solutions under development |
| 4. Crystalline & Nano-Engineered Enhancers (CA + Nano-$SiO_2$) | Crystalline admixtures (e.g.,commercial crystalline admixture gies ( and Nano-silica (≤100 nm $SiO_2$) | In-situ crystallization and secondary pozzolanic nucleation | Insoluble Ca-silicate crystals + additional C–S–H clusters densifying the matrix | Proprietary CA compounds (Ca salts + reactive silicates) + Nano-$SiO_2$ dispersion sols or powders | Secondary enhancers that seal pores, fill microcracks, and amplify existing C–S–H/ C–A–S–H networks | Greatly reduce permeability and chloride ingress; dose-sensitive; scaling and dispersion control critical |

| | | | | | | |
|---|---|---|---|---|---|---|
| 5. Pozzolanic Feedstock (Supporting Precursors) | Fly ash (Class F & C), Metakaolin, Natural Pozzolans (pumice, scoria), Rice-husk ash, Silica fume, Oil shale ash (OSA) | Supply reactive Si and Al for secondary gel formation | Secondary C–S–H or N–A–S–H / C–A–S–H depending on activation | $SiO_2$–$Al_2O_3$–rich materials activated by $Ca(OH)_2$ or alkali solutions in hybrid systems | Feedstock / reactive precursors enabling macro-chemical glue formation in other systems | Variability by source; require grading and controlled activation to ensure consistent reactivity |

*Note. Emerging non-conventional systems (CSA/CAC, MPC, phosphate- and carbonation-bonded, and bio-mineral MICP) map primarily onto the crystalline/hybrid end of Category 4 and are evaluated within the same mechanistic lens (rapid crystallization, acid–base polymerization, or biomineralization)*

roles within the unified framework.

### Interpretive Summary

**Full Binders**

Categories 1–3 (C–S–H, C–A–S–H, N–A–S–H) → complete macro-chemical glues.

**Enhancers**

Category 4 (CA + Nano-$SiO_2$) → strengthen and seal existing networks.

**Feedstock**

Category 5 (Pozzolanic materials) → supply Si–Al reactivity for gel or crystal growth.

Together they form a hierarchical spectrum of macro-chemical bonding mechanisms ranging from primary gel formation to secondary densification and precursor supply.

### Operationalization of the Comparative Matrix

Given the conceptual focus of this study, parameter scoring relies on reported values and standardized indices where available, and on qualitative mapping otherwise:

**Kinetics**

Time-to-set; 1-, 7-, and 28-day strength trends (for cementitious/geopolymeric systems).

**Microstructure**

Evidence from MIP, XRD/FTIR, SEM/TEM, nano-indentation (gel continuity, Ca/Si or Na/Al trends, crystalline infill).

**Macro-Performance**

Compressive/tensile strength ranges; permeability/ion diffusion; durability against sulfate, carbonation, and chloride.

**Constructability & Safety**

Handling of alkali activators or lime/slag; one-part activation feasibility; curing demands in low-humidity/high-temperature environments.

**Adoption Readiness**

Presence/absence of harmonized standards (ASTM/EN/AASHTO/RILEM), and demonstrated field trials.

**Hot-Arid Weighting**

when multiple datasets exist, we prioritize (or annotate) results obtained at elevated temperature/low humidity; otherwise, we infer sensitivity using activation energy or shrinkage/carbonation tendencies reported in the literature.

**Asphalt Baseline (for contrast)**

binder rheology (DSR/BBR, MSCR nrJ) and mixture susceptibility (Hamburg, TSR), acknowledging the absence of a macro-chemical network.

### Scope and Limitations

The methodology is designed as a synthesis of mechanisms and comparative evaluation, not as a laboratory program. While quantitative performance values (e.g., compressive strength, permeability coefficients) are referenced in the discussion section, the focus is conceptual: identifying how each binder family can be reframed as a macro-chemical bonding system rather than a supplementary material. The scope is therefore analytical and preparatory, intended to establish foundations for future experimental validation and eventual codification.

## RESULTS AND DISCUSSION

### Cement Hydration as the Benchmark of Macro-Chemical Glue

The hydration of OPC serves as the reference model of a macro-chemical bonding system. As described in the Methods section, the hydration of silicate phases ($C_3S$ and $C_2S$) generates C–S–H gel-the principal adhesive phase-while aluminate and ferrite phases ($C_3A$ and $C_4AF$) yield ettringite and related hydrates that regulate setting and early stability. This combination creates a multi-phase adhesive network that provides strength development, durability, and volumetric stability at the macro scale. Despite its success, the reliance on clinker production imposes high carbon costs, motivating the search for alternative glues that can deliver equivalent macro-scale performance through different chemistries.

### Comparative Evaluation of Alternative Systems

To structure the analysis, Table 5 compares the cement baseline (C–S–H system) with four candidate families of binders-alkali silicates (AAMs), lime/slag systems, crystalline admixtures, and nano-silica. The evaluation applies the seven-parameter matrix introduced in the Methods section, focusing on reaction pathway, primary products, gel/crystal topology, microstructural effects, macro-scale bonding performance, constructability, and institutional readiness.

**Table 5:** Comparative Framework of Macro-Chemical Bonding Systems

| **System** | **Reaction Pathway** | **Primary Binding Phase** | **Gel/Crystal Topology** | **Microstructural Effects** | **Macro-Scale Bonding** | **Constructability / Safety** | **Institutional Readiness** |
|---|---|---|---|---|---|---|---|
| Cement Hydration (Baseline) | Hydration of $C_3S$, $C_2S$, $C_3A$, $C_4AF$ | C–S–H gel, Ettringite, CH | Poorly crystalline C–S–H; AFt needles | Pore refinement, ITZ densification, CH as reactive feedstock | Proven high compressive/tensile strength, durable under standards | Widely available, safe, familiar to industry | Fully codified (ASTM, EN, ACI) |
| Alkali Silicates / AAMs | Dissolution–polycondensation of aluminosilicates with $Na_2SiO_3$ / NaOH | N–A–S–H gel | 3D aluminosilicate networks, highly polymerized | Low permeability, refined microstructure, shrinkage/carbonation risks | High strength/durability shown in lab; sensitive to mix ratios | Handling of alkaline activators (safety issue); one-part methods improving | Not yet codified; pilot standards under RILEM |
| Lime / Slag Systems (AAS) | Activation of slag with lime or moderate alkali | C–A–S–H gel | Cross-linked calcium-aluminosilicate chains | Dense ITZ, fast early strength; carbonation shrinkage risk | Cement-like mechanical performance; variability with slag source | Safer than NaOH; compatible with blended cements | Limited codification; recognized as SCM not as independent glue |
| Crystalline Admixtures (CA) | Nucleation and growth of insoluble crystals in pores | Modified C–S–H + insoluble crystalline deposits | Crystalline infill within voids and cracks | Self-sealing effect, permeability reduction | Enhanced durability; strength improvements variable | Easy to dose; proprietary composition limits reproducibility | No dedicated standards; accepted as admixture not binder |
| Nano-Silica (NS) | Secondary pozzolanic reactions + nucleation sites | Additional C–S–H gel | Nanoscale clusters, high-surface nucleation | Refines pore structure, strengthens ITZ | Increases strength, reduces chloride ingress | Sensitive to dispersion; scaling challenges | Widely studied; accepted only as additive |

## Discussion of Comparative Trends

### Reaction Diversity

Whereas OPC relies exclusively on hydration, alternatives demonstrate broader pathways-dissolution–polycondensation (AAMs), lime-induced C–A–S–H growth, in-situ crystal propagation (CA), and nucleation amplification (NS). This diversity suggests multiple possible chemistries can achieve macro-scale adhesion.

### Binding Phase Characteristics

N–A–S–H gels provide highly polymerized frameworks, while C–A–S–H mimics C–S–H but with enhanced alumina incorporation. Crystalline admixtures differ by producing discrete crystals rather than gels, while nano-silica intensifies gel continuity.

**Microstructural Impacts**

All alternatives share a trend toward pore refinement and ITZ strengthening, though shrinkage and carbonation remain risks for AAMs and slag systems. Crystalline admixtures uniquely address permeability through self-sealing.

**Macro-Bonding Performance**

Laboratory evidence shows comparable or superior strength and durability relative to cement. However, reproducibility depends on precursor consistency and processing.

**Practicality and Standards**

While cement remains fully codified and universally accepted, the alternatives remain constrained by limited codification and concerns about handling, scalability, and long-term validation.

### Detailed Comparative Discussion

### Alkali-Activated and Alkali-Silicate Systems (N–A–S–H Pathway)

Alkali-activated binders (AAMs) represent the most direct chemical analogue to cement hydration in terms of forming a continuous gel phase. Their dissolution–polycondensation mechanism transforms amorphous aluminosilicate precursors into a three-dimensional sodium–alumino–silicate hydrate (N–A–S–H) framework. This gel operates as a macro-chemical glue, developing a cohesive skeleton that bonds aggregate surfaces in much the same way C–S–H does for OPC. At comparable curing regimes, compressive strengths above 60 MPa and permeability reductions of more than one order of magnitude have been documented (Juenger *et al.*, 2025). Yet, the polymerization degree-and therefore macro-bond quality-depends heavily on Na/Al and Si/Al ratios as well as curing humidity.

Under hot-arid exposure, uncontrolled moisture loss can disrupt the gel network, leading to shrinkage micro-cracks that weaken macro-scale continuity. One-part (dry) activator technologies now address safety concerns of liquid $NaOH/Na_2SiO_3$ and offer improved field constructability (Kastiukas *et al.*, 2024). Conceptually, Within the MCB framework, N–A–S–H gels satisfy the chemical and structural criteria of macro-scale adhesion and are interpreted as distinct mechanistic families within the MCB lens, rather than supplementary modifiers.

### Lime/Slag Systems (C–A–S–H Pathway)

Lime- or slag-activated systems form calcium–alumino–silicate hydrate (C–A–S–H) gels that are structurally similar to the C–S–H of cement yet denser and more cross-linked due to aluminum incorporation. In the macro-chemical context, this means a tighter gel network and improved adhesion continuity across the aggregate–binder interface. The high calcium content also accelerates early-age bonding, producing strength gains within 24 hours that rival OPC (Aydın *et al.*, 2022). However, dimensional instability under carbonation remains a weakness, especially under Gulf-like dry heat, where rapid $CO_2$ diffusion alters the Ca/Si ratio and disrupts the gel's cohesive integrity (Zhang *et al.*, 2021). Despite these challenges, the Ca-rich chemistry offers a bridge between familiar cement technology and next-generation binders: a hybrid macro-chemical system capable of integrating with existing codes once long-term durability data are consolidated.

### Crystalline Admixtures (Self-Growing Networks)

Crystalline admixtures (CA) diverge fundamentally from gel-forming systems by relying on in-situ crystal propagation rather than polymeric gelation. When moisture penetrates the matrix, reactive compounds within the admixture use free $Ca(OH)_2$ and unhydrated silicates to precipitate insoluble crystalline salts that fill pores and microcracks. This progressive infilling converts an initially porous cement matrix into a self-sealed continuum-effectively a reactive macro-crystalline glue. In macro-chemical terms, CA introduces a secondary bonding phase that enhances durability without changing the original gel chemistry. Reported permeability reductions reach 70–90%, and repeated wetting–drying cycles can trigger self-healing behavior (Snoeck & De Belie, 2021). Yet, variability across proprietary formulations makes reproducibility difficult; overdosing may inhibit hydration, while under-dosing yields negligible improvement (Tiwari *et al.*, 2022). Nevertheless, crystalline admixtures demonstrate that controlled crystal growth can complement gel networks as an additional bonding pathway.

### Nano-Silica and Nano-Engineered Additives (Amplified C–S–H Networks)

Nano-silica (NS) differs from the other alternatives in that it enhances rather than replaces the existing macro-chemical glue. Acting as nucleation centers, NS particles accelerate C–S–H formation, refine pore structure, and improve the interfacial transition zone (ITZ). From a bonding perspective, this translates to a denser, more continuous adhesive network and improved aggregate–paste coupling. Strength gains of 15–25% and permeability reductions up to 60% have been reported at optimized dosages below 3 wt% (Kashani *et al.*, 2024). However, benefits are highly dose-sensitive. Excess nano-silica can agglomerate, trapping air and raising water demand-effects that fragment rather than reinforce the macro glue (Zhang *et al.*, 2023). At its best, nano-silica functions as a macro-chemical amplifier, intensifying the continuity of existing gel phases (C–S–H or C–A–S–H) and thereby improving the mechanical and durability performance of macro-chemical framework applicable to various composite systems.

### Comparative Insights

Viewed through a unified macro-chemical lens, the four mainstream families express distinct yet convergent mechanisms:

- AAMs → polymeric N–A–S–H gel generation;
- Lime/Slag → Ca–Al–Si (C–A–S–H) hybrid gels;
- Crystalline admixtures → in-situ crystal propagation/ self-sealing networks;
- Nano-silica → nucleation-driven amplification of C–S–H/C–A–S–H gels.

All target the same outcome-a continuous, load-bearing adhesive network at the macro scale-via different chemistries. The central challenge is scaling from laboratory maturity to field reliability under variable temperature–humidity regimes and construction logistics. Institutional inertia compounds this gap: asphalt benefits from a century of codification and OPC from decades, whereas these emerging glues lack harmonized design and test standards. This motivates the next step: examining non-conventional chemical glues that attain macro-scale adhesion through rapid crystallization or acid–base polymerization-e.g., CSA/CAC (ettringite- and aluminate-rich networks), MPC and broader phosphate-bonded systems, and carbonation-bonded matrices-which expand the design space beyond silicate gels.

## Emerging and Non-Conventional Chemical Glues

Beyond the mainstream families of alkali-activated, lime/ slag, crystalline, and nano-engineered systems, several non-conventional binders have recently re-emerged as potential macro-chemical glues. These materials differ from both Portland cement and alkali activation in that they generate distinct chemical networks-often faster, denser, or more thermally stable-capable of forming cohesive macro-scale adhesion.

## Magnesium Phosphate Cements (MPCs)

Magnesium phosphate cements form through acid–base reactions between lightly calcined magnesia (MgO) and a soluble phosphate salt such as ammonium dihydrogen phosphate ($NH_4H_2PO_4$). The main product, struvite ($MgNH_4PO_4·6H_2O$), crystallizes rapidly, producing an interlocked crystalline network that achieves compressive strengths above 30 MPa within two hours (Wang *et al.*, 2023). In the context of macro-chemical bonding, MPCs illustrate how ionic substitution and rapid crystal growth can produce an immediate macro-scale adhesive matrix. Their fast setting, low shrinkage, and ability to bond to asphalt and concrete substrates have positioned them for rapid pavement repair and precast applications, although cost and moisture sensitivity remain limiting factors.

## Calcium Sulfoaluminate and Aluminate Systems (CSA/CAC)

Calcium sulfoaluminate (CSA) cements, rich in ye'elimite ($C_4A_3\overline{S}$), develop strength primarily through massive

$$C_4A_3\bar{S} + 2C\hat{S}H_2 + 34H \rightarrow C_6A\hat{S}_3H_{32} + 2AH_3$$

Note: In cement chemistry notation, $S^{-}$ represents $SO_3$ within clinker phases, while S^ denotes $SO_4^{2-}$ from gypsum. The overbar on C is not used; CaO is simply denoted as C.

The resultant ettringite provides a crystalline glue characterized by rapid hardening and low $CO_2$ footprint-approximately 30–40 % lower than OPC. Similarly, calcium aluminate cements (CACs) hydrate to form $CAH_{10}$, $C_2AH_8$, and $C_3AH_6$, producing dense, chemically resistant matrices suitable for hot or aggressive environments (Lothenbach *et al.*, 2021). These systems demonstrate alternative aluminate-dominated macro-chemical pathways, with potential for sustainable, high-temperature-resistant pavements.

## Phosphate- and Carbonation-Bonded Systems

Beyond magnesium phosphates, broader phosphate-based binders-including Ca- and Al-phosphates-create M–O–P frameworks that bond strongly at ambient temperature and exhibit exceptional acid resistance (Zhou *et al.*, 2024).

Parallel research into carbonation-bonded materials, which cure under controlled $CO_2$ exposure, forms $CaCO_3$ networks that act as low-carbon macro-chemical glues. Such systems invert the conventional view of carbonation as degradation, reframing it as a constructive bonding reaction for near-net-zero construction materials.

## Bio-Chemical and Bio-Mineral Glues (MICP)

At the frontier of sustainable binding lies microbially induced calcite precipitation (MICP). Here, ureolytic bacteria such as Sporosarcina pasteurii hydrolyze urea, raising pH and inducing precipitation of $CaCO_3$ within pore spaces (DeJong *et al.*, 2022). The resulting biogenic calcite crystals bridge particles and fill voids, creating a self-healing, low-carbon, biologically driven macro-chemical bond. While mechanical strengths remain below engineered cements, MICP demonstrates that biochemical reactions can act as true macro-scale glues, opening an entirely new research axis within the macro-chemical bonding paradigm.

## Synthesis

Together, these non-conventional binders expand the conceptual map of macro-chemical bonding from purely silicate-based gels to include phosphate, carbonate, and even bio-mineral networks. Each system reinforces the central thesis of this paper: that macro-scale adhesion can arise from diverse chemical pathways-gelation, crystallization, or biomineralization-so long as they produce a continuous, load-bearing network. Their inclusion underscores the need for an integrative research framework that classifies binders not by raw material origin, but by the nature of their macro-chemical bonding mechanisms.

## Mechanistic Synthesis & Cross-System Summary (Table 6)

Table 6 consolidates the chemical, structural, and performance characteristics of all known macro-chemical bonding systems, positioning them along a spectrum from purely physical adhesion (asphalt) to advanced chemically engineered glues. The data illustrate three principal insights that clarify how binding materials should be classified. First, systems dominated by silicate gel formation-including OPC, alkali-activated (N-A-S-H), and lime/slag (C-A-S-H)-constitute the backbone of macro-chemical bonding science. They generate continuous, load-bearing networks through polymeric or cross-linked gelation, producing mechanical strengths and durability equal to or exceeding traditional cement. These systems confirm that gel formation, not merely hydration, is the governing mechanism of chemical adhesion at the macro scale. Second, crystalline and phosphate systems expand the paradigm beyond gels. Their bonding arises from rapid crystal growth or acid–base polymerization, creating dense, interlocked matrices that function as crystalline macro-glues. Magnesium-phosphate and calcium-sulfoaluminate cements exemplify how alternative ionic chemistries can produce equivalent adhesive performance while reducing $CO_2$ emissions or enabling ultra-fast setting. In these materials, crystallization replaces gelation as the route to cohesion-an equally valid form of macro-chemical bonding.Third, emerging systems-nano-engineered, carbonation-bonded, and bio-mineral binders-illustrate auxiliary or next-generation pathways. Nano-silica strengthens existing glues through nucleation amplification; carbonation-bonded matrices exploit $CO_2$ reactions to form carbonates as low-carbon glues; and microbial calcite precipitation demonstrates that even biological processes can yield structural bonding through controlled biomineralization. These categories signal a transition from purely inorganic chemistry toward hybrid and bio-chemical adhesion frameworks. From an engineering perspective, the comparative evaluation indicates that at least five families-alkali-activated (AAMs), lime/slag (C-A-S-H), magnesium-phosphate (MPC), calcium-sulfoaluminate (CSA), and calcium-aluminate (CAC)-possess the maturity and performance potential to act as full macro-chemical binders, capable of functioning as full macro-chemical binders that may, in specific applications and under appropriate standards, substitute for cement and, in some contexts, asphalt. Others, such as crystalline and nano-silica systems, play complementary or amplifying roles that enhance durability when blended with existing matrices. Collectively, these findings reinforce the central thesis of this study: macro-chemical bonding is not confined to a single chemistry but represents a family of adhesive mechanisms-gelation, crystallization, and biomineralization-that can each achieve macro-scale cohesion through engineered chemical networks. This broader framework now sets the stage for the final synthesis and concluding discussion on how these diverse pathways can be unified into a coherent

**Table 6:** Comparative Summary of Macro-Chemical Bonding Systems and Their Potential as Full Binders

| **Binder / System** | **Dominant Chemistry** | **Main Reactive Species / Rich in** | **Primary Binding Mechanism** | **Resulting Network Type** | **Relative Strength & Durability** | **Potential as Full Binder Alternative to Cement/ Bitumen** |
|---|---|---|---|---|---|---|
| Asphalt (baseline physical) | Hydrocarbon viscoelastic | Bitumen hydrocarbons | Physical coating and cohesion via viscosity | None (no chemical bonding) | Moderate strength; poor thermal durability | Not chemical; purely physical adhesion |
| Portland Cement (OPC) | Hydration (Ca–Si–O–H) | **$Ca0, Si0_2, Al_20_3, Fe_20_3$** | Hydration → C–S–H + Ettringite | Semi-crystalline C–S–H gel | High compressive strength; good durability; high $CO_2$ footprint | Reference chemical glue |
| Alkali-Activated / Alkali-Silicate (AAMs) | Alkali activation / polycondensation | $Na_2O$, $SiO_2$, $Al_2O_3$, $Na_2SiO_3$ (sodium silicate activator; Si-rich) | Dissolution → N–A–S–H gel formation. $Na_2SiO_3$ modulus controls gel polymerization and bond density. | 3-D polymeric aluminosilicate gel | Very high strength (>60 MPa), low permeability; shrinkage risk. Note: High strength (>60 MPa) when $Na_2SiO_3$/NaOH ratio optimized. | Strong candidate; requires standards |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Bio-Mineral (MICP) | Carbonation-Bonded Systems | Phosphate-Bonded (Ca/ Mg/Al) | Calcium Aluminate (CAC) | Calcium Sulfoaluminate (CSA) | Magnesium Phosphate Cements (MPC) | Nano-Silica (NS) | Crystalline Admixtures (CA) | Lime / Slag (C-A-S-H) |
| Biochemical precipitation | $CO_2$ curing | Acidic polymerization | Aluminate hydration | Ettringite-forming hydration | Acid–base reaction | Secondary pozzolanic / nucleation | Nucleation–growth | Ca–Al–Si hydration |
| $Ca^{2+}$ + urease activity → $CO_3^{2-}$ | $Ca(OH)_2$, $Mg(OH)_2 + CO_2$ | $Ca^{2+}/Mg^{2+}/Al^{3+} + PO_4^{3-}$ | $Al_2O_3$, CaO | CaO, $Al_2O_3$, $SO_3$ | $MgO + PO_4^{3-}$ | $SiO_2$ (nano-scale) | $Ca^{2+}$, silicates, proprietary salts | CaO, $SiO_2$, $Al_2O_3$ (from slag) |
| Microbial-induced $CaCO_3$ deposition | Carbonation → $CaCO_3$ / $MgCO_3$ matrix | Formation of M–O–P networks | Hydration → $CAH_{10}$ / $C_2AH_8$ / $C_3AH_6$ | Ye'elimite + gypsum → Ettringite | Precipitation → $MgNH_4PO_4{\cdot}6H_2O$ (Struvite) | Nucleation → extra C–S–H formation | Crystallization within pores | Lime/alkali activation → C–A–S–H gel |
| Discrete calcite bridges | Dense crystalline carbonate network | Amorphous–crystalline hybrid | Dense crystalline hydrates | Needle-like crystalline network | Interlocked crystalline matrix | Densified micro-gel network | Interlocking crystalline network | Cross-linked gel similar to OPC |
| Self-healing; limited strength (<15 MPa) | Moderate strength; excellent sustainability | Strong chemical adhesion; acid-resistant | High chemical resistance; thermal stability | Rapid hardening; lower $CO_2$; durable | Very high early strength (>30 MPa in 2 h) | +15–25 % strength; refines ITZ | Excellent impermeability; moderate strength gain | High strength, fast set; carbonation sensitivity |
| Emerging bio-glue; developmental | Low-carbon niche binder | Specialized macro glue | High-temperature macro glue | Low-carbon cement alternative | Effective rapid-set chemical glue | Enhancer of existing glue | Complementary glue; not standalone binder | Hybrid system; promising for hot climates |

classification and research roadmap.

### Feedstock–Driven Effects of Pozzolanic Precursors Across Macro-Chemical Systems

Treating pozzolanic precursors as feedstock-rather than independent binders-clarifies how precursor chemistry governs the continuity of macro-chemical glues in both gel-forming (C–S–H/C–A–S–H/N–A–S–H) and crystal-forming pathways. Three design levers dominate: (1) Amorphous/glassy content and fineness, which set dissolution kinetics and nucleation density; (2) Oxide envelope ($SiO_2$–$Al_2O_3$–CaO–MgO–$Fe_2O_3$, with minor $SO_3$/alkalis), which steers the target gel family and crystal propensities;(3) Boundary conditions of $CO_2$–$H_2O$–T, which control shrinkage/carbonation risks, self-sealing potential, and early network continuity. Beyond common fly ash (Class F/C), metakaolin, and GGBFS, practical feedstocks include natural pozzolans (volcanic ash/pumice/scoria), calcined clays/shales, silica fume and rice-husk ash, and oil shale ash (OSA) from oil-shale combustion.

Volcanic pozzolans are typically high-silica/low-lime and favor highly polymerized N–A–S–H or low-Ca C–S–H networks; silica fume (≥≈85% $SiO_2$) acts primarily as an ultra-reactive nuclei provider and CH-consumer; rice-husk ash (amorphous $SiO_2$ if well-burnt) delivers similar micro-silica effects with agricultural circularity; while OSA is Ca- and $SO_3$-rich and can express latent hydraulic/alkali-activated behavior depending on fineness and blending strategy, enabling hybrid C–A–S–H development or accelerated early stiffness in mixed systems (representative ranges reported in the literature).

**Implementation cue (Table 7)**

A sensitivity map crossing precursor class (FA-F/FA-C, MK, GGBFS, natural pozzolans, silica fume, rice-husk ash, calcined clays/shales, oil shale ash) × reactivity indices (amorphous/glassy content, fineness, basicity, soluble alkalis/minor oxides) × target network family (C–S–H / C–A–S–H / N–A–S–H / crystalline infill) × environmental envelope (T–RH–$CO_2$; moisture/ion exposure) → recommended activator modulus/dosage, w/b and curing windows, and early-age shrinkage/carbonation risk levels. The table. 7 below operationalizes these links for design/specification across climates (including but not limited to hot-arid): it maps precursor class → oxide envelope → reactivity levers → target network tendency → risks/mitigations → standards

**Table 7:** Pozzolanic Precursors as Feedstock Across Macro-Chemical Systems (design-oriented summary)

| **Precursor class** | **Typical oxide envelope (wt%)** | **Reactivity levers** | **Target gel / network tendency** | **Activation & mixability** | **Climate risks** | **Mitigations / design cues** | **Standards anchor*** |
|---|---|---|---|---|---|---|---|
| Class F Fly Ash (FA-F) | $SiO_2$ ~50–65; $Al_2O_3$ ~20–30; CaO <10; $Fe_2O_3$ 4–10 | Glass↑; fineness↑ | N–A–S–H (AAM); secondary C–S–H (OPC blends) | $Na_2SiO_3$/NaOH (AAM); CH consumption in OPC | Slow early strength; drying shrinkage | One-part activators; internal curing; fine limestone filler | ASTM C618 (Class F) |
| Class C Fly Ash (FA-C) | $SiO_2$ ~35–50; $Al_2O_3$ ~15–25; CaO ~15–30 | Latent hydraulicity; fineness | Mixed C–A–S–H/ N–A–S–H (AAM); robust secondary C–S–H | Moderate alkali or lime activation | Carbonation susceptibility in dry $CO_2$ | Early membrane curing; low w/b; SCM synergy | ASTM C618 (Class C) |
| Metakaolin (MK) | $SiO_2$ ~50–55; $Al_2O_3$ ~40–45; CaO <2 | High amorphous Al–Si; platelets | Highly cross-linked N–A–S–H; dense secondary C–S–H | Low-to-moderate alkali demand; strong filler effect | Heat evolution; rheology penalties at high dose | Dispersants; staged dosing (≤10% bwb typical) | (Covered as natural pozzolan under ASTM C618) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Oil Shale Ash (OSA) | Fly ash: $SiO_2$ ~20–30; CaO ~30–40. Bottom ash: $SiO_2$ ~5; CaO ~50; $SO_3$ often elevated | Fineness; free-lime/ anhydrite content; blending | Hybrid C–A–S–H; latent hydraulic/alkali-activated response | Lime/alkali co-activation; ternary blends (e.g., MK/RHA) | Expansion/carbonation if unmanaged; variability by source | Tight grading; sulfate balance; early curing; binary/ternary SCM design | (No dedicated international spec; classify by ASTM C618 testing analogs) |
| Calcined Clays / Shales (incl. LC²/ LC³ blends) | $SiO_2$ ~45–55; $Al_2O_3$ ~30–40; CaO <5 | Dehydroxylation degree; fineness | Secondary C–S–H; Al-rich C–A–S–H | OPC blends; hybrid LC³-type | Early shrinkage in dry heat | Wet curing; limestone synergy; shrinkage reducer | EN 197-5 families (CEM II/CEM VI) |
| Natural Pozzolan (Volcanic ash / pumice / scoria) | $SiO_2$ often >50; $Al_2O_3$ 10–20; CaO low (source-dependent) | Glassy phase; fineness | Low-Ca C–S–H; highly polymerized N–A–S–H (AAM) | OPC blends or alkali activation | Variability; slower early strength | Fine grinding; alkali/lime co-activation | ASTM C618 “natural pozzolan” |
| Rice-Husk Ash (RHA) | $SiO_2$ ~85–95 (amorphous if well-burnt) | Porous/high SSA; controlled burn | Secondary C–S–H; contributes to N–A–S–H | Lime or alkali activation; blends | Water demand; variability | Controlled calcination; grinding; superplasticizer | (Guides/local; aligns with C618 intent) |
| Silica Fume (SF) | $SiO_2$ ≥~85 (amorphous) | Extreme fineness; nucleation | Additional C–S–H; ITZ densification | OPC blends; micro-dosage in hybrids | Workability loss; agglomeration | High-range WR; slurry form; ≤10% typical | ASTM C1240 ($SiO_2$ ≥85% typical) |
| GGBFS (slag) | $SiO_2$ ~30–38; $Al_2O_3$ ~8–14; CaO ~35–45; MgO ~8–12 | Glass content; basicity ($CaO/SiO_2$) | C–A–S–H dominant; hybrid gels | Lime or moderate alkali; one-part feasible | Carbonation shrinkage at low RH | Moisture-retentive curing; $Al_2O_3$ tuning; micro-silica blend | ASTM C989/C989M (slag cement) |

**Standards anchor = common normative references used to classify/accept the precursor; local equivalents may apply.*

anchors where applicable.

Takeaway. This feedstock map supports a mechanism-first specification logic-selecting and conditioning precursors to preserve gel/crystal continuity under the expected $CO_2$–$H_2O$–T envelope-while leaving room for region-specific optimization (e.g., hot-arid, temperate, coastal).

**Synthesis Discussion**

The comparative results across all binder families reveal that macro-chemical bonding is best understood not as a material class but as a mechanistic paradigm-a shift from what a binder is made of to how it achieves cohesion. Traditional classifications (cementitious, bituminous, polymeric, or geopolymeric) describe composition, whereas the macro-chemical approach classifies binders according to the mechanism of adhesion they produce at the macro scale: gelation, crystallization, or biomineralization.

**From Material to Mechanism**

At its core, every successful binder performs three universal functions: (i) creating a continuous load-bearing network, (ii) distributing stresses uniformly across the granular skeleton, and (iii) resisting environmental degradation. In cement, this occurs through the formation of C–S–H gel that interlocks particles into a rigid continuum. In alkali-activated systems, the N–A–S–H network accomplishes the same task through polycondensed aluminosilicate chains. In crystalline and phosphate systems, the interlocking occurs through rapid crystal growth and ionic cross-linking rather than amorphous gelation. In bio-mineral systems such as MICP, the same structural continuity is achieved biologically through calcite precipitation. Thus, while chemistries differ, the functional outcome-a chemically generated macro-scale glue-remains consistent.

### A Unified Framework of Macro-Chemical Adhesion

When examined collectively, three mechanistic categories emerge:

### Gel-Based Bonding

Dominated by silicate or aluminosilicate polymerization (C–S–H, C–A–S–H, N–A–S–H); characterized by semi-crystalline continuity and strong mechanical integration.

### Crystal-Based Bonding

Formed through precipitation and growth of ordered mineral networks (Ettringite, Struvite, $CaCO_3$); excels in permeability control and dimensional stability.

### Hybrid / Bio-Chemical Bonding

Encompassing nano-enhanced, phosphate, and microbial systems that combine gelation, nucleation, or biomineralization; represents the frontier of low-carbon and adaptive binders.

This tripartite framework provides a rational taxonomy for future research: instead of segregating materials by composition (cementitious vs. geopolymeric), they can be evaluated by bonding mechanism, facilitating cross-disciplinary design and codification.

### Performance Convergence and Divergence

Despite chemical diversity, convergent trends appear. All effective macro-chemical glues achieve microstructural densification, ITZ strengthening, and permeability reduction-metrics directly correlated with long-term durability. Divergence arises mainly in kinetic behavior and institutional acceptance: fast-setting systems (MPC, CSA) contrast with slower-evolving AAMs, and while OPC enjoys full codification, most alternatives remain trapped at the pilot or standardization stage. Addressing this gap requires performance-based codes that evaluate adhesion and cohesion as functional outcomes, rather than prescribing material composition.

### Implications for Pavement Engineering

For pavement and infrastructure applications, the macro-chemical bonding perspective introduces new design flexibility. Instead of optimizing asphalt content or cement dosage, engineers can design the chemical glue itself-selecting whether the target mechanism should be rapid crystallization (for fast repair), polymeric gelation (for high strength), or bio-mineralization (for self-healing and sustainability). This reframing aligns with the principles of the circular economy and material decarbonization, enabling future pavements that are engineered from chemistry upward rather than from material tradition downward.

### Transition Toward Institutional Recognition

Finally, the discussion highlights the structural barrier that persists between laboratory innovation and field acceptance. The success of Portland cement as the first macro-chemical glue was not purely technical-it was institutional. To unlock similar adoption for next-generation binders, research must converge with codification, creating test protocols that measure macro-chemical bond integrity across gels, crystals, and biomineral matrices. Only through such codification can alternative binders evolve from academic materials to standardized macro-chemical systems with the credibility to complement-and where appropriate, substitute for-incumbent asphalt- and cement-based solutions in critical infrastructure.

### Design Implications for Climate-Specific Macro-Chemical Binders

The synthesis suggests a pragmatic route for hot-arid pavements: (i) prioritize gel continuity resilient to drying (e.g., Ca-rich C–A–S–H or hybrid gels) and validate carbonation resistance; (ii) use one-part activation or benign activator chemistries to improve constructability and safety; (iii) combine gel-formers with crystalline self-sealing (CA) and nano-silica amplification to stabilize the ITZ; and (iv) adopt performance-based acceptance that couples surface-energy-based adhesion metrics with durability under high-temperature/low-humidity curing. This design logic operationalizes macro-chemical bonding into a field-ready path for next-generation binders in desert climates.

## CONCLUSION

This study introduces the macro-chemical bonding (MCB) framework to reinterpret binding systems in pavement and construction materials through their chemical cohesion mechanisms rather than material origin. Using ordinary Portland cement (OPC) as the baseline and comparing gel-, crystal-, and hybrid-based binders, the results show that multiple chemistries can form dense, load-bearing networks capable of structural performance and environmental durability. Gel-based systems (C–S–H, C–A–S–H, N–A–S–H) demonstrate the ability to create durable matrices comparable to conventional cement, while crystal-based binders such as magnesium–phosphate and calcium sulfoaluminate/aluminate form low-permeability crystalline networks acting as strong chemical glues. Hybrid and bio-chemical systems such as nano-silica enhancement and microbial calcite precipitation- extend the paradigm toward adaptive and low-carbon bonding pathways.

Beyond its analytical outcomes, this paper establishes Macro-Chemical Bonding as a foundational research discipline a scientific school that frames future innovation in alternative binders and sustainable pavements. The framework serves as the intellectual basis for upcoming applied systems, without disclosing or depending on any proprietary formulations. The study consolidates a five-category taxonomy: (1) C–S–H as the hydration baseline, (2) C–A–S–H for lime/slag systems, (3) N–A–S–H for alkali-activated binders, (4) crystalline and nano-engineered enhancers, and (5) pozzolanic feedstock as reactive precursors. This structure bridges traditional cement chemistry with next-generation binders, showing that all converge on the same functional outcome a continuous macro-scale chemical glue that bonds aggregates and distributes stresses. Future research can build on this framework to quantify bonding efficiency, durability indices, and thermal resilience across different macro-chemical systems. The primary barrier to adoption remains institutional, not scientific. Developing performance-based standards and climate-specific specifications is essential for enabling the codification and large-scale adoption of macro-chemical bonding in future sustainable pavement systems.

## Disclosure Note

This paper presents a conceptual and theoretical framework only. It does not include or rely on any proprietary composition, formulation, or system under patent evaluation.

## REFERENCES

Adamson, A. W., & Gast, A. P. (1997). *Physical chemistry of surfaces* (6th ed.). Wiley.

American Association of State Highway and Transportation Officials. (2017). *AASHTO T 324-17: Standard method of test for Hamburg wheel-track testing of compacted asphalt mixtures.* AASHTO.

American Association of State Highway and Transportation Officials. (2021). *AASHTO M 332-21: Standard specification for performance-graded asphalt binder using multiple stress creep recovery (MSCR).* AASHTO.

American Association of State Highway and Transportation Officials. (2022). *AASHTO T 283-22: Standard method of test for resistance of compacted asphalt mixtures to moisture-induced damage.* AASHTO.

American Association of State Highway and Transportation Officials. (2022). *AASHTO T 313-22: Standard method of test for determining the flexural creep stiffness of asphalt binder using the bending beam rheometer (BBR).* AASHTO.

American Association of State Highway and Transportation Officials. (2022). *AASHTO T 315-22: Standard method of test for determining the rheological properties of asphalt binder using a dynamic shear rheometer (DSR).* AASHTO.

American Association of State Highway and Transportation Officials. (2023). *AASHTO M 320-23: Standard specification for performance-graded asphalt binder.* AASHTO.

American Association of State Highway and Transportation Officials. (2023). *AASHTO T 393-23: Standard method of test for indirect tensile cracking test (IDEAL-CT) for asphalt mixtures.* AASHTO.

Alves, B. I. A., Pereira, E., & Teles, R. (2024). Alkaline activation of binders: A comparative study of slag, fly ash, and metakaolin systems. *Materials, 17*(1), 152. https://doi.org/10.3390/ma17010152

Ammar, M. A., Chegenizadeh, A., Budihardjo, M. A., & Nikraz, H. (2024). The effects of crystalline admixtures on concrete permeability and compressive strength: A review. *Buildings, 14*(9), 3000. https://doi.org/10.3390/buildings14093000

ASTM International. (2018). *ASTM D4124-09(2018): Standard test method for separation of asphalt into four fractions.* ASTM International.

ASTM International. (2018). *ASTM C989/C989M-18: Standard specification for slag cement for use in concrete and mortars.* ASTM International.

ASTM International. (2019). *ASTM D8225-19: Standard test method for determination of cracking tolerance index of asphalt mixture using the indirect tensile test (IDEAL-CT).* ASTM International.

ASTM International. (2020). *ASTM C1240-20: Standard specification for silica fume used in cementitious mixtures.* ASTM International.

ASTM International. (2023). *ASTM C618-23: Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete.* ASTM International.

Aydın, S., Baradan, B., & Yılmaz, G. (2022). Early strength development and durability of lime–slag binders: Comparative analysis with OPC. *Construction and Building Materials, 349,* 128750. https://doi.org/10.1016/j.conbuildmat.2022.128750

Bernal, S. A., & Provis, J. L. (2014). Durability of alkali-activated materials: Progress and perspectives. *Journal of the American Ceramic Society, 97*(4), 997–1008. https://doi.org/10.1111/jace.12831

Cui, Y., Ai, W., Tekle, B. H., Liu, M., Qu, S., & Zhang, P. (2023). State-of-the-art review on the production and bond behaviour of reinforced geopolymer concrete. *Discover Sustainability, 3,* 27. https://doi.org/10.1007/s43621-023-00127-1

De Belie, N. (2018). A review of self-healing in cementitious materials. *Materials and Structures, 51,* 130. https://doi.org/10.1617/s11527-018-1257-5

DeJong, J. T., Mortensen, B. M., Martinez, B. C., & Nelson, D. C. (2022). Bio-mediated soil improvement and carbon sequestration through microbial-induced calcite precipitation. *Cement and Concrete Research, 157,* 106815. https://doi.org/10.1016/j.cemconres.2022.106815

Elahi, M. M. A., Hossain, M. M., Karim, M. R., Zain, M. F. M., & Shearer, C. (2020). A review on alkali-activated binders: Materials composition, curing regimes and performance. *Construction and Building Materials, 260,* 120452. https://doi.org/10.1016/j.conbuildmat.2020.120452

Elzeadani, M., Bompa, D. V., & Elghazouli, A. Y. (2022). One-part alkali-activated materials: A state-of-the-art review. *Journal of Building Engineering, 57,* 104874. https://doi.org/10.1016/j.jobe.2022.104874

European Committee for Standardization. (2015). *EN 450-1: Fly ash for concrete—Definitions, specifications and conformity criteria.* CEN.

European Committee for Standardization. (2021). *EN 197-5: Common cements—Part 5: CEM II/CEM VI cements containing calcined clay and limestone.* CEN.

Fernández-Jiménez, A., Palomo, A., & Shi, C. (2020). Variability in blast furnace slag reactivity: Implications for performance of alkali-activated binders. *Cement and Concrete Research, 136,* 106182. https://doi.org/10.1016/j.cemconres.2020.106182

Gartner, E., & Quillin, K. (2007). Low-$CO_2$ cements based on calcium sulfoaluminate. *Environmental Science & Technology, 41*(17), 6136–6141. https://doi.org/10.1021/es062907k

International Energy Agency. (2023). *Cement – Analysis.* https://www.iea.org/reports/cement

Juenger, M., Provis, J., & Shi, C. (2025). State-of-the-art report on alkali-activated materials. *Cement and Concrete Research, 180,* 107655. https://doi.org/10.1016/j.cemconres.2025.107655

Kashani, A., Al-Majidi, M., & Thomas, P. (2024). Advances in nano-silica–modified cementitious composites: A critical review. *Construction and Building Materials, 392,* 131932. https://doi.org/10.1016/j.conbuildmat.2024.131932

Kastiukas, G., Malaiškienė, J., & Perković, V. (2024). Advances in one-part alkali-activated binders: From precursors to performance. *Construction and Building Materials, 390,* 131850. https://doi.org/10.1016/j.conbuildmat.2024.131850

Lesueur, D. (2009). The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science, 145–146,* 42–82. https://doi.org/10.1016/j.cis.2008.08.011

Lothenbach, B., Ben Haha, M., & Winnefeld, F. (2021). Thermodynamic modeling of calcium aluminate cements. *Cement and Concrete Research, 149,* 106534. https://doi.org/10.1016/j.cemconres.2021.106534

Mohammed, A., Rashid, K., & Al-Khalaf, S. (2023). Effect of crystalline admixtures on the permeability and mechanical performance of concrete. *Construction and Building Materials, 371,* 130949. https://doi.org/10.1016/j.conbuildmat.2023.130949

Petersen, J. C. (2009). *A review of the fundamentals of asphalt oxidation* (Transportation Research Circular E-C140). Transportation Research Board.

Provis, J. L. (2022). Alkali-activated materials and geopolymers: Past, present, and future. *Cement and Concrete Research, 156,* 106774. https://doi.org/10.1016/j.cemconres.2022.106774

Provis, J. L., & van Deventer, J. S. J. (Eds.). (2014). *Alkali-activated materials: State-of-the-art report* (RILEM TC 224-AAM). Springer.

Rossi, L., de Lima, L. M., Sun, Y., Dehn, F., Provis, J. L., Ye, G., & De Schutter, G. (2022). Future perspectives for alkali-activated materials: From existing standards to structural applications. *RILEM Technical Letters, 7,* 159–177. https://doi.org/10.21809/rilemtechlett.2022.160

Scrivener, K., Martirena, F., Bishnoi, S., & Maity, S. (2018). Calcined clay limestone cements (LC3). *Cement and Concrete Research, 114,* 49–56. https://doi.org/10.1016/j.cemconres.2017.08.017

Shell Bitumen. (2015). *The Shell Bitumen handbook* (6th ed.). ICE Publishing.

Shi, C., Palomo, A., & Zhang, J. (2023). Carbonation of alkali-activated materials: Mechanisms and implications. *Cement and Concrete Composites, 138,* 104934. https://doi.org/10.1016/j.cemconcomp.2023.104934

Shi, C., Roy, D., & Krivenko, P. (2022). Alkali-activated slag binders: Recent advances and future challenges. *Cement and Concrete Composites, 132,* 104616. https://doi.org/10.1016/j.cemconcomp.2022.104616

Snoeck, D., & De Belie, N. (2021). Self-healing of cementitious materials by mineral admixtures: A review. *Cement and Concrete Research, 142,* 106365. https://doi.org/10.1016/j.cemconres.2020.106365

Taylor, H. F. W. (1997). *Cement chemistry* (2nd ed.). Thomas Telford.

Tiwari, A., Goyal, S., & Singh, R. (2022). Crystalline admixtures for concrete durability: Mechanisms, performance, and limitations. *Journal of Building Engineering, 50,* 104183. https://doi.org/10.1016/j.jobe.2022.104183

van Oss, C. J., Chaudhury, M. K., & Good, R. J. (1988). Interfacial Lifshitz–van der Waals and polar interactions in macroscopic systems. *Chemical Reviews, 88*(6), 927–941. https://doi.org/10.1021/cr00088a006

Wagh, A. S. (2016). *Chemically bonded phosphate ceramics* (2nd ed.). Elsevier.

Wang, L., Zhang, D., & Li, X. (2023). Magnesium phosphate cements for rapid repair of pavement and structural materials: A review. *Construction and Building Materials, 378,* 130912. https://doi.org/10.1016/j.conbuildmat.2023.130912

Zhang, Y., Chen, B., & Wang, Q. (2022). Role of Si/Al and Na/Al ratios in the polymerization of alkali-activated gels. *Journal of Materials in Civil Engineering, 34*(10), 04022245. https://doi.org/10.1061/(ASCE)MT.1943-5533.0004522

Zhang, Y., Chen, B., & Wang, Q. (2023). Effects of nano-silica on hydration and performance of cementitious systems. *Journal of Materials in Civil Engineering,* *35*(7), 04023112. https://doi.org/10.1061/(ASCE)MT.1943-5533.0004789

Zhang, Z., Provis, J. L., Reid, A., & Wang, H. (2021). Carbonation mechanisms in alkali-activated slag concretes: Impacts on pore structure and durability. *Cement and Concrete Research, 140,* 106292. https://doi.org/10.1016/j.cemconres.2021.106292

Zhou, T., Yang, J., & Wang, H. (2024). Advances in phosphate-bonded cements and composites: Chemistry, microstructure, and performance. *Journal of Building Engineering, 72,* 107628. https://doi.org/10.1016/j.jobe.2024.107628