Oral presentation

The crystallographic diversity of pozzolanic phases in ancient Roman concrete

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The use of pozzolanic materials to trigger low-temperature hydraulic reactions in calcium-based inorganic binders has been the most relevant technological evolution in the field of construction materials since the beginning of pyrotechnology. After the first applications by ancient Mediterranean societies of the Second and First Millennium BCE, the potential of pozzolanic binders was fully exploited by ancient Romans, which used them for large-scale structural purposes through the formulation and development of Roman concrete, the so-called *Opus Caementicium*, whose enhanced durability properties are testified by the massive occurrence of well- preserved structures, even in extreme conditions. Several scholars attempted at determining the key factors of such excellent resilient behavior, imputed both to the self-healing characteristics of the employed raw materials and to the post-pozzolanic behavior of the binding composites triggered by secondary transformative processes. Nevertheless, the incidence of the hypothesized reactive dynamics in most of the dedicated scientific studies seems circumscribed to specific compositional and environmental factors, besides impacting on the overall cohesive properties of ancient binding composites only at a local, microstructural scale.

In this study, a combined mineralogical-spectroscopic-microstructural analytical approach has been adopted for the characterization of the crystal-chemical features of Roman pozzolanic binders, considering several samples collected from various archaeological sites in the Italian peninsula and around the Mediterranean region. Materials have been investigated by scanning electron microscopy and energy-dispersive X-ray spectrometry (SEM-EDS), integrating the obtained microstructural and microchemical information with an in-detail mineralogical and crystallographic characterization by X-ray powder diffraction (XRPD) and solid state nuclear magnetic resonance (NMR) on both bulk and binder-concentrated samples. Furthermore, forefront total scattering methods, based on the innovative synchrotron Wide Angle X-ray Total Scattering (WAXTS) modelling based on the Debye Scattering Equation, were applied to investigate pozzolanic phases at the atomic to the nanometre scale.

The obtained results showed a systematic shift of the investigated binding systems from the conventional lime-silica-alumina ternary diagram and its associated mineralogical assemblage of chain-like calcium silicate hydrate (C-S-H) phases with tobermoritic structure and sheet-like calcium aluminate hydrate (C-A-H) phases with layered double hydroxide structure. Indeed, most of the investigated materials are characterized by the widespread occurrence of paracrystalline calcium aluminosilicate hydrate (C-A-S-H) gels with a hybrid ino- and phyllo-silicate structure, while crystalline tobermorite has been observed only in isolated case studies employing unconventional pozzolanic materials such as highly amorphous pyroclastic products derived from rapid cooling of acidic magmas.

Furthermore, the study proved the leading role of magnesium in stabilizing the bulk cohesive framework of Roman concrete, even in extreme, saltwater-saturated environments, triggering resilient properties such as an improved resistance to acidic attack not observable in standard, calcium-based binding systems. Under a mineralogical perspective, such alternative reactive paths led to the massive precipitation of magnesium silicate hydrate (M-S-H) and magnesium aluminosilicate hydrate (M-A-S-H) phases with a phyllosilicate-like layered structure fundamentally different to that of C-S-H and stable in a wider pH range. The occurrence of active magnesium in reactive binding systems is related not only to the abundance of the element in the most common pozzolanic additives, either natural (pyroclastic sediments and structurally disordered clays) or anthropogenic (crushed ceramics and combustion residues), but also to dissolution processes of conventional carbonate aggregates such as dolostones and magnesian limestones. Such secondary processes, conventionally gathered under the broad term alkali-carbonate reactions (ACRs), are generally considered detrimental in conventional cementitious systems. Nevertheless, it has been observed that their common incidence in ancient, lime-based binding composites, together with alkali-silicate reactions (ASRs) on cryptocrystalline silicate aggregates, is able to trigger para-pozzolanic processes even when conventional pozzolans are absent, guaranteeing a hydraulic behaviour and improved resilience to degradation to mortars and concretes prepared with carbonate-rich sands.

By unravelling the crystallographic diversity of pozzolanic phases and their role in the performance and durability behaviour of ancient binding composites, this research not only enhances the understanding of Roman concrete technology but also provides valuable insights for contemporary construction practices. Harnessing the lessons from antiquity, material scientists and engineers can develop innovative cementitious materials with improved performance and sustainability, ensuring the legacy of Roman concrete continues to inspire future generations of builders.