Lessons from a lost technology: the secrets of Roman concrete

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'Roman concrete' was used as building material during Roman Imperial times for a great number of famous constructions with different functions. Well-known examples are aqueducts, for example the Pont du Gard in France and the Aqua Alexandrina in Rome, and numerous monuments such as the famous Coliseum and Pantheon in Rome. While visually less apparent today, ancient harbors also were an important part of constructions supporting the power of the Roman imperial system and were invaluable to control the Mediterranean Sea trade. The article 'Unlocking the secrets of Al-tobermorite in Roman seawater concrete' by Jackson et al. (2013) describes the investigation of a number of extremely interesting samples drilled from 2000-year-old Roman maritime concretes in 11 harbors along the Mediterranean coast (the ROMACONS project 2002-2009 (Oleson et al. 2004)).

This article delivers an outstanding contribution because the described research integrates interdisciplinary findings from mineral physics, geochemistry, engineering and archaeometry to investigate and explain reasons for the exceptional quality of these

Roman constructions even after two thousand years exposure to an aggressive sea-water environment. The article also gives novel results regarding the role of Al-tobermorite as the main cementitious binder in Roman concrete. These results offer a source of new perspectives in future research on new binder types in the context of more sustainable and more durable concrete structures.

Ancient 'Roman concretes' are complex composite cementitious materials with a hydraulic binder ('hydraulic' refers to the ability of the binder to harden under water) composed of a mixture of hydrated lime with volcanic material. Both the ancient Greeks and Romans knew that certain volcanic deposits when finely ground and mixed with lime and aggregates yielded hydraulic mortars and concrete with superior compressive strength (Blézard 1998). The Greek knowledge of the use of highly siliceous volcanic Santorini Earth (volcanic ash) goes back to 500-300 B.C., and around the third century B.C. the Romans discovered the effective use of 'Pulvis Puteolanus' (meaning earthy material from the region of Puteoli and currently named pozzolana) near Mount Vesuvius. The use of these natural pozzolana and other SCMs (Supplementary Cementitious Materials (Snellings et al. 2012)) will help in achieving improved durability of modern concretes and sustainable binder systems.

The advanced experimental methods utilized by the multidisciplinary authored team demonstrate that sharing knowledge and technical expertise from different scientific areas opens up fertile grounds for breakthrough research. In this case especially scanning transmission X-ray microscopy shed new light on the distribution of Al in the Al-tobermorite and C-A-S-H (calcium-aluminosilicate-hydrate) minerals, which form the main reaction products of Roman seawater concrete. The application of Al and Si X-ray absorption spectroscopy on dedicated instruments using synchrotron radiation at a nanometer spatial resolution is a first in the field and will certainly find more widespread application in construction materials science, applied mineralogy and archaeometry. This analytical combination, with established characterization techniques in the field of historic mortars and concrete, such as solid state Al and Si NMR spectroscopy, and EMPA and SEM-EDX microanalysis, allowed the novel results to be compared and interpreted within the current state-of-the-art on cementitious binders.

The result is that the investigated ancient Roman seawater concrete is a highly complex and composite cementitious system with a remarkably heterogeneous structure. Its mix design needed no more than 10 wt% lime (quicklime, CaO) hydrated purposely in seawater after mixing with the key ingredient of alumina-rich volcanic ash. This notably unique combination formed the fundamental cementitious binding component, the glue, which, when mixed with pozzolanic coarse aggregates of zeolitic tuff, composed a unique concrete mixture that could set quickly under seawater, become extremely strong, and remain cohesive and intact in aggressive seawater for over 2000 years. The extraordinary durability of this massive seawater concrete is exceptional and must be related to the stability of the binder phase in an aggressive marine environment. Among the most interesting findings of the paper is the high content and differential distribution of Al in the C-A-S-H and Al-tobermorite binder phases. The chemical action of alkali cations, both from the volcanic ash and seawater, and the self-elevated moderate temperatures (< 85 °C) reached during the hydration of quicklime and formation of poorly crystalline C-A-S-H were identified to be critical to the formation of Al-tobermorite. Another eye-catching finding is related to the presence of sulfate which is known to cause severe damages (i.e. delayed ettringite formation, expansion and cracking) in today’s concrete when it experiences internal temperatures above 70°C, but surprisingly has no harm to this ancient seawater concrete. This particular performance is because sulfate ions are not bound in C-A-S-H but produce individual clusters of ettringite integrated soundly in the overall cementitious matrix. In this respect, the role of Al in stabilizing the phase assemblage, prohibiting dissolution, and deleterious expansive reactions is becoming clear (Chappex and Scrivener 2013), and connects to insights on mineral dissolution gained in the field of mineralogy and geochemistry (Schott et al. 2009). Furthermore, the work of Jackson et al. (2013) delivers an important fact that pozzolanic aggregates rich in silica, alumina and alkalis undoubtedly contribute to the extended durability of this pozzolana-containing concrete without causing any damage from alkali-silica reaction, as opposed to today's common perception of concrete durability.

These findings clearly demonstrate successful ancient practice of Al- and alkali-rich binders which are now appearing as sustainable and durable alternatives to Portland cement (Juenger et al. 2008). The well-recognised but overlooked superiority of the ancient seawater concrete containing natural pozzolan is obviously a tribute to the ingenuity of Roman scientists some 2000 years ago, as well as a proven model of extended durability and sustainability from which we should learn in order to achieve improved durability of modern concrete structures and sustainable binder systems incorporating Al-tobermorite.

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