Roman Concrete 2: Discovery of the chemical processes could lead to the commercialisation of Roman-inspired hot-mixed concrete mixtures

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In 2018 Risk Frontiers published a briefing note titled 'Why is Roman volcanic concrete more durable than modern concrete?' (Risk Frontiers Briefing 365). Over the last six years further research has been conducted, and researchers now understand the processes to develop such a concrete mixture. The researchers now aim to commercialise this mixture in the hope of developing durable, resilient, and sustainable concrete mixtures (Seymour 2023).

Recap

Concrete used in modern construction projects is porous and degrades in contact with seawater. Some submerged concrete objects such as concrete piles can last less than 10 years. The seawater seeps into the pores of concrete, and once dried out the salts crystalize causing pressure, which results in stresses that lead to the formation of cracks and spalls. There are also other chemical processes such as sulfate sulphate attack, lime leaching and alkali-aggregate expansion all of which also degrade the concrete structures.

Meanwhile, 2000-year old concrete structures, constructed during the Roman Empire, are still standing. The composition of Roman concrete has been long known to be a mixture of volcanic ash, lime and volcanic rock. However, the science behind its resilience to seawater had remained unknown, until research performed by Jackson et. al. (Jackson 2017). They discovered that when sea water interacted with the Roman concrete mixture it formed the rare minerals aluminous tobermorite and phillipsite. This interaction with the environment is credited with strengthening the concrete, with tobermorite having long plate-like crystals which allow the material to bend rather than crack under stress.

New Findings

Recent research by Seymour et. al. (Seymour 2023) has found that the materials used to create Roman concrete are slightly different from what was previously believed, as well as determining the processes used to mix them. This was achieved by studying the lime clasts found in Roman concrete.

Within Roman concrete there are often small, white chunks of lime that are present. It was originally believed that these lime clasts were due to poor mixing of the materials. However, the Romans put significant effort into making such an outstanding well-mixed concrete, spending centuries optimising the mixture. Researchers did not believe that this aligned with the belief that they would then put little effort into the mixing of the materials.

Through a combination of scanning electron microscopy and energy dispersive x-ray spectroscopy, Powder x-ray diffraction, and Raman spectroscopy on the lime clasts, it was discovered that the nature of the lime used was different to previous understanding, as high temperature associated compounds were present. It was originally thought that the Romans used slaked lime. This is the process where limestone is heated at high temperatures to produce a highly reactive caustic powder called quicklime (calcium oxide), which is then mixed with water to produce slaked lime (calcium hydroxide), a slightly less reactive and a less caustic paste. However, the experimental results suggested that quicklime was mixed directly with the volcanic material and water at extremely high temperatures (potentially slaked lime was included too), a process called hot-mixing. With the concrete mixture being heated to high temperatures, it allowed chemistries to occur that are not possible if only slacked lime was used.

Benefit of Lime Clasts

The lime clasts within Roman concrete enable it to self-healing when exposed to the environment. When cracks form in modern concrete, they present structural durability issues. However, with Roman concrete, when a crack forms it typically travels towards the lime clasts as they have the highest surface area within the concrete. When water seeps into the cracks it reacts with the lime clasts to form a highly alkaline solution. This solution then carbonates as calcium carbonate and seals the crack.

The authors note that the 'entire self-healing mechanism occurs upon stimulation from external forces that would, otherwise, cumulatively result in material failure if left unchecked', and that 'the calcium-rich phases within the lime clasts remain stored until they are needed'. They credit these functions of the Roman concrete in allowing Roman structures to persist over millennia.

The authors also tested these results by making a replica of Roman concrete made using quicklime and comparing it to a control. They then performed crack tests, exposing the samples to water flow over 30 days. Whilst the control concrete remained cracked, the Roman concrete sample had been completely filled with a newly precipitated mineral phase identified as calcite.

They are now working on commercialising this Roman concrete mixture, noting that it could expand the service life of these concretes as well as improve the durability of 3D-printed concrete formulations.

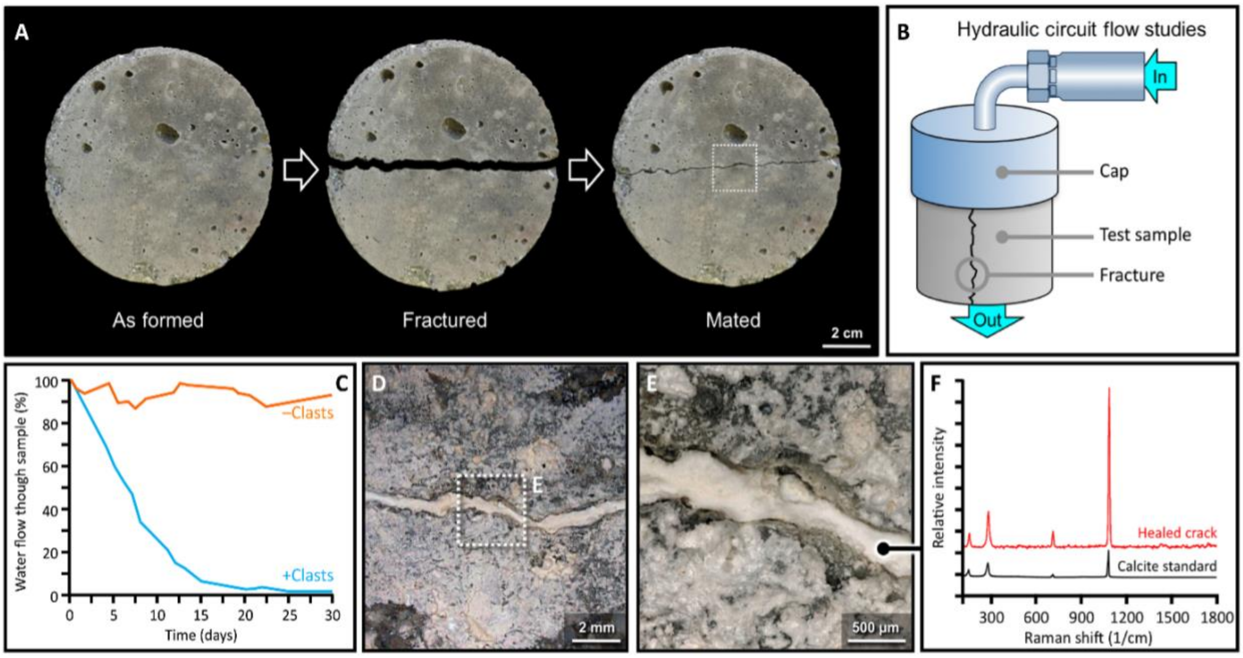

Figure 1. *Modern mortar self-healing experiments. After casting, the Roman-inspired hot-mixed concrete samples were mechanically fractured and then re-mated (with a gap of 0.5 ± 0.1 mm) and preconditioned for our crack-healing studies (A). Using an integrated flow circuit (B), water flow through the sample over the course of 30 days was documented with a flow meter. Compared to the lime clast–free control (orange line), after 30 days, water flow through the lime clast-containing sample (blue line) ceased (C), and examination of the cracked surface revealed that it had been completely filled with a newly precipitated mineral phase (D and E), which was identified as calcite from Raman spectroscopy measurements (F). Source: Fig. 5, Seymour 2023.*

Benefits

It is envisioned that Roman concrete mixtures could help reduce the environmental impact of cement production. The Roman concrete mixture has an extended functional lifespan and could lead to the development of lighter-weight concrete forms. Concrete production currently accounts for at least eight percent of global greenhouse gas emissions (Ellis 2020).

The Roman concrete mixtures could also be used in high degradation environments. Construction along the coast, where saltwater poses a degradation threat to concrete structures, could be made more resilient. Similarly, for structures within the ocean, such as piles for bridges, it could improve the lifespan and reduce the maintenance. It could also help with the structural stability of dams, with over 200 notable dam failures happening worldwide between 2000 and 2009 (Jonkman 2008).

REFERENCES

Ellis, Leah D., et al. "Toward electrochemical synthesis of cement—An electrolyzer-based process for decarbonating $CaCO_3$ while producing useful gas streams." Proceedings of the National Academy of Sciences 117.23 (2020): 12584-12591.

Jackson, M.D. et. al. Phillipsite and Al-tobermorite mineral cements produced through low-temperature water-rock reactions in Roman marine concrete. American Mineralogist: Journal of Earth and Planetary Materials, 102(7), pp.1435-1450 (2017).

Jonkman, Sebastiaan N., and Johannes K. Vrijling. "Loss of life due to floods." Journal of Flood Risk Management 1.1 (2008): 43-56.

Seymour, Linda M., et al. "Hot mixing: Mechanistic insights into the durability of ancient Roman concrete." Science advances 9.1 (2023): eadd1602.

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Jacob has been involved in the development of our FloodAUS, CyclAUS and QuakeAUS Cat-Loss models. He specialises in data science and mathematics.
Jacob received his PhD in Condensed Matter Physics from Macquarie University. Jacob's interests include data science, numerical modelling, physics and mathematics.

Joining Risk Frontiers in 2017, Jacob has worked across a range of projects from model development and climate risk management to resilience and portfolio modelling.

Notably, Jacob has employed techniques such as machine learning and statistical analysis to understand the vulnerability of risk across Risk Frontiers catastrophe suite, as well as applying machine learning algorithms for flood, cyclone and earthquake models. He also works on hazard and loss modelling.