Saverio Russo
Università degli Studi di Genova
e Accademia Ligure di Scienze e Lettere

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LONGEVITY OF ANCIENT ROMANS' CONSTRUCTIONS EXPLAINED BY CHEMISTRY

***For centuries it has been believed that the exceptional longevity of the building material used by ancient Romans was due to the presence of a specific pozzolanic ingredient. Very recent experiments, however, have suggested a much more plausible explanation. Their concrete was not produced from slaked lime, as in modern times, but from quicklime by a hot mixing process forming clasts with a very reactive architecture. With rainwater an exothermic reaction occurs and calcium carbonate is eventually formed, healing the microcracks* in situ.**

Introduction

The exceptional longevity of the civil engineering works carried out in many areas of the world by the ancient Romans has always been a mystery. Their constructions have been quite often preserved for millennia even in very severe climatic conditions, *e.g.* in areas prone to earthquakes or in direct contact with sea water. Compared to modern concrete structures that often begin to collapse in a few decades, the most famous architectures of the ancient Romans are surprisingly still standing, at least for the most part, after more or less two thousand years from their construction and are destined to last a long time to come. When their buildings suffered damage, it has often been caused by the looting of stones rather than by structural failures.

Let us give a few examples: the Pantheon, with its unreinforced concrete vault which is the largest in the world (diameter of 43.44 m, weight over 5,000 tons) has been presumably built between 112 and 128 AD. The construction of the Colosseum (originally known as the Flavian Amphitheatre, the largest Roman amphitheatre in the world) must be placed between 70 and 80 AD under Vespasian and Titus. The beautiful Mausoleum of Cecilia Metella on the Roman Appian Way is even older by at least a century. Its building dates back to between 30 and 10 BC in the Augustan age. The aqueducts are further evidence of the exceptional longevity of the buildings

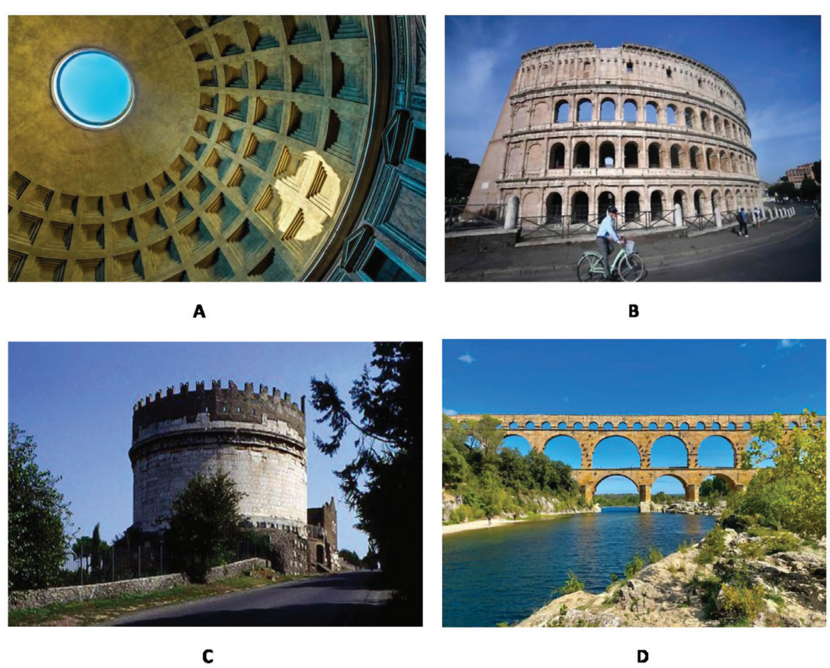

Fig. 1 - A: Pantheon; B: Colosseum; C: Mausoleum of Cecilia Metella; D: Pont du Gard

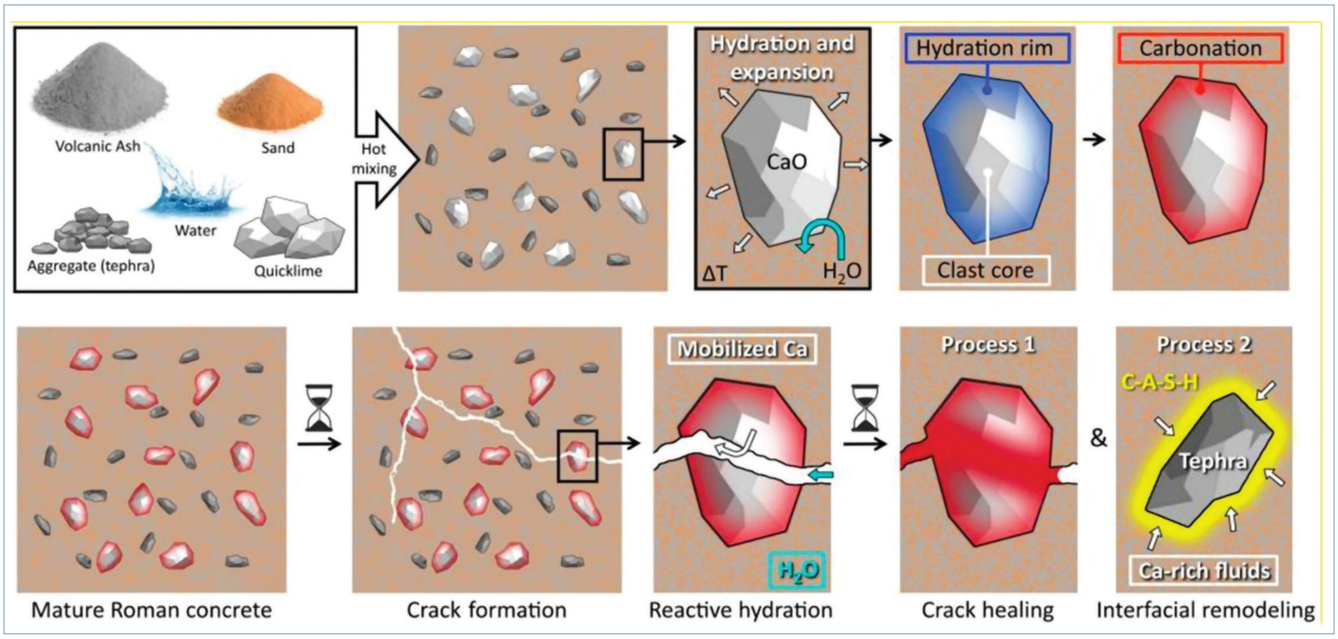

Fig. 2 - Proposed mechanism for self-healing within ancient Roman mortars (taken from [3])

made by the ancient Romans. The Pont du Gard, in the south of France, was part of an aqueduct almost 50 km long and was built around 17 BC by Agrippa under Emperor Augustus. Fig. 1 depicts the excellent status of the four constructions mentioned above to the present time.
From the third century BC to the present day, it has always been believed that the extraordinary durability of the building material used by the Romans was linked to the presence of a specific pozzolanic material, consisting of volcanic ash from the Pozzuoli area between Cumae and the promontory of Minerva in the Gulf of Naples. This ash was in fact shipped throughout the Roman territories to be used as a key ingredient in the production of concrete. In particular, but not only, it was used in the construction of foundations immersed in water for ports and bridges over rivers, according to detailed formulations widely described in *De Architectura* by Marcus Vitruvius Pollione [1], engineer and architect of the first century BC, and by contemporary Pliny the Elder [2] in *Naturalis historia*.
A very recent investigation has however suggested an alternative explanation for such exceptional performance [3]. The international research group author of the aforementioned publication has put forward a proposition, supported by very solid experimental evidence, which starts from the constant presence of small whitish and needle-like mineral inclusions of millimeter size, identified as calcium carbonate, in all ancient Roman concretes. Its formation has been considered possible only due to reactions starting from quicklime (calcium oxide) and conducted at high temperature, unlike current concrete formulations produced instead from slaked lime (calcium hydroxide).

Characterization of ancient Romans' concrete

Concrete is a composite material formed by prolonged mixing of cement, sand, gravel and any additives. Cement is produced by calcination, *i.e.* by extended heating at high temperature (T≥1500 °C), of an intimate mixture of limestone, with calcium carbonate as main component, and clay, *i.e.* hydrated aluminosilicates with dimensions less than 2 μm. Calcination produces the so-called clinker which, finely ground with the addition of small quantities of gypsum (*approx.* 2÷4%) and any additives, forms cement. The term derives from the Latin *caementum*, binder, *i.e.* material capable of binding other materials such as sand and crushed stone otherwise disaggregated.
The authors of the cited study were able to take a fragment of *ca.* 2 cm. of ancient Roman concrete from the boundary wall of the archaeological site of Priverno (second century BC) south of Rome,

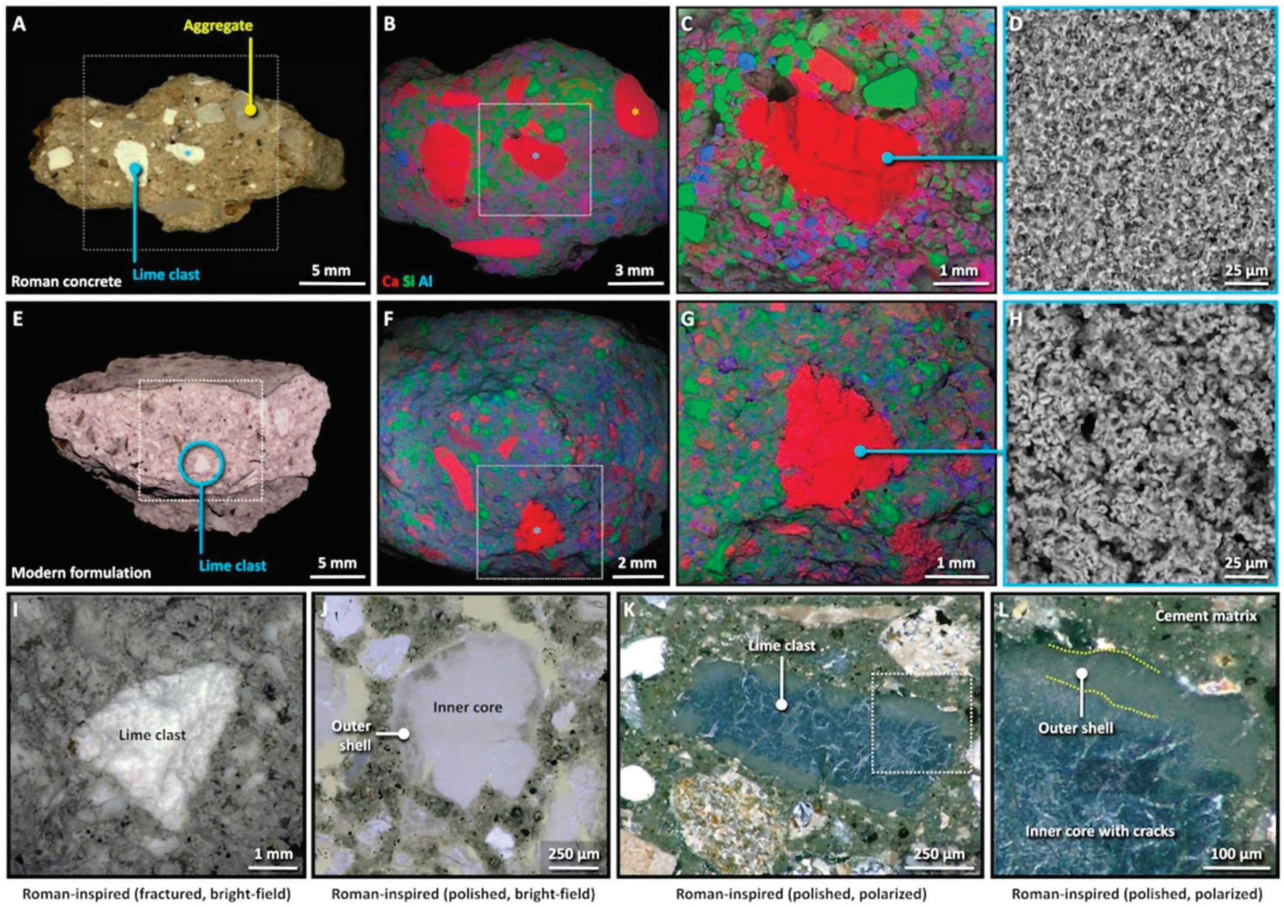

Fig. 3 - Compositional and morphological characterization of ancient and modern lime clasts (taken from [3]). A, E: Optical micrographs of quicklime clasts belonging to ancient Roman concrete and 'ancient roman-like' concrete, respectively; B, C: Elemental mapping *via* quantitative SEM-EDS of clasts of A; F, G: Elemental mapping *via* quantitative SEM-EDS of clasts of E; D, H: micro-particle architecture; I: Magnified view of a single fractured clast of E; J: inner core and outer shell of the clast (bright field); K, L: self-healed microcracks inside the clast (polarized illumination)

subjecting it to complete characterization with different analytical tools, of which the most relevant was EDS spectroscopy. The latter is an analytical technique that allows chemical characterization by elemental analysis of materials.

Based on the whole set of their analytical results, using multiscale imaging techniques and chemical mapping, Masic *et al.* [3] have proposed that the production of concrete by the ancient Romans took place by hot mixing (*e.g.* firing in an oven at high temperatures) with undoubted advantages such as the production of chemicals associated only at high temperatures, as well as a remarkable increase of the reaction rate with the ultimate result of buildings constructed in a shorter time. The predominant effect of hot mixing resulted in the formation of clasts, *i.e.* small lumps of quicklime characterized by a very fragile and highly reactive nano- and micro-particle architecture. Paradoxically, until the publication of the work of Masic *et al.* [3] these very porous clasts were considered as clear evidence of the use of poor-quality raw materials and/or of deficiencies in effective mixing. Clasts, on the contrary, proved to be essential components to ensure the exceptional resistance to deterioration present in the constructions of the ancient Romans, as they constituted a perennial source of calcium ions at the origin of the in situ formation of calcium carbonate. In fact, the quicklime clasts in the presence of microcracks were able to react with water penetrated by rain, humidity or rising from the ground, creating a saturated solution of calcium ions capable of carbonating and crystallizing as calcium carbonate, quickly filling the microcracks. In addition, calcium ions were also able to react with the aggregates of pozzolanic material, called tephra, present in the concrete, further reinforcing the latter through the formation of hydrated calcium aluminosilicates (identified by the acronym C-A-S-H), thus supporting at least in part the fundamental role of pozzolanic ash claimed by Vitruvius [1] and Pliny the Elder [2]. Fig. 2 schematizes the self-repair mechanism proposed by Masic *et al.* [3].

To endorse the above hypothesis, a pilot experiment was conducted by the same authors with the making of a sample of hot mixed concrete according to the formulations of the ancient Romans, *i.e.* using quicklime, compared with a sample based on modern formulations linked to slaked lime. A micro-crack was made on both samples that allowed the introduction of water into the cracks. In the 'ancient Roman-like' concrete after a few weeks the cracks were completely healed, while in the 'modern' concrete the water continued to flow into the cracks, thus reaffirming the full validity of the proposed self-repair mechanism.

Fig. 3 shows the characterizations of both an ancient concrete sample and a modern sample inspired to the ancient Roman one, that highlight the strong microstructural similarities between the two samples. On the 'Roman-like' specimen some self-repairing microcracks inside the clast (v. L) are also shown.

This was the secret that most probably guaranteed to the ancient Romans the achievement of the highest results in the field of civil engineering, making roads, bridges, aqueducts and buildings that lasted for millennia [4].

A modern self-repairing cement

On the basis of the very interesting results achieved and the related patent (WO 2019/204776 owned by MIT [5]), after years of tests conducted in Switzerland at the Institute of Materials Mechanics in Grancia directed by De Tommaso (one of the authors of the work in question), all the industrial certifications necessary to enter the market have been obtained and it has been possible to concretize some marketing hypotheses to be used in modern construction with new formulations of lighter and stronger concrete, capable of lasting longer and reducing environmental impact. An Italian startup called DMAT [6] was founded by Masic and Sabatini (another author of the aforementioned publication), which began to sell to various customers the formulations to make a self-healing concrete called D-Lime which, among other things, is claimed to emit a 20% lower amount of carbon dioxide during production with costs reduced by 50% compared to similar products. DMAT has recently landed in the USA giving life to a newco that deals with the development and marketing of concretes having the new characteristics. The next step will be to develop formulations for 3D printers to make eco-friendly, self-healing concrete produced without waste.

The most relevant parameters to be monitored in order to optimize commercial formulations will be those related to the control of both dosage and granulometry of quicklime, for which it is necessary to minimize contraindications such as excessive heat of hydration and initial volumetric instability.

Further developments

In few years the successful investigation by Masic *et al.* [3] on the real causes of durability in ancient Roman concrete due to its self-healing characteristics has brought to modern formulations of a more resilient, sustainable and durable concrete [5, 6], thus paving the way for the development of far-reaching applications in many different areas. Namely, three-dimensional printing looks as a very promising effort to minimize waste in concrete industry [7] and could efficiently be extended also to the self-healing process mentioned above.

Note 1

The concrete construction industry has a huge environmental impact, producing about 8% of the total greenhouse gases. If it were a nation, it would be in third position after China and the United States in CO_2 production [8]. Producing one ton of cement roughly involves the emission of one ton of CO_2 into the atmosphere.

For one cubic metre of concrete (2.2÷2.4 tonnes) approx. 300 kilograms of cement, 600 kilograms of sand, 1300 kilograms of gravel and 120 litres of water are needed [9].

Global cement production (2022 data) was about 4.37 billion tons [10], from which the production of 14 billion cubic meters of concrete was derived.

Note 2
Self-healing materials are a class of intelligent materials capable of recovering, partially or totally, mechanical damage autonomously or in response to an external stimulus. The basic idea is to integrate repair mechanisms into materials that counterbalance the degradative mechanisms resulting from their normal use [11, 12].

Note 3
During the Balkan War, which broke out in March 1992, Admir Masic was a Bosnian refugee who got asylum in Croatia, where he studied as a chemical scholar and won all the 'Olympics' in Chemistry. He collaborated with the Turin volunteer organization Collettivo Azione Pace which invited him to Italy at the end of the war, helping him to enroll at the University of Turin, finding him accommodation and financing him with economic aids from their benefactors. He graduated in Chemistry in 2001 with 110 cum laude and subsequently did a PhD in Physical Chemistry. Then after, he worked on the restoration of the Reggia di Venaria on behalf of the Piedmont Region and was a research fellow. Without a residence permit as he did not have an employment contract, he was forced to leave for Germany where he easily got a passport and started working in a renowned research center (Max Planck Institute of Colloids and Interfaces). In that context he began to interact with leading international scientific circles. He is currently a professor at the Massachusetts Institute of Technology (MIT) in Boston. As an inventor, he patented with Linda M. Seymour (WO 2019/204776, MIT property [5]) a concrete that self-repairs and allows buildings to be kept standing for a very long time, perhaps for a thousand years or even more. Furthermore, he has launched MIT ReACT [13], Refugee Action Hub (now called MIT Emerging Talent), a free program for talented refugees from all over the world to study Computer Science and Management, selecting 150 students from more than 20 countries in 7 hubs every year. The term Action in the program is an appreciation for the help he got from Collettivo Azione Pace.

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La longevità delle costruzioni degli antichi romani spiegata dalla chimica

La straordinaria longevità delle opere di ingegneria civile degli antichi romani, sorprendentemente ancora in piedi dopo due millenni, è sempre stata un mistero. Per moltissimi secoli si è creduto che l'eccezionale resistenza del loro materiale da costruzione fosse dovuta alla presenza di una specifica cenere vulcanica. Ricerche molto recenti, tuttavia, hanno suggerito una spiegazione molto più plausibile. I loro calcestruzzi non erano prodotti da calce spenta, ma da calce viva cotta ad alte temperature con formazione di clasti molto reattivi. A contatto con l'acqua piovana avviene una reazione esotermica con formazione finale di carbonato di calcio che cristallizza e salda *in situ* le microfessure, agendo da ottimo agente autoriparante.