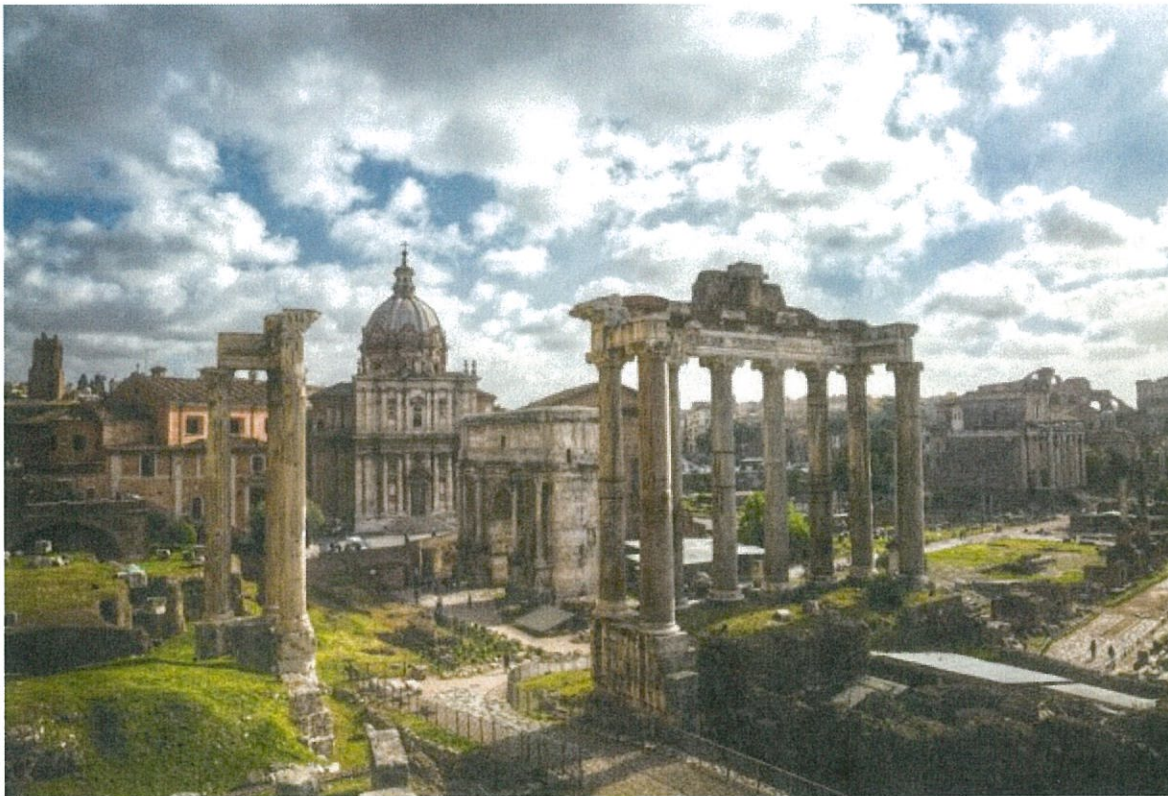


RECLAMATION

Managing Water in the West

Final Report ST-2014-01-7137

Improving Concrete Longevity and Durability: Lessons from Roman Concrete



Audrey Rager
MERL-2014-94



Research and Development Office
Bureau of Reclamation
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Mission Statements

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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Executive Summary

NEED AND BENEFIT

The manufacture of Portland cement accounts for approximately 5 percent of annual industry-produced carbon dioxide emissions (Mahasenan et al., 2003). If we can increase the durability and longevity of concrete, we can ultimately reduce carbon emissions by reducing concrete repairs and concrete structure replacement.

The manufacture of concrete releases carbon from burning fuel, required to heat a mix of limestone and clays to 1,450 degrees Celsius (2,642 degrees Fahrenheit). The heated limestone (calcium carbonate) releases carbon dioxide. Lawrence Berkeley Laboratory scientists Marie Jackson and Paulo Monteiro determined that the Romans, by contrast, used less lime and made concrete from limestone baked at 900° C (1,652° F) or lower. Thus requiring far less fuel than Portland cement (Yang, 2013).

In addition to reducing carbon emissions through lower baking temperatures, Roman concrete may be the key to stronger, longer-lasting structures. As Monteiro states "In the middle 20th century, concrete structures were designed to last 50 years, and a lot of them are on borrowed time." In contrast, Roman concrete structures have survived for 2,000 years (Yang, 2013).

The Romans made concrete by mixing lime, volcanic rock, and a small amount of water. The lime was hydrated and reacted with the ash to create cement. According to surviving writings of Vitruvius, an engineer for the Emperor Augustus, and Pliny the Elder, the best maritime Roman concrete was made with ash from the seaside town of Pozzuoli. Volcanic ash (or natural pozzolan) with similar mineral characteristics is found in many parts of the world, including the western United States. Jackson et al. (2009, 2013) argue that Romans deliberately selected alkali- and alumina-rich ash for optimal performance of pozzolanic concretes.

CURRENT RESEARCH

Modern Portland cement is a compound consisting of calcium, silicates, and hydrates (C-S-H). Monteiro and Jackson investigated concrete from Pozzuoli Bay (Yang, 2013) and found that Roman concrete differs from modern concrete in at least two important ways: (1) aluminum substitutes for silicon in poorly crystalline calcium-silicate-hydrate (C-S-H or tobermorite gel) to form calcium-aluminum-silicate-hydrate (C-A-S-H or Al-tobermorite gel) and (2) Al-tobermorite gel crystallizes over time to form mineral fibers of Al-tobermorite (Yang, 2013).

The cement in Roman concrete contains more aluminum and less silicon than modern concrete. This resulting calcium-aluminum-silicate-hydrate (C-A-S-H) is an exceptionally stable binder. The substitution of aluminum for silicon in C-A-S-H may be the key to the longevity of Roman concrete (Jackson et al., 2013; Yang 2013).

In theory, hydration of Portland cement resembles a combination of naturally occurring layered minerals including tobermorite. However, in reality, this ideal crystalline form of tobermorite is rarely found in modern concrete. Instead, tobermorite (C-S-H) occurs as an amorphous gel. Roman concrete, on the other hand, does contain crystalline tobermorite. Monteiro and Jackson and Jackson et al. (2013) used X-ray diffraction and tomography to clarify the role of aluminum in the crystal lattice of tobermorite. They believe this Al-tobermorite has a greater stiffness and is one of the reasons Roman concrete is so durable.

In modern concrete made with Portland cement, uncontrolled hydration at temperatures above about 65 °C causes the developing C-S-H to absorb sulfate. As the concrete cools and ages, the sulfate is expelled to form deleterious ettringite (Taylor et al., 2001). Ettringite does not occur in the C-A-S-H matrix of Roman concrete. Instead, sulfate ions are isolated in discrete crystalline ettringite microstructures in relict voids or along the perimeters of relict lime clasts (Jackson et al., 2012). Deleterious chloride ions are isolated in the same way resulting in discrete crystalline structures of hydrocalumite.

Crystalline Al-tobermorite forms diagenetically over time in the Roman concrete and appears to begin crystallization at the center of relict lime clasts (Jackson et al., 2013). The crystalline Al-tobermorite give strength to the concrete and may also help sequester deleterious sulfide and chloride ions, contributing to the concrete's durability and longevity.

IMPLICATIONS AND FUTURE RESEARCH QUESTIONS

Recent research indicates that Roman concrete may get its strength, durability and longevity from the crystalline form of Al-tobermorite. Research questions related to Reclamation's research interests may include the following:

1. How can we promote the growth of crystalline Al-tobermorite in modern concrete?
2. Where are sources of alkali- and alumina-rich volcanic tuff in the western United States that might be used to reproduce Roman-style concrete?
3. Can we change the chemistry (alkali and aluminum content) and physical form (pumaceous clasts) of commercial fly-ash to resemble the volcanic ash used in Roman-style concrete? Will doing so promote the growth of crystalline Al-tobermorite?
4. Roman concrete is about 45 vol% glassy zeolitic tuff and 55 vol% hydrated lime-volcanic ash mortar with lime forming <10 wt% (Jackson et al., 2013). Glassy volcanic rocks are considered to be highly reactive with the alkali cement forming alkali-silica gel and are to be avoided for

use as concrete aggregate (ASTM, 2011). Why were the Romans able to use glassy volcanic rocks in their concrete with no alkali-silica reaction? Does it have anything to do with the high aluminum content of the glassy volcanic rocks? If so, can adding aluminum to a concrete mix reduce the chance of alkali-silica reaction?

5. Roman concrete has shown very little cracking after 2000 years. This implies it is resistant to deterioration due to freeze-thaw cycles. In modern concrete, entrained air-void systems help prevent damage from freeze-thaw cycles. Does Roman concrete have an air-void system? In particular, do the vesicles in pumice act as an air-void system?

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