455

Screenings
from the Soil Research Lab

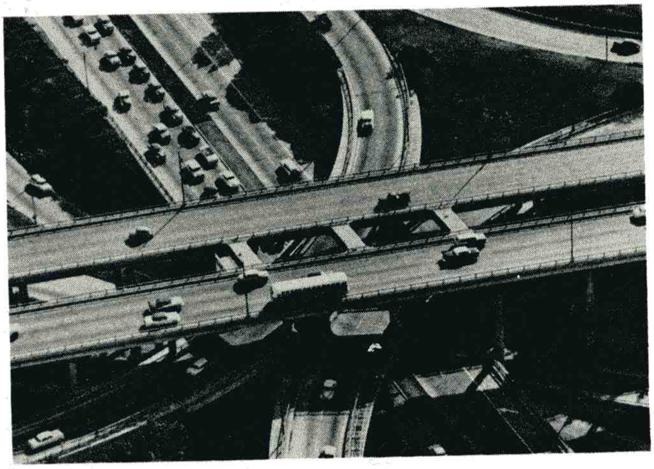
Vol. 8*
December, 1964

IOWA ENGINEERING EXPERIMENT STATION
IOWA STATE UNIVERSITY of Science and Technology
AMES, IOWA

Subject: PORTLAND CEMENT

Pardon us, but have you looked up, down, or sideways lately? Please do; we'll wait.

All right, what did you see? Please, not television or old election posters or more work. What you're supposed to see is CONCRETE. Because...



CONCRETE is the world's most abundant building material. The U.S. annual tonnage is about 5 times that of the nearest rival (steel), and last year the total world production of concrete was about 3 billion tons. With a world population of 3 billion people that means an average of about 1 ton per person. In the U.S.A. the quota is over 2 1/2 tons per person annually[2].

Furthermore, annual production of portland cement has doubled in the last 20 years. Since the world population is doubling only every 40 years, anybody with a grain of feeling for advanced arithmetic will see that by the year 2400 the world will not be covered by people, but by CONCRETE. Also it should be pretty obvious to anybody but a social scientist that we've been pushing the wrong pill.

How To

Portland cement concrete appears rather simple but has a complicated inner chemistry, being more than a bit like women in this respect. Easy to get along with (and they claim impossible to get along without), an apparently minor mismanagement can bring disaster. In fact, concrete is rather abstract, in spite of dictionary definitions.

Cement: The basic recipe for portland cement is as follows: Take one cup limestone, crushed; add one-half cup of clay or pulverized shale (plus perhaps some sandstone or iron ore, depending); mix thoroughly and grind up fine; bake in a white-hot oven, 1400 or 1500°C; cool, add one tablespoon gypsum, and grind very fine. If you can do this for a dollar a bag (94 lb) you can almost compete.

Concrete: To make CONCRETE, take one cup portland cement, 2 of sand and 3 1/2 of gravel, blend thoroughly, and marinate in just enough water to make a thick batter. The thicker the batter the stronger the concrete.

The concrete is now ready to pour. Be sure to grease your pan first, and after pouring you'll want to slap it around a bit or vibrate to get the excess air out. Cover with wet towels for one week, and we guarantee you will look like a new slab.

Now you know the business, please do not say "cement" sidewalk or "cement" structure. There is no such thing as a "cement" sidewalk. The sidewalk is CONCRETE. Or wood or bricks or grass or gravel or muck or tank traps. Our neighborhood speciality is pitfalls, dog manure and chewing gum.

Apartments, Chicago. From the bottom, boats, cars, and people.

(Top photo). Four-level highway interchange, California.

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*This is the first Screenings of 1964, the last being V. 7 No. 1 on foundation engineering. The reason we waited so long was to wish you a Merry Christmas.

[2] If you have not received yours, write the Portland Cement Assoc. Our thanks to the PCA for photos.

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Histerical Aspects

Portland cement, like the vote for women, is a 20th century innovation based on an 18th century invention that was in developmental stages from the time of the Pyramids. The Egyptians cooked up crude plaster-of-Paris to stick their masonry together, with hieroglyphics as follows:

gypsum + heat → plaster-of-Paris + steam
$CaSO_4 \cdot 2H_2O$ → $CaSO_4 \cdot 1.5H_2O$ + $0.5H_2O$

Mix the resulting powder with water, and the operation shifts into reverse:

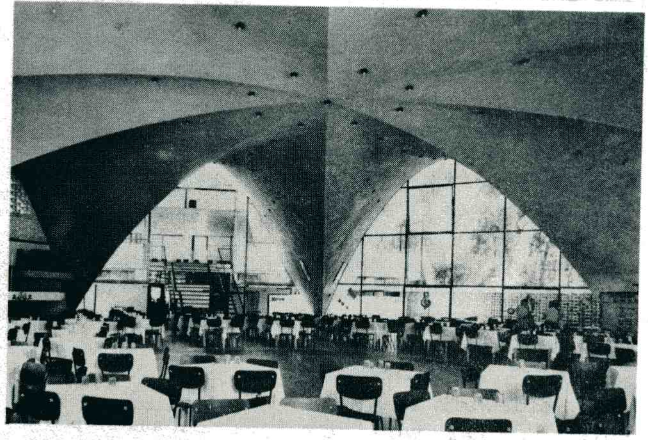
plaster-of-Paris + water → gypsum

Or as the great Egyptian philosopher AOK (Dogface) put it, Hot Rock make Magic Powder; Magic Powder plus Water plus Magic Words (now so-called Countdown) make Rock.

Blimey

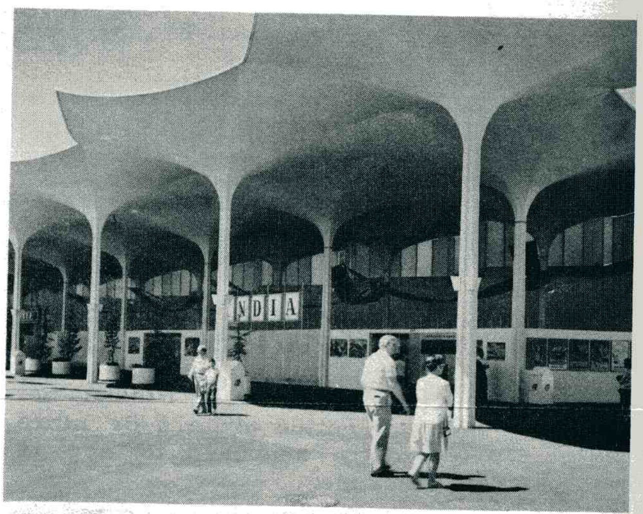
Gypsum cement slowly dissolves in wet climates, so it's a good thing Egypt never tried to export any pyramids. After a few thousand years the Greeks and the Romans began to resent oblique references to backward areas in the North, and they decided to get with it and build their own civilizations. Naturally a first requirement was good mortar, and they discovered if they cooked limestone they got lime:

limestone + heat → lime + gas
$CaCO_3$ → CaO + CO_2



Restaurant, Xochimilco, Mexico. The sky is not falling; thin reinforced concrete shells behave as membranes in distributing stresses. The earliest thin shells were on eggs.

(Above, right) Century 21 Exposition, Seattle



For mortar, the reaction is essentially the reverse; lime first hydrates or slakes to $Ca(OH)_2$, which in turn reacts with CO_2 from air to make limestone plus water:

hyd.lime + carb.dioxide → limestone + water
$Ca(OH)_2$ + CO_2 → $CaCO_3$ + H_2O

Both the lime and the gypsum mortars are still widely used in plastering, in case anybody wants to get plastered.

Carbonation behind closed doors can be slower than loss of prejudice, and some of the more compact Roman mortars still are not carbonated after a couple thousand years.

Pozzolanic CONCRETE

Roman dabbling in lime concrete soon led to a momentous discovery which ushered in the era of silicate cement chemistry, not to mention Tiberius and the Roman Empire. According to Vitruvius, who was the first engineer who knew how to write (and some say the last):

> "There is a species of sand which, naturally, possesses extraordinary qualities. It is found... in the neighborhood of Mt. Vesuvius; if mixed with lime and rubble, it hardens as well under water as in ordinary buildings".

This underwater deal made a rather catchy slogan, and the new concrete, we mean CONCRETE, caught on like a sweaty girdle. Most of the famous Roman structures, such as the Coliseum, employ this concrete. The Pantheon has a solid concrete dome with 142 foot span.

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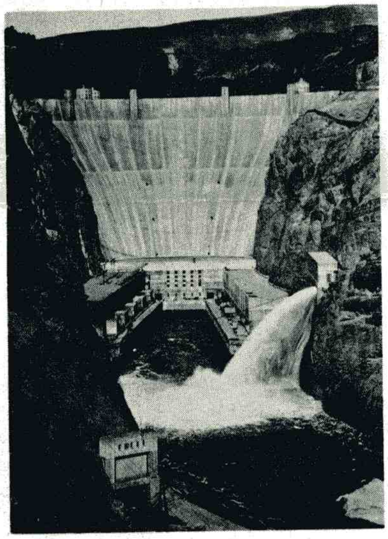
The special ingredient of Roman concrete was a volcanic ash called pozzolan after the Italian town. Other much-used pozzolans are Santorin earth, from the Greek island; trass, from terraces along the Rhine; burned clay or pottery; and fly ash, from burnt flies.[3]



Concrete dams provide a big, big incentive for cement chemistry research. Hoover Dam (right) led to development of a new low-heat (Type IV) cement. In the 1950's, Hungry Horse brought on a return to pozzolans.

Middle Ages

A Middle-Aged burst of conservatism revived stone cutting at the expense of pozzolanic concrete, while foreign policy turned off on a series of righteous Crusades. Finally after about the 14th century they quit enough of their Holy Grailing to rediscover pozzolanic concrete, as well as art, science, and a few other little incidentals like America.

Merrie Olde Milestones

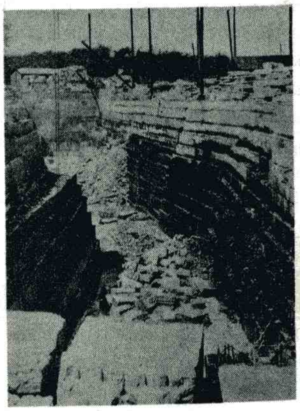
And so we leave the sunny shores of the Mediterranean[4] for the misty shores of Ye England. In 1756, famous English engineer John Smeaton was commissioned to build a lighthouse on account of the fog. Through kitchen table experiments and the Scientific Method, Smeaton learned that the best lime for lighthouses came from dirty limestone, or one with clay in it. The new lime set under water even without pozzolan, and is therefore a "hydraulic lime".

Some 40 years later James Parker discovered "Roman" cement, named for its fancied resemblance to Roman pozzolan which it did not resemble, but then that's advertising. Parker's cement was made from naturally occurring clay-limestone nodules or concretions. Similar "natural cements" were soon in production in France and the U.S., and dominated the market until about 1850. Natural cement was used in the Thames Tunnel, Brooklyn Bridge, and Erie Canal. Natural cement differs from hydraulic lime in that after burning it requires grinding.

Portland

In 1824 Joseph Aspdin patented a "Portland Cement", named for a fancied resemblance to Portland stone. Aspdin kept his process such a secret that nobody knows just what he invented or when he invented it. Key principles are to add clay to limestone if the stone does not already contain it, and to mix thoroughly and heat very hot. The first were known prior to Aspdin, so his secret must have been in the heating, but it may have been 1850 or so before he finally made things hot enough.

Portland cement concrete caught on and soon took over, and by 1905 most of the stone cutters were again out of business.



Main construction materials B.C. (Before Concrete) were brick and stone. This eastern Iowa quarry, opened in 1894, was about the last word in the Iowa cut stone industry. Around 1900 the bottom fell out (cf. photo).

CLINKER

Look out, Little Egypt; here come the hieroglyphics again. Burned and unground cement is called clinker. Four compounds are now known to put the clink in clinker:

Table 8[5]

C_3S = tricalcium silicate
C_2S = dicalcium silicate
C_3A = tricalcium aluminate
C_4AF = tetracalcium alumino-ferrite

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[3] This is a slight misrepresentation, but then it's a political year. Actually fly ash is from burnt coal.

[4] There's no very good way to take them with us.

[5] In the interest of brevity we have eliminated the first seven tables. Plus a whole bunch of chairs.

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Chemists with previous educational bias may see something strange about these formulas: C does not mean carbon; it means CaO. Likewise S stands for SiO_2, A for Al_2O_3, F for Fe_2O_3, and H for H_2O. It's a cement chemist Zip Code.[6]

Table 9

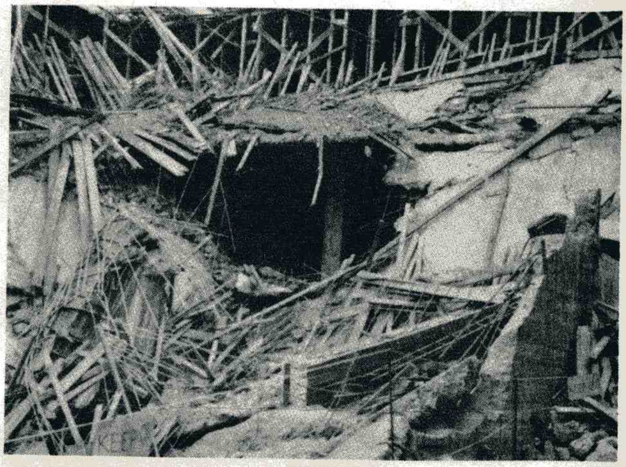
Compound	Setting Rate	Strength	Heat Evolved
C_3S	Fast	Strong	Temperate
C_2S	Slow	Strong	Cool
C_3A	Fast	Weak	Torrid
C_4AF	Fast	Weak	Tropical

C_3S is current No. 1 compound in portland cement. C_3S is for engineers who prefer their cement like their women—fast, strong and hot. C_3S is the major compound in high-early strength cement, which is ground extra fine so it will react faster.

C_2S. Engineers who think cool prefer more C_2S in their portland—great for big dams, where cooling of the mass concrete is one big dam problem.

C_3A fits into the picture about like the Other Woman: a real trouble-maker, useful mainly to flux the clinker. Unguarded, it reacts so fast with water it causes "flash" set.[7] C_3A is usually guarded with gypsum, which reacts to make a sulfoaluminate coat and slow things down.

Unfortunately C_3A compounds also react with sulfates coming in later, after the concrete has hardened. Very pretty little sulfoaluminate crystals ("ettringite", or "cement bacillus") then grow in place and blast everything apart. To avoid such importune reactions C_3A content may be minimized.



One footing failed. From Feld, "Lessons from Failures of Concrete Structures." Am. Conc. Inst. and ISU Press, 1964.

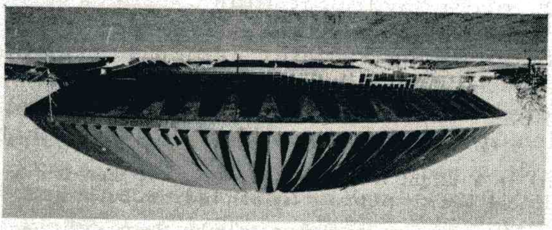
C_4AF is useful as a burning aid and doesn't have all the bad qualities of C_3A; hence the need for an occasional shot of iron ore in the raw batches. C_4AF gives cement its gray color, and may be left out for a white cement.

Table 10

Average Compositions of Portland Cement

	C_3S	C_2S	C_3A	C_4AF
High-early (Type II)	58%	16%	8	8
Ordinary (Type I)	53	24	8	8
Moderate heat (Type II)	47	32	3	12
Low heat (Type IV)	26	54	2	12

Other compounds. Add up the figures across Table 10 and you see we've been short-changed about 8%—too much for rounding off and too little for income tax. Included are the gypsum (about 2-3%), plus free lime and other oxides MgO, Na_2O and K_2O. MgO is limited to 4 or 5% because it slowly hydrates and expands; the alkalis Na and K are minimized where they may react with local aggregate.



Fieldhouse, University of Illinois, Urbana; site of many a startling upset.

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[6] The eventual goal of the Zip and similar schemes is of course to eliminate names altogether:

> Dear 442-50569-8812 (Mom): How strange to know who I am again, after all these years as a wrong number. You remember they started sending all my mail to my license plate; meanwhile I sold my car. Then 729-40438-0036 (my wife) thought my Number was Up (drafted and killed in the war) so for the next 17 years I went under an assumed number. Now it looks like all our children are bastards unless I can get things straightened out. Also we're expecting a .6 any day now, so there's the question of one more tattoo...As ever, your loving son, OOX.

[7] Not to be confused with "false" set, which is usually caused by gypsum going to plaster-of-Paris during grinding.

Storyline HYDRATION

So much for lights and camera; now for the action. That is, in building anything from a romance to a football team the main concern is the end product or the coach gets fired. So getting back to today's romance:

The end product of portland cement hydration is mainly a calcium silicate hydrate (C-S-H) similar to the mineral tobermorite, named for Tobermory, Scotland. The crystals are so fine they can be seen only with an electron microscope, and can be identified only by X-ray diffraction. They have such a large surface area they are usually tagged tobermorite gel.

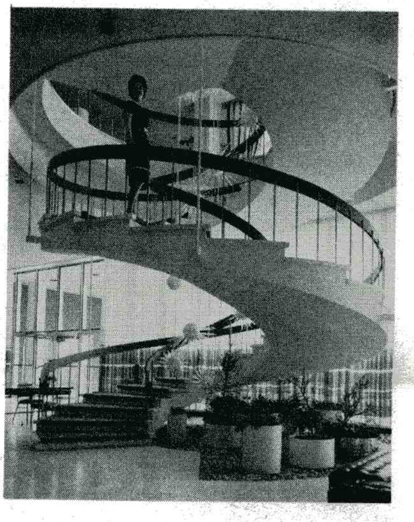
Cement paste after 16 hours, magnified 30,000 times. Intermeshed fibrous crystals are tobermorite gel, the heart and strength of concrete.

The C/S ratio in tobermorite varies from about 0.8 to 1.7 or more; in concrete it's about 1.5:

1. $$2C_3S + 6H \rightarrow \underset{\text{tobermorite gel}}{C_3S_2H_3} + \underset{\text{lime}}{3CH}$$

2. $$2C_2S + 4H \rightarrow C_3S_2H_3 + CH$$

Note that both C_3S and C_2S give the same hydration products; the main differences are in rates of hydration and the amounts of released lime.



Tripping down the tobermorite. Or, Dude Decending the Staircase, (Houston, Texas).

In high structures where light weight is an advantage, artificially expanded aggregates are often used in the concrete.

Although tobermorite gel is by far the most important product, chemistry buffs may be disappointed if we don't mention what else happens:

3. $C_3AH + H = C_4AH_{19}$
or C_4AH_{13} (hexagonal plates)
or C_3AH_6 (cubes)[8].

4. $C_4AF + H + CH = C_3AH_6 +$
C_3FH_6 (both cubic)[9].

Apparently relatively large (but still microscopic) cubes and hexagonal plates do little for strength, because there's not much muscle from either reaction 3 or 4.

The gypsum necessary to keep reaction 3 from going too fast behaves as follows:

5. $$CaSO_4 \cdot 2H + C_3A + H = \underset{\text{ettringite}}{C_3A \cdot 3CaSO_4 \cdot 32H}$$

Ettringite coats the C_3A grains like a steady date, delaying rival reactions but not stopping them indefinitely.

Water-cement ratio

Engineers claim more concrete has been ruined by morons standing at the concrete mixer with a water hose than by anybody else except architects. Water makes the mix sloppy and easy to pour, but reduces ultimate strength in proportion. A water-cement ratio of 0.4 (by weight) is apparently about sufficient for hydration and filling capillary voids; in practice the ratio is ordinarily upped to 0.5 to 0.6 for easier placement.

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[8] Actually, C_3AH_6 is seldom observed, and C_4AH_{19} may be something else like a hemi-carbonate, $C_3A \cdot \frac{1}{2}CH \cdot \frac{1}{2}CaCO_3$.

[9] Actually, C_3AH_6 and C_3FH_6 form solid solutions with garnets C_3AS_3 and C_3FS_3, the resulting mixed-up-mess being termed hydrogarnets, or $C_3(A,F)(S,H_2)_3$ for short. Sometimes we just say CASH, which is always short.

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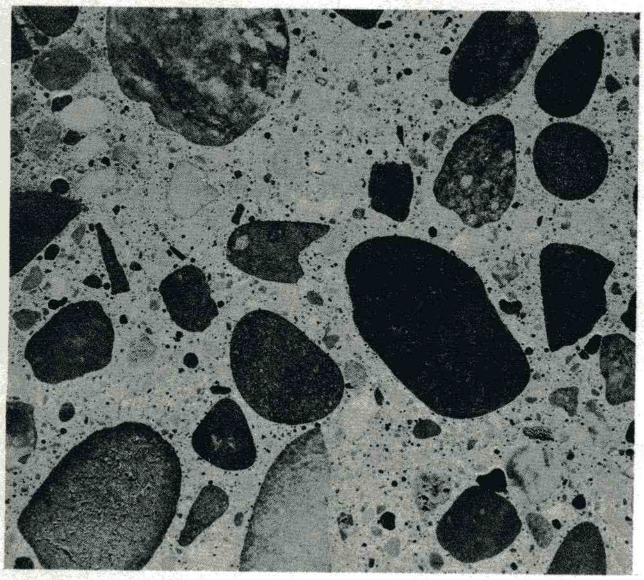


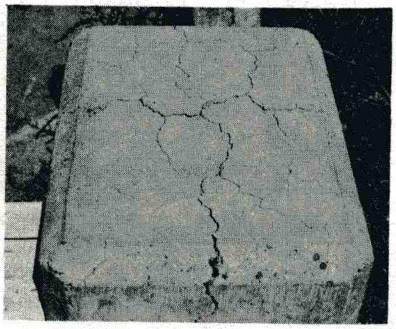
Tiny Bubbles

One of the most fantastic detective stories in the annals of cement research concerns a rather casual use of beef tallow as a grinding aid. A few concrete jobs were found to have unusual tolerance to frost action or scaling.

The answer was found in billions of tiny bubbles dispersed throughout the mortar, providing cushions against expansive pressures of ice or salts. Today air entraining agents (oil, soap, resin, etc.), either added at the mixer or already in the cement, are used for most exposed concrete work.

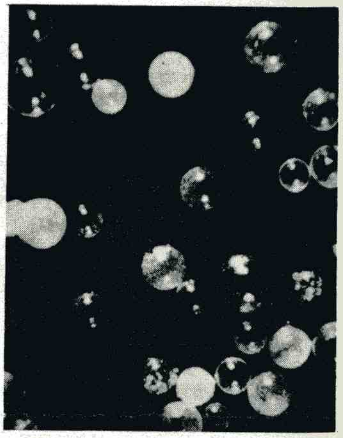
Puzzlin's

Hydrating portland cement liberates a collossal amount of lime (CH in eq. 1 and 2). Thanks to clues from the Romans, pozzolans are often used to tidy up the reaction; they are cheap, and convert lime into additional cementing agents. Used in sufficient quantity they help resist chemical attack and prevent the alkali-aggregate reaction (below), which is one reason pozzolan is puzzlin'.



The alkaline interior of concrete can give problems, such as alkali-aggregate reaction. Alkali reacts with certain aggregates to make silica gel, which expands and goes blast.

The most commonly used pozzolan in the U.S. is fly ash, from burning of pulverized coal. Fly ash is → mainly microscopic spheres which give a ball bearing aspect to the mix, good for workability and especially pumpability, as in grouting or cementing oil wells.



Some of the other admixtures to concrete are even more puzzlin': Calcium chloride speeds the set by some devious means. Dispersing agents ("Pozzolith") disperse the cement and increase fluidity with the same water content. Aluminum powder reacts with released lime to make gas bubbles, offsetting shrinkage or making a lightweight concrete. Other chemicals are catalysts, wetting agents, water repellants, accelerators, retarders, plasticizers, stiffeners, or a combination of ingredients like your doctor recommends.

Other cements

The old-fashioned natural cements in the U.S. are mainly C_2S plus 10 to 20 percent MgO; because of the low burning temperature the MgO hydrates fairly rapidly and doesn't make trouble. Recent work at ISU indicates certain dolomitic limes are cements, MgO converting to $Mg(OH)_2$.

Aluminous cement uses bauxite instead of clay as raw material, and is mainly CA. It hydrates so fast the product is gel, with full strength in 24 hours. Portland-blast furnace slag cement blends have pozzolanic properties. Masonry cements are mainly portland plus plasticizer, such as hydrated lime.

Not to mention oil well cements, which have enough iron in the raw mix for zero C_3A content, or utilize pozzolans or special retarders for slower set at high temperatures. Supersulphated cement and some experimental expansive cements have generous calcium sulphate which reacts with C_3A (eq. 5) to make ettringite and bulk up the concrete. Where else in this mad, mad world will you find anything so wild and substantial as concrete? Nowhere, man, but no where . . .

RLH

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