The concrete conundrum

Concrete is the single most widely used material in the world – and it has a carbon footprint to match. James Mitchell Crow looks at some of the approaches being used to ease the material’s environmental impact.
Concrete has a problem. Already pilloried through its use in countless architectural eyesores, from tower blocks to carparks, concrete’s environmental credentials are also now coming under scrutiny. The material is used so widely that world cement production now contributes 5 per cent of annual anthropogenic global CO₂ production, mainly because such vast quantities are used.

Humans have used concrete for millennia – its basic ingredients date back to ancient Egypt. CO₂ is a product of the main reaction that makes cement – concrete’s key ingredient. Development of new concrete additives could produce a stronger, more workable material whilst reducing the amount of cement required and the resulting CO₂ emissions.

‘The reason concrete has such a big carbon footprint is because such huge quantities are used.’

Already 605 metres high, the Burj skyscraper in Dubai will be the world’s tallest building.

Concrete is used in such large amounts because it is, simply, a remarkably good building material: not just for basic road construction, but also for rather more glamorous projects. The Burj Dubai skyscraper, still under construction but already well over half a kilometre high – the final height remains secret, but the building is set to dwarf all other man-made structures – relies on a highly flowable concrete mixture that doesn’t harden before it can be pumped to the top of the tower, yet forms a strong and robust final product. And Japan’s construction industry has pioneered ultra-strength varieties from which to build its earthquake-proof bridges, and the Tokyo apartment blocks that form some of the most expensive real estate in the world.

With the loss of Roman concrete expertise as the Empire fell into decline, concrete’s secrets didn’t re-emerge until just 200 years ago. Modern concrete was born in the early nineteenth century, with the discovery of Portland cement, the key ingredient used in concretes today. The process of roasting, and then grinding to a powder, limestone and clay to make ‘artificial stone’ was patented in 1824 by Joseph Aspidin of Leeds, UK, and later refined by his son William into a material very close to the cement used today.

The main reaction occurring in Aspidin’s kiln was the formation of calcium silicates, from calcium carbonate (limestone) and silicates that make up clay. At temperatures approaching 1000°C, the two raw materials break down into their component oxides – and as the temperature rises further, then combine into di- and tri-calcium silicate. The lesser quantities of iron and aluminium in the clay also react with calcium, giving the minor components of Portland cement. Finally, this mixture, called clinker, is ground to a powder, and gypsum is added.

To convert this powdery mixture into a concrete, which Aspidin senior claimed was as beautiful as Portland stone (hence its name),
just add water and aggregate. The resulting calcium silicate hydrates form an extended network of bonds which bind together the solid aggregate. However, the exact role of the lesser components of the cement remains vague.

While the chemistry of concrete may still not be entirely understood, what has become increasingly clear is the material's environmental impact. ‘The rule of thumb is that for every tonne of cement you make, one tonne of CO\textsubscript{2} is produced,’ says Marios Soutsos, who studies concrete at the University of Liverpool, UK. ‘Modern cement kilns are now more efficient, and produce about 800kg of CO\textsubscript{2} per tonne – but that is still a big emission.’

Concrete production is responsible for so much CO\textsubscript{2} because making Portland cement not only requires significant amounts of energy to reach reaction temperatures of up to 1500°C, but also because the key reaction itself is the breakdown of calcium carbonate into calcium oxide and CO\textsubscript{2}. Of those 800kg of CO\textsubscript{2}, around 530kg is released by the limestone decomposition reaction itself.

A complex mix
Several ways of reducing the environmental impact of concrete are now being investigated – one possibility being to produce ultra-strong varieties – so less concrete is required to do the same job.

Achieving strong concrete is a fine balancing act. Too many pores filled with unreacted water weaken the final structure, but a certain amount of water is required to keep the mixture workable. However, this threshold of workability can be lowered using additives called plasticisers.

The concrete lorries that rumble along our roads today are likely to be carrying a complex mixture of chemical additives, in addition to the basic ingredients of concrete. But like most aspects of concrete chemistry, this is not a new development – the Romans are known to have included additives such as animal blood to improve concrete performance, and the Chinese added sticky rice to their mixtures when building the Great Wall during the Ming dynasty.

‘People do dispute this, but I would say the water: cement ratio for complete hydration was 0.32,’ said Marios Soutsos. ‘But to get the strength you don’t need to have complete hydration. We are going down to a ratio of 0.16, with admixtures, and that gives higher strength than a completely hydrated system. The only thing preventing us from going below that is the workability of the concrete. More efficient chemical admixtures may allow us to.’

One company hoping to extend that limit further is BASF. Their construction chemicals business – greatly expanded by the purchase of Degussa’s construction business on 1 July 2006 – is one of the main drivers of admixture chemistry, according to Soutsos.

While there have been several families of concrete additives used by the construction industry since animal blood went out of fashion, the most recently developed, and best performing, are the polycarboxylate ethers (PCEs), says Sven Asmus, head of technical services and development of admixture systems at BASF, based in China, where close to half of the world’s cement is produced. As a polymer, the PCE’s structure and properties can readily be tailored by changing the monomers used to make it.

Many acrylic acid derivatives [PCE monomers] are manufactured in large scale, and we’ve been looking at different combinations that give good properties,’ says Asmus. ‘Initially this was by trial and error, but we have now built up such expertise that we can use a directed approach to designing new mixtures.’

Plasticisers work by preventing the cement particles from clumping together. ‘In physical terms, these are dispersants, and they act through absorbing onto the surface of the particle which they are supposed to.'
to disperse,’ says BASF’s Christian Hübsch, marketing support, branches and industries, Europe. ‘Polycarboxylates act by a steric repulsion, so in simple terms they act as a spacer between two particles.’

To make ultra-high strength concrete, you need very strong plasticisers. ‘Final strength is achieved by maximum water reduction, which needs ultra-strong dispersant molecules,’ adds Hübsch. ‘These are the molecules with the longest side chains, because they provide the strongest dispersing forces. Due to their sheer size, they provide the longest-range repulsion forces.’

Ultra-high strength concrete was pioneered in Japan, where the added cost of the material was offset by the need for earthquake-resistance, and the fact that property in Tokyo area costs up to €160 000 per square metre, encouraging the construction of buildings with the thinnest possible concrete superstructure. ‘But we also see huge potential in Europe, and cost is a major issue here,’ adds Hübsch. ‘The solution is not at hand yet; nevertheless we see higher and higher strength classes coming up with almost normal mix designs, applying specially designed concretes which have a lower cement content. Cement is the most expensive component of ultra-high strength concrete, and if you can substitute some of this with alternatives such as slag or fly ash, this is, economically, beneficial.’

Cut the clinker
Replacing Portland clinker, either partially or entirely, with alternative cements is also being investigated as an approach to tackling concrete’s CO$_2$ emissions. Waste materials, such as slag (from blast furnaces) and fly ash (from coal-fired power stations), are already being used as supplementary cementitious materials (SCMs) – and have been for some decades.

‘Replacement of Portland cement is key, absolutely, and the challenge is to address the negative effects of this substitution, which is mainly related to early strength development,’ said Hübsch. ‘With 50 per cent clinker replacement with fly ash, early strength goes down dramatically. We had a discussion with the big contractors in Germany about this– ideally they would like to cast concrete in the afternoon, and then de-mould the next morning, to go on with the construction. At colder temperatures this can really become a problem.’

However, Scrivener says that the potential of clinker replacement is ultimately limited. ‘The uptake of SCMs has been pretty good – but the production of these materials is dwarfed by the demand for cement,’ she explains. ‘And while making cement from a blend of slag and Portland cement is fairly straightforward, entirely replacing clinker with slag requires alkali to be added to the mixture to activate it – and that alkali can then go on and attack the aggregate. ‘Alkali-silica reaction is becoming more and more of a problem, because as time goes on we’re discovering that more and more aggregates are reactive,’ adds Scrivener. ‘For example, here in Switzerland 70 per cent of our power comes from hydro, we have 300 dams built in the 1950s and 60s, and more and more of them are starting to show signs of this reaction. So this is the problem – it can take 60 years before the problem manifests itself.’

A more viable long-term clinker substitute, certainly in terms of availability, is finely-ground limestone, suggests Scrivener. ‘Adding up to 5 per cent can have positive effects, by improving the microstructure. And for buildings such as individual houses, where you don’t need great strength, there you can substitute 20 per cent with good performance.’

Sticking with less cement
An additional approach to the carbon footprint problem is to reduce the amount of cementitious material altogether – be it Portland cement or an SCM. This is another area being researched by BASF, and also by Ravindra Dhir, director of the concrete technology group at the University of Dundee, UK.

‘We’ve found that you can take out at least 20 per cent of the cement content while retaining durability,’ Dhir says. And it turns out that reducing the cement levels can

The Tatara bridge in Japan is the world’s longest cable-stayed concrete bridge

‘It’s almost impossible to find out the optimal material for a particular structure’
actually improve the durability of the final concrete. ‘If you think about concrete in terms of cement paste and aggregate, it is the cement paste that is more porous, so it is the cement that provides a route by which elements of exposure can go in and out. So in theory, the less you use, the better the concrete should be.’ Pores in the material allow corrosive materials such as chlorides and sulfates to penetrate the structure and attack the metal reinforcement – the cause of well over 90 per cent of problems of concrete durability, adds Scrivener.

However, Dhir points out that the ultimate strength of the concrete is equally if not more important than short-term CO₂ saving. ‘The challenge is to translate thinking and laboratory findings into the real world – and in the world of concrete that’s not easy, and it will always be a slow pace. You’ve got to be sure about variability of materials, the issue of quality assurance, and they may come to the conclusion that it’s not worth the risk, and I would not argue with them.’

‘I think we’re really moving towards a breakthrough – and I think it’s high time we did – of designing concrete intelligently for performance, both the engineering requirements and the exposure requirements.’

Scrivener agrees that a key obstacle to using concrete efficiently is our current inability to easily predict the performance of a particular mixture. ‘Under the current European standards, there are something like 170 different cement types available, and if a person wants to build a structure it’s an almost impossible task to decide the optimal material for the structure he wants to build. We’re starting to work towards good prediction of performance, which is one of the first things you need to start working towards.’ This current lack of knowledge means that often concrete is used that is stronger than the job requires – unnecessarily using up more raw materials than were really needed.

This ability to predict performance depends on our ability to understand the complex chemical reactions involved in concrete formation. ‘Historically, because we have very complex materials, and it hasn’t been possible to precisely understand the chemistry, people have fallen back on a kind of empirical approach,’ says Scrivener. ‘Now, because of the way characterisation techniques have advanced – we have atomic force microscopy, scanning and transmission electron microscopy, x-ray diffraction, NMR – this enables us to have a real understanding of the chemistry, which we need to be able to work on a less empirical basis.’ To improve our understanding of the performance of different concrete mixtures, it’s simply a matter of applying these techniques, Scrivener adds, which just comes down to time and effort.

Hübsch also sees a revolution on the horizon in the field of chemical admixtures, with the potential to dramatically change concrete’s properties. ‘Admixtures of the future will actively interfere with the hydration processes, and ideally control these processes in terms of reaction rate, and in terms of the composition and ideally the morphology of hydration products. This will be the quantum leap everybody is trying to achieve. I’d say, on a five to 10 year basis, we might be able to fundamentally change the properties of concrete on a nanoscale.’

But perhaps the most significant reason for optimism is the increasing engagement of the cement industry itself. ‘One of the main things I’ve been involved in over the last five years is putting together a consortium called Nanocem, which has brought together, for the first time, the leading academic groups throughout Europe with the industry,’ says Scrivener. ‘For the first time ever, we have all the major cement producers signed up to support fundamental research in this area, and of course one of our major preoccupations is sustainability. It’s very important that we have all the major producers involved, because they’re the people, at the end of the day, who are going to be able to make a difference.’

Further reading