A hard sell? Metakaolin in high-performance concrete

Adding metakaolin to cement can improve the strength, corrosion resistance and appearance of concrete, but as *Frank Hart** explains, the construction industry is yet to be fully won over by its performance benefits.

Metakaolin is an amorphous, alumino-silicate mineral, manufactured by calcining kaolin at temperatures between 650°C and 850°C. It is classed as a pozzolan, defined by international standards agency ASTM as a siliceous or aluminous and siliceous material, which reacts chemically with calcium hydroxide (lime) at ordinary temperatures, to form compounds possessing cementitious properties.

Sold in bags as a fine dry powder, the colour of metakaolin varies from white to orange or pink, depending on the amount of coloring oxides present, such as iron oxide (Fe_2O_3) and titanium dioxide (TiO_2).

According to *Transparency Market Research*, the global metakaolin market was valued at $91.8m in 2012 and is expected to reach $124.2m by 2019, expanding at a compound annual growth rate (CAGR) of 4.4%.

In terms of volume, demand was 250,000 tonnes in 2012. The amount of metakaolin sold to the concrete market that year was valued at $48m, accounting for more than 50% of total consumption.

Calcination of metakaolin is traditionally performed using gas-fired rotary kilns, in which the temperature and rate of throughput are carefully controlled in order to maximise the amount of amorphous metakaolin produced. Over-calcining, at temperatures above 900° C, will alter the material's mineralogical structure to spinel and mullite, which are non-pozzolanic.

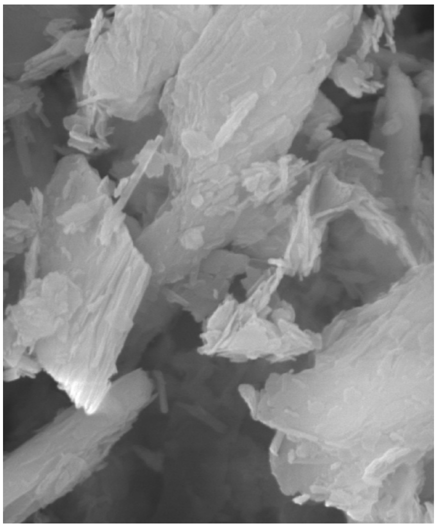
Flash calcination can also be used, a process which often forms spherical agglomerates. The spherical structure of flash-calcined metakaolin can impart additional benefits compared to traditionally calcined material, including lower water demand, better workability and higher cement substitution. According to California, US-based materials technology firm Demeter Technologies Inc., energy consumption of flash-calcined metakaolin material is up to two and a half times less than that of traditional calcining.

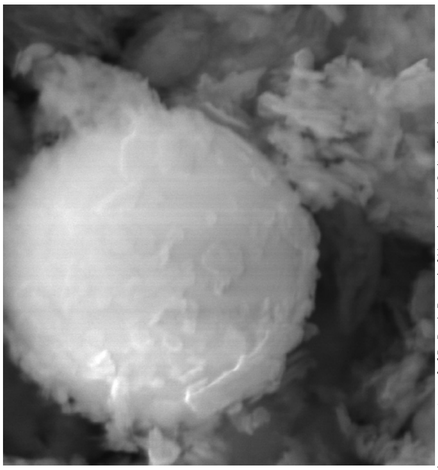
High-reactivity metakaolin (HRM) is metakaolin produced from consistent, refined kaolin, and is distinct from that produced from low-grade, unrefined kaolin. The latter often includes unwanted non-pozzolanic minerals such as quartz and feldspar. Another aspect of HRM is that the sum of aluminium oxide (Al_2O_3) and silicon dioxide (SiO_2) in the chemical composition is greater than 90%.

The presence of significant potassium oxide (K_2O) or sodium oxide (Na_2O) in metakaolin suggests that mica or feldspar were present in the pre-calcination feed. As a result, the metakaolin product will contain unreactive glass.

Producing metakaolin

$Al_2Si_2O_5(OH)_4$ (kaolin) → $Al_2Si_2O_7$ (metakaolin) + $2H_2O$





Rotary-calcined metakaolin Flash-calcined metakaolin

SEM images courtesy of of Dr Denis Bezard of Newchem AG, Switzerland

Pozzolans in concrete

The raw materials used to produce cement include limestone or chalk and shale or clay. After crushing and milling, the mineral powder is heated in huge rotary calciners to around 1,450°C to form cement clinker, which is then ground back to powder. It can be mixed with water and poured to set as a solid mass or used as an ingredient in making mortar or concrete, which are combinations of cement, water and aggregate.

Pozzolanic materials containing high proportions of silica and/or alumina are known as supplementary cementing materials (SCMs) and include fly ash, granulated ground blast furnace slag (GGBFS), silica fume, pumice and metakaolin.

SCMs may be added to concrete to reduce the volume of cement required to make it and

Reaction of metakaolin with calcium hydroxide

Metakaolin + $Ca(0H)_2$ + H20 → Calcium silicate hydrate (cementitious gel)

Anthony Quintano, via Flickr

432 Park Avenue, New York City. At 425 metres tall, this is the third highest building in the US and the tallest residential building in the western hemisphere. HRM supplied by German chemicals manufacturer BASF was used in the formulation of the 760mm-thick concrete walls to achieve a compressive strength of 16,100 psi.

to improve its physical properties, such as strength and durability. This enhanced concrete is known as high performance concrete (HPC), defined by the American Concrete Institute as "a concrete which meets combinations of performance and uniformity requirements that cannot be achieved routinely using conventional constituents and normal mixing, placing and curing practices".

Despite being more expensive than conventional concrete, HPC is economical because it extends service life, guaranteeing reduced damage through corrosion and lowering overall cost.

When ordinary Portland cement reacts with water it produces a hard cementitious substance but also releases calcium hydroxide ($Ca(0H)_2$), an unwanted by-product which can lead to concrete cancer ** and other problems. High concentrations of $Ca(0H)_2$ are found at the interfacial zone – the layer of cement paste directly adjacent to particles of aggregate. Metakaolin has the effect of densifying this zone by reacting with $Ca(0H)_2$, increasing its strength and reducing porosity.

Unlike competitor SCMs, such as fly ash, GGBFS and silica fume, metakaolin is manufactured for its intended use, with its chemical composition, brightness, particle size distribution, chapelle reactivity and other properties tailored to produce a consistent and effective pozzolan.

The pozzolanic performance of metakaolin and other SCMs can be measured using procedures outlined by ASTM, in which 7 and 28-day compressive strengths of mortar cubes with a 20% mass replacement of cement by pozzolan are compared to those of a control without pozzolan.

Other test procedures include the Chappelle Test, which measures the ability to absorb calcium hydroxide and the Fratinni Test, which measures the OH-content (contained in calcium hydroxide) of concrete mixes after eight days of curing.

When used to replace cement at levels of 5-15% by weight, the concrete produced is more cohesive and less likely to bleed (experience water separation), thereby reducing the intensity of pumping and finishing required. The compressive, tensile and flexural strength of the hardened concrete is also improved, increasing stability and reducing deflections in tall buildings. The cement matrix has lower porosity and permeability, increasing resistance to corrosion by sulphate and chloride ions and mineral and organic acids. Freeze-thaw resistance is also enhanced.

The amount of heat needed to hydrate cement can be reduced by 50% when metakaolin is used, which is important for very large structures such as dams where an increase in temperature during the early setting stages can lead to thermal stress and cracks. Fly ash and GGBS provide similar benefits, but silica fume, which is highly reactive, accelerates temperature rise.

Using HPC allows for tall but slender tower blocks to be built where space is at a premium in city centres. A good example is 432 Park Avenue in Manhattan, US – a building distinguished by a height-to-width ratio of 15:1 (anything greater than 7:1 is considered to be slender) and a low footprint of only 28.5 metres^2.

At 425 metres tall, it is the third highest building in the US (*see image*) and the tallest residential building in the western hemisphere. HRM supplied by German chemicals manufacturer BASF was used in the formulation of the 760mm-thick concrete walls to achieve a compressive strength of 16,100 psi (ordinary Portland cement concrete is approximately 4,500 psi).

In some cases, like 432 Park Avenue, the aesthetics of a structure are important, often requiring a white finish. Metakaolin manufactured in the US, India, China and elsewhere from low-iron and titania-feed kaolin can achieve brightness levels of 80-85 and are the preferred materials for such applications.

There is still a large market for low-brightness metakaolin, however, where the emphasis is on its technical rather than aesthetic qualities, such as in concrete used for dams, aqueducts and bridges.

Another important application is the exploration of oil and gas deposits, where concrete is used to fill the space between the borehole walls and the outer steel casing of the drill. Metakaolin improves the compressive and flexural strength of the hardened concrete and reduces its permeability to liquids and gases. Finished oil wells are plugged with concrete to prevent leakage.

Main benefits of adding metakaolin to concrete

- Increased compressive, tensile and flexural strength
- Reduced permeability
- Reduced sulphate and chloride corrosion
- Reduced freeze-thaw damage
- Prevention of alkali silica reaction
- Prevention of efflorescence
- Reduced CO_2 footprint

**Concrete cancer is a term given to the reaction which occurs over time in concrete between the highly alkaline cement paste and the reactive non-crystalline (amorphous) silica found in many common aggregates

Table 1: Chemical Properties of metakaolin and other SCMs

Metakaolin	Company	Country	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	CaO	MgO
Optipozz*	Burgess	US	51.7	43.2	0.4	2.1	N/A	N/A	N/A	N/A
MetaMax	BASF	US	-	-	-	-	-	-	-	-
Powerpozz	Advanced Cement Technologies	US	55	41	<1.4	<3.0	0.05	0.4	0.1	0.1
HP Ultra	Metacaulim	Brazil	57	34	2.0	1.5	<0.1	<0.15	<0.1	<0.1
Whitemud MK	Whitemud	Canada	62.5	31	1.1	0.6	0.16	1.81	0.4	0.3
Argical M1200S*	Imerys	France	55	39	1.8	1.5	**	**	***	***
Metacon	English Indian Clays	India	53	45	0.9	0.65	0.10	0.03	0.09	0.03
Other SCMs (typical values)										
Fly ash	-	-	40	18	10	1	3	3	20	3
Silica Fume	-	-	92	0.5	1.4	-	0.3	0.7	0.5	0.3
GGBFS	-	-	34	10	3	-	0.6	0.5	45	4.5

*Flash Calcined ** K_2O + Na_2O = 1.0% *** CaO + MgO = 0.6%

Source: Published technical data sheets

Table 2: Physical properties of metakaolin and other SCMs

Metakaolin	Company	Country	Particle size (microns)	Surface area (m_2/g)	Chapelle (mg $Ca(OH)_2$ /g)	Brightness (%)
Optipozz*	Burgess	US	50% <1.4	-	-	White
MetaMax	BASF	US	50% <1.3	-	1146	85
Powerpozz	Advanced Cement Technologies	US	-	20	1313	White
HP Ultra	Metacaulim	Brazil	-	23	880	Light cream
Whitemud MK	Whitemud	Canada	50% <8	-	-	Off-white
Argical M1200S*	Imerys	France	50% <1.1	19	1400	-
Metacon	English Indian Clays	India	-	-	740 - 1000	Off-white
Other SCMs (typical values)						
Fly ash	-	-	100% <45	-	700	Grey
Silica fume	-	-	50% <0.1	25	800	Grey
GGBFS	-	-	Variable	-	400	Grey

*Flash calcined

Source: Published technical data sheets

CO_2 emissions

According to the US Environmental Protection Agency, production of Portland cement releases approximately one tonne of carbon dioxide (CO_2) per tonne of cement, accounting for around 6% of total man made global CO_2 emissions (1.2 tonnes in every 20).

The Swiss Federal Institute of Technology investigated CO_2 emissions from the production of metakaolin and calculated a typical figure of 270kg per tonne, which included clay extraction, drying and gas-fired calcination. The use of biogas, as used by Argeco Development, a metakaolin producer based in southwest France, is calculated to produce around 92kg of CO_2 tonne.

The LC3 Project, funded by the Swiss Agency for Development and Cooperation through its global programme for climate change, is an initiative that aims to develop a new blend of concrete based on 50% clinker; 30% metakaolin; 15% limestone; and 5% gypsum.

It is claimed that LC3 can reduce CO_2 emissions by up to 30% and can be made in existing cement plants without the need for capital-intensive modifications.

Table 3: Typical prices of metakaolin

SCM	Form	Origin	Price/tonne Ex-works unless otherwise stated
Metakaolin	Bags	India and China	\$120-400 (Typically \$200-300)
Metakaolin	Bags	US (High brightness)	\$400-550
Other SCMs			
Fly ash	Bulk	India	\$80-85 delivered UAE
GGBFS	Bulk	India	\$10
GGBFS	IBCs	India	\$42
Silica fume	IBCs	China	\$150-300
Silica fume	IBCs	US	\$300-700

Source: First Test Minerals

Global metakaolin producers

The US, China and India are the major global producers of metakaolin. Tables 1 and 2 list some of the major players in the industry and detail chemical and physical properties for leading commercial grades of metakaolin compared to other SCMs (fly ash, silica fume and GGBFS).

US

Most US production is based in Georgia and Carolina, where metakaolin is manufactured from bright sedimentary feedstock. Companies including BASF, French industrial minerals conglomerate Imerys and US producers Thiele Kaolin Co. and Burgess Pigment Co. sell high-brightness metakaolin for use in concrete and other industries such as paints and PVC.

Canadian firm I-Minerals Inc. is developing a new metakaolin plant in Idaho to produce material exclusively for the concrete industry. The facility is expected to be on stream by 2018.

India

India is home to several metakaolin producers, notably 20 Microns Ltd, English Indian Clays Ltd (EICL) and Ashapura Minechem Ltd.

These companies and a number of others are located close to India's west coast, in Kerala or Gujarat and are logistically well placed to supply the Middle East, where significant infrastructure and construction investment is planned in the Gulf Cooperation Council (GCC) countries in the coming years.

China

Leading Chinese metakaolin companies include Jinyu Kaolin Chemical Co., Shanxi Jinyang Calcined Kaolin Co., Beihai Rede Kaolin Co. and Shijiazhuang Jinli Mineral Co. China is also the world's largest producer of fly ash and GGBFS.

Outside these major metakaolin-producing countries, notable suppliers include Imerys in France and Ukraine; Poraver in Germany and Canada; Whitemud Resources Inc. in Canada: Metacaulim do Brasil in Brazil; Plast Rifey LLC in Russia; and Calix Ltd in Australia.

Outlook for metakaolin demand

According to Ruben Snellings of the Sustainable Materials Management section of Vlaams Institute of Technology in Belgium, global cement production in 2015 was 4.2bn tonnes, corresponding to the use of approximately 800m tonnes of SCM's (20% replacement of cement by SCM's).

Concrete manufacture is expected to grow significantly between now and 2019 due to an increasing number of civil engineering projects in both developed and developing economies.

In April 2015, the UAE made it mandatory to use SCMs in concrete, the first and so far the only country to do so, but the move is likely to encourage other GCC countries to pass similar legislation.

In the US, more than 50% of all concrete production includes SCMs.

Fly ash dominates the SCM market, accounting for around 70% of global volume. GGBFS is the next biggest seller, followed by much smaller volumes of silica fume and metakaolin.

To meet growing demand for cement and concrete while cutting CO_2 emissions, cement producers will need to investigate the use of more SCMs without compromising performance and durability. GGBFS supply is already limited and an increase in metals recycling is likely to lead to further reductions, while fly ash supply is not likely to expand at the pace of concrete demand.

www.twin-loc.fr, Via Flickr

The Bacalan vertical lift bridge in Bordeaux was built using metakaolin-based concrete.

Structural uses of metakaolin

Jupia Dam, Brazil (1962)

This was the first use of metakaolin in concrete. The primary purpose was to suppress alkali silica reaction (sometimes called concrete cancer).

Brayton Point Cooling Towers, Massachusetts, US (2012)

Metakaolin was used in the concrete of two cooling towers in a coal-burning power plant adjacent to the sea, providing reduced permeability, improved chloride resistance and increased durability and strength.

Palais Royale, Mumbai, India (2013)

One of the first projects in India where metakaolin was used in HPC, the Palais Royale is approximately 300 metres high.

Bacalan Bridge, Bordeaux, France (2013)

"Argical" metakaolin supplied by Imerys was used in the construction of concrete pillars which form the vertical lift structure for the $195m bridge, providing improved strength and aesthetic colouring.

This opens up opportunities for metakaolin and other materials such as pumice in concrete markets.

But for consumption of these materials to grow, suppliers need to convince architects, ready-mix concrete manufacturers and other decision makers in the construction sector that metakaolin is a beneficial option.

Research into further improvements for concrete includes the development of ultra-high performance concrete (UHPC) and geopolymers, both of which benefit from the inclusion of metakaolin.

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