Necessity is the mother of invention

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Synopsis

Research and development is governed not only by market related strategies, but also by other factors, including changes in the environment and safety issues as well. This presentation is aimed at providing a few examples on how cement and concrete technology has developed to assist in providing solutions for the needs brought about by changes in strategic thinking as a result of global and external pressure. The change in strategy could be related to health issues such as that in the asbestos cement industry, environmental restrictions, or other related factors, placing demand on new development.

The four examples presented are:

- Value added to products in the search for asbestos fibre replacement in the fibre cement industry
- Advanced performance in concrete structures for construction in earthquake prone areas and light weight structures
- Innovative cements developed as a result of the Kyoto Protocol
- High performance concrete developed for nuclear waste disposal

Keywords: Fibre, Concrete, Cement, Nuclear Waste, Ductile, Reinforcement, Industry, Environmental

1. Introduction

"Necessity is the mother of invention": an expression so often used, the impact however, often under estimated.

Prime examples are:
- The inventions of the wheel
- Leonardo da Vinci aircraft concepts
- Telephone, Alexander Graham Bell
- Steam engine

Some inventions, are not related to in-depth thought about the subject, but rather as a result of unrelated, serendipitous discoveries, for example;
- 3 m Glue for yellow sticky papers
- Invention of Asbestos Cement which was a coincidence brought about by a mistake adding cement instead of gypsum to the Hatschek machine
- and recently Viagra

In this paper, I have used four examples of development or research initiated specifically to respond to new needs brought about by changed circumstances. These are:

a. The asbestos cement industry which faced serious problems due to health related lung cancer issues. The need to replace asbestos fibres in fibre cement products resulted in a completely new focus on product development.
b. Innovative design of concrete with fibre reinforcement for earthquake prone areas and lightweight structures.
c. The development of new innovative cements brought about by the Kyoto Protocol on CO2 emissions.
d. Research on cements arising from the concepts of the nuclear power industry for radioactive waste disposal.

2. Fibre Cement industry using Hatschek Technology

Background

The first and most successful industrialization of fibre cement was the invention of asbestos cement at the beginning of the 20th century. This innovative product is still being produced today and developed from slates to corrugated sheets and pipes. It is well known that this product needed to be replaced due to health issues associated with asbestos fibres.

In 1975 the first asbestos free New Technology (NT) research was initiated in Switzerland. The technology was designed to be used on the Hatschek fibre cement process. The range of products able to be produced using this very flexible process comprises flat and corrugated sheets, tiles, low pressure pipes, and a variety of hand- or machine molded conduits, bends, tees and guttering (rain water goods). The technology concentrated on air curing or steam curing at elevated temperatures not higher than 80°C. Almost at the same time James Hardie in Australia, were given the mandate to convert asbestos cement products to asbestos free fibre cement. As James Hardie used mainly autoclaved technology for asbestos cement, the emphasis was based on asbestos free autoclaved technology.
In Europe the choice of using synthetic fibres combined with cellulose fibre was the approach adopted, however in Australia the autoclaved approach using cellulose fibre only was the preferred technology. Both technologies used the classical Hatschek process as the manufacturing process.

The two technologies developed are described as follows:

Air and / or steam cured products:

An air curing time of 28 days using cellulose, synthetic fibres, cement, micro silicate, additives and water. In some factories steam is introduced with no pressure during the curing in order to speed up the curing process.

Autoclaved products:

Using cellulose fibres only, cement, silicate, other additives and water.
Autoclaved at 8 to 10 bars for 16 hours (temperature 180°C).

Basic principles of fibre cement technology and applications

The basic objective in the production technology of fibre reinforced cement based composites is to arrange the fibres in the matrix in such a way, to allow the fibres to perform their designed functional role and to achieve a composite between the fibres and the matrix. Fibres can be arranged in a regular or random array, the choice depending on the type of fibre, the application of the composite and stress distribution. The fibre/matrix interfacial bond is possibly the most important factor influencing the efficiency of the composite. This depends, on the one hand, on the properties of the fibre such as its affinity to the matrix, (its surface texture and mechanical bonding properties); on the other hand on the effectiveness of the manufacturing process in reducing the entrapped air between the individual filaments at the interface.

Fibre cement sheet machines may have three or four vats and sieve cylinders, the greater number of vats resulting in increased production. Also the laminate at the making roll comprises thin films. Pipe machines usually have one or two vats in series, and the pressure imposed on the mandrel by press rolls is much greater than in sheet formation, so as to make a dense product.

Raw material selection is of prime importance, not only by way of suitable blend of cellulose and synthetic fibres, but by choice of a cement of particle size, which has a bearing on the drainage properties of the mix.

After the green product has been formed at the machine it needs to be cured. Some acceleration of this process can be effected by primary curing in steam tunnels. If the sheets are autoclaved the curing time is accelerated even more and products are able to be sold within a few days after manufacture.

The properties of the fibre cement product is usually related to the quality of the fibres and cement. Coarser cement than normal is prepared in order to minimize filtration losses. The soluble alkali content of cement is also sometimes considered detrimental and should preferably be as low as possible.

Hatschek fibre cement has about 20 % open porosity. It is found that higher fibre content increases this porosity, with the result that strength does not increase in proportion to the increase in the fibre content. The dispersion of the fibre is in two dimensions not only because of the laminated structure but also, because of the rotation of the primary sieve in the vat, there is a predominant alignment of the fibres in the direction of rotation.

Alternative fibres to asbestos are PVA (Polyvinyl alcohol), PP (Polypropylene), PAN Polyacrylnitril and Cellulose. Conventionally the addition of fibre is given on the basis of a percentage weight of the total raw material mix. Volume fractions are however more realistic for fibre cement manufacture. For example low density fibres like PP (0.9 kg/m2) will occupy more volume than a PVA fibre (density 1.3 kg (m2) when dosed at the same weight fraction.

Asbestos cement products rely upon the natural network of asbestos fibres to support cement particles in the manufacturing process. This is possible because of the variable length and diameters of asbestos fibres, which is an inherent property of this natural product. While the longer fractions of asbestos make a major contribution to reinforcement in asbestos cement, the shorter fractions of the fibres have an important function as a retentive carrier for cement particles in the manufacturing process. Only cellulose fibre come close to providing a similar retentive function. Synthetic fibres such as PVA , PAN and PP fibres are offered as replacements in finite lengths and diameters, and as such do not provide filtration properties. They cannot be used in conventional Hatschek cement manufacturing processes without the additional support of cellulose pulp.

PP fibres are hydrophobic and require a surface treatment in a cement matrix. PVA, on the other hand, is hydrophilic and is more amenable to inclusion in cement products. PVA and PP fibres cannot be used for the manufacture of autoclaved sheets. In this case the autoclaved products rely entirely on the mechanical strength properties of the cellulose fibres alone.

Although there has been (and still is) a tremendous thrust in research programs to seek for more fibre alternatives, the fibre cement producers world wide have used only a few of the fibre types researched for products produced for the market today. The reason for this is that choice of a particular fibre type is based on price, availability, compatibility with cement, durability and the reinforcing potential in the cement composite.

The products made with synthetic fibre technology are expensive (cost estimates 20 % more than asbestos cement), where as the Autoclaved technology is priced similar to asbestos cement. It is clear that when a fibre cement manufacturer needs to convert from asbestos to asbestos free technology, the choice between the two technologies is strongly influenced by the cost factor. However, costing is not the only factor involving this choice; a <u>fundamental difference</u> in the choice is also based on the fact that roofing products like <u>corrugated sheets and slates can only be</u> produced successfully with the synthetic fibre approach. This is because of the more extreme exposure of roofing products to natural weathering and therefore durability becomes an issue. Flat sheets for façade application on the other hand can use both technologies. Pipes and moulded goods are in some cases cheaper to produce using synthetic fibre technology due to space constraints in the Autoclave. However, James Hardie have produced autoclaved pipes in Australia for many years. In general it is evident that the change from asbestos fibres to synthetic fibres has provided the fibre cement industry with a more ductile product which improved impact resistance properties.

The following product range exists today in the fibre cement production:

Corrugated sheets

Corrugated sheets are produced in varied lengths from 1 m to 3.5 m. For reasons mentioned above, the synthetic fibre approach is used to manufacture this product. It is used for housing in countries like Brazil, South Africa, Asia, etc.

In Europe it was used for industrial buildings for many years, but recently due to the innovative competitive steel corrugated sheeting market, there has been a very significant drop in the market for industrial applications. Today the major use is for the farming sector.

Roofing slates
This product is very popular in Europe as a replacement for natural slates, which are very heavy and require expensive sub-structure. The product is expensive and competition is high with cement tiles and clay tiles. In European alpine areas it is the preferred product used on farm houses and holiday houses. The product needs to be frost resistant and the synthetic fibre approach is used for this product.

Façade
The user's requirements for façade material are:

High price to performance ratio
Acceptable appearance
Long lifetime
Low combustibility
High impact resistance
UV stability of the surface
Large size façade boards are offered in the measurements up to 3 m lengths with a width of 1.2 m for high rise buildings. The drilling of holes for fastening the boards to the wall is done on site. Hidden fixings were developed for sophisticated application systems.
To fulfill certain American as well as the Australian market requirements, other autoclaved product developments were found to be very useful from economic considerations. For the application of cellulose fibre cement materials such as lap siding or panels, the materials should have sufficient frost resistance and must be flexible. The products are not predrilled; the nail is driven through the wood fibre cement material.
All façade products can be produced, using both synthetic fibre and Autoclaved technologies; the choice depending on the economics and strategic raw material supply.

Interior applications
Important requirements are: Water resistance and low thermal and hygroscopic expansion . For computer-room flooring, very high lumped loads have to be carried by the material, and floor underlay has to secure a very high dead sounding with the respective installation material. There is a very big market for internal walls and ceilings. The major technology used for internal applications is Autoclaved.

Moulded Goods
Garden articles and fittings are produced using mainly synthetic fibre technology.
Finishing ends, ridge caps, etc. for corrugated sheets is a prerequisite for the sale of corrugated sheets. The products are not very profitable, as a lot of manpower is required, nevertheless, it is regarded as an essential part of the sale of corrugated sheets. Garden articles on the other hand are sold as special products and high prices can be requested, depending on the creative aspect of the material and design.

Pipes
This is a dying market as there is no replacement for Asbestos cement pressure pipes. One of the only factories producing synthetic fibre non-pressure pipes today, is in South Africa. James Hardie apparently still produce very small amounts of Autoclaved pipes.

Concluding remarks

The fibre cement industry successfully replaced asbestos cement with a new technology which brought about many new innovative ideas. For example the new material was found to be very tough (less brittle) than asbestos cement and therefore the added value of more impact resistant corrugated sheets and façade panels have been used to their advantage.

Also innovative designs and coating systems have emerged from the new technology which made the product very much more aesthetically appealing than the old dull gray asbestos cement products.

3. Advanced performance in concrete structures in earth quake prone areas and light weight structures

The basic principles of adding fibres to materials to improve the performance of the product has certainly been the fascination of people for many centuries. It is also not per chance that nature was a source of inspiration. Two examples being the structure of a leaf and bird wings, classical examples of how thin materials can be intelligently reinforced to provide strong light-weight structures.
An ancient Greek legend (Icarus and Daedalus) reminds us of this application:
Daedalus was an engineer who was imprisoned by King Minos. With his son, Icarus, he made wings of wax and feathers. Daedalus flew successfully from Crete to Naples, but Icarus, tried to fly too high and approached the sun. The wax melted and the wings fell apart. Icarus fell to his death in the ocean.
In 1485 Leonardo da Vinci designed the first aircraft – the ornithopter – the modern day helicopter is based on this concept.
Concrete engineers followed similar thoughts in the 1960's using fibres to reinforce concrete structures in order to reduce the weight of the structure. It became the trend to design structures with higher strength in conjunction with lighter structural elements. However not all the design engineers understood completely the durability aspects associated with steel fibre reinforcement in concrete structure. This resulted in failure in the field and now new codes of practices needed to be adopted with special emphasis on durability. Deterioration in steel fibre reinforced structures is a combination of mechanical loading and environmental factors. It has been reported by Prof. Victor Li of Michigan University (1) that the American Society of Civil Engineers assessed damage to concrete structures caused by engineering design errors to be more than US$ 1.6 Trillion to be spent over the next five years to repair the damaged structures. In Asia the damage repair is estimated at US$ 2 Trillion and in Germany, Japan, Korea and Thailand it has been reported that damage repair is costing more than new constructions. The major cause of this has been due to the inherent brittle nature of concrete which tends to crack and spall under surface loads. Once the material has cracked, depending on the size of the crack, the ingress of water and other liquids is then evident. This results in corrosion of the steel, sulfate attack and leaching. In countries where sub-zero temperatures prevail in the winter months the cracks are filled with water and therefore freezing and thawing of the concrete inevitably results in destruction of the material.

In the last decade much work has been done to improve the ductility of concrete using fibre reinforcement and cement modifications. One of the pioneers in this field is Prof. Victor Li, see www.engineeredcomposites.com . He has been the master mind behind ECC (Engineered Cementitious Composites) and has published numerous papers in this field. He investigated many types of fibres ranging from Polypropylene, Polyethylene to Polyvinyl alcohol and claims to have produced a very ductile concrete. The material design allows for the so-called strain hardening characteristics which is the particular characteristic of this invention. In January 2007 ECC was named as one of the five winners by Architectural Records in the Concrete and Masonry category. ECC was given the special credit as being the years most interesting and innovative new building products available to architects, designers and specifiers. This invention certainly has a large potential for future consideration in earth quake applications.

Basically the fibre reinforced materials can be put into two categories;
Category 1 (Ductility)
Fibres which have a low modulus and high strain to failure. The interfacial bond between the fibre and the matrix is generally weak and poisson contraction high. This results in a system which can absorb large amounts of energy and ideally suited for impact resistant structures. Typical fibres which fall into this category are Polypropylene, Nylon, etc.
Category 2 (Strength)
Fibres in this category have a high modulus, high strength and low strain to failure. The fibre/matrix bond strength is strong. These types of composites are generally strong with lower impact resistance.
The two categories of fibre reinforced materials can be tailor made to suit the needs of the end user. Engineers have basically used these principles for design criteria for structures, such as industrial floors, nuclear power industry, shotcrete, football and sport stadiums, highways, bridges, etc., etc.
Having realized the vast potential for light weight concrete structures, Lafarge were very innovative and developed a product under the brand name "Ductal". This product essentially uses a powdery premix of cement, siliceous materials together with other potential additives and a special super plasticizer. The type of fibre used for the reinforcement is steel. Lafarge pursued an active

partnership policy with the construction industry, designers, consultants and architects. This resulted in very unique concrete structural designs; one example being the famous villa Navarra with its roof made from Ductal (see fig. 1 below).

Figure 1 Villa Navarra Philipp Rualt

The roof was designed by the architect Rudy Ricciotti, together with the structural engineer Romain Ricciotti and the concrete engineer from Lafarge Mouloud Behloul. The structure is a roof of 40 meters long with a cantilevered surface of 7.8 meters. It is a very bold design and the first Ductal roof construction of its kind

A second example of excellence and creative construction is the 0-14 building in Dubai (Reiser + Umemoto). This concrete structure consists of a lattice like shell exterior 22 story office tower. The structure is load bearing and provides an appealing shading solution for glass towers exposed to the blazing sun in the very hot climate of Dubai. The architects worked together with a structural engineer Ysrael A. Seinuk from New York to create this unique structure cutting down on direct light while still permitting strategically placed views. Another feature of this construction is the deep cavity (1 meter) between the shell and the building which creates a chimney effect drawing hot air away from the building and at the same time cooling down the tower's inner glass surface. The perforated shell was constructed by pouring a concrete with the correct flow properties around a mesh of woven steel reinforcement

Figure 2 During and after construction Dubai 0-14 building

Textile concrete Technology

The first applications using Polypropylene nets in fibre reinforced cements were investigated by Hibbert and Hannant (2). This product demonstrated the useful impact properties which could be derived from placing continuous Polypropylene nets in corrugated sheets. Textile reinforced cements developed over the last decades and much research was done at the University of Aachen and Dresden amongst others. In South Africa Don Hourane (3), an inventor used unique applications of woven textiles (CemForce) For example in certain built-up areas where access for large trucks is limited, the innovative ideas for making "rocks" out of textile fabrics for swimming pools or features in back gardens, a unique example of necessity being the mother of invention. Here chicken wire is used to create the shape of the rock or feature and CemForce was then placed on top of this. The cement/sand mixture was brushed into the woven mat. The required thickness is achieved by using a multiple layered technique with the matrix applied by hand. Obviously this type of application is intended for niche market applications with unique characteristics. See Figure 3 below

Figure 3 Special application of CemForce for niche market applications

4. Innovative cements developed as a result of the Kyoto Protocol

The manufacture of cement requires high temperatures greater than 1400° C. This together with the decomposition of limestone itself (the main ingredient in cement) results in very large quantities of CO2 gas emissions. Roughly 1.6 tons of dry, non calcined minerals are required to produce 1 ton of cement. This is due to loss of CO2, combined water, other volatiles and some fine dust. About 180 – 350 kg of coal is used per ton of cement in coal-fired plants. For every ton of cement produced approx. 1 ton of CO2 is released into the atmosphere. The world cement consumption is increasing rapidly. In 1975 about 1 billion tons of cement was consumed – in 2000 about 1.5 billion tons – and the forecast for 2025 is 4 billion tons. It is estimated that over 6 billion tons will be consumed in 2050. This accounts for very large amount of CO2 potentially released to the atmosphere.

At the Kyoto meeting in 1997, the major industrial nations, with the exception of the USA, agreed to reduce their emissions of these so-called greenhouse gases over the next decades. For example, the target reductions for EU countries was to reduce the emission of greenhouse gases by 8 % by 2008 compared with the 1990 levels. In 2012, further CO2 reduction targets are likely to be adopted by the EU: the discussions suggest that a further 20 – 30 % reduction by 2020, and a 50 % reduction by 2040 may be targeted. This forced cement manufacturers to look for alternative fuels to heat the furnace for cement production. The fuel for the furnace can be oil, gas, powdered coal or various inflammable waste materials, such as used tires or waste oil. In Germany, for example, approx. 350'000 tons of scrap tires are burned each year. About 70 % of this goes to energy production, mainly as fuel in cement kilns. As the burning of clinker requires such high energy consumption, cutting back on clinker production and blending in alternative mineral products were seen as desirable objectives.

Substitute fuels can be classified according to energy potential as follows:

- High-grade fuels, such as scrap tires, plastics, used oil

- Medium-grade fuels include materials such as electrode coke, biogas, biological wastes (such as pellets from paper recycling sludge and ground slaughterhouse waste), sawdust, olive pips, waste from cooking fats and oils.
- Low-grade fuels, cardboard, paper, sewage sludge, etc.

The co-grinding of industrial waste products, such as fly ash or blast furnace slag, to give blended cements is now widely accepted and forms the basis of European standards. The increased use of such blended cements is seen as a viable way of reducing the energy consumption of the cement and concrete industry. For example see Table 1 below:

Cement type	Designation	Notation	Clinker %	Other main ingredient %	Minor Additives %
CEM I	Portland cement	I	95 - 100	0	0 – 5
CEM II	Portland slag cement	IIA-S	80 – 94	6 – 20	0 – 5
		IIB-S	65 – 79	21 – 35	0 – 5
	Portland silica fume cement	IIA-D	90 – 94	6 – 10	0 – 5
	Portland pozzolanic cement	IIA-P	80 – 94	6 – 20	0 – 5
		IIB-P	65 – 79	21 – 35	0 – 5
		IIA-Q	80 – 94	6 – 20	0 – 5
		IIB-Q	65 – 79	21 – 25	0 – 5
	Portland fly ash cement	IIA-V	80 – 94	6 – 20	0 – 5
		IIB-V	65 – 79	21 – 25	0 – 5
		IIA-W	80 – 94	6 – 20	0 – 5
		IIB-W	65 – 79	21 – 25	0 – 5
	Portland burnt shale cement	IIA-T	80 – 94	6 – 20	0 – 5
		IIB-T	65 – 79	21 – 25	0 – 5
	Portland limestone cement	IIA-L	80 – 94	6 – 20	0 – 5
		IIB-L	65 – 79	21 – 25	0 – 5
	Portland composite cement	IIA-M	80 – 94	6 – 20	0 – 5
		IIB-M	65 – 79	21 - 25	0 – 5
CEM III	Blast furnace cement	IIIA	35 – 64	36 – 65	0 – 5
		IIIB	20 – 34	66 – 80	0 – 5
		IIIC	5 – 19	81 – 95	0 – 5
CEM IV	Pozzolanic cement	IVA	65 – 89	11 - 35	0 – 5
		IVB	45 – 64	36 - 55	0 – 5
CEM V	Composite cement	VA	40 – 64	36 - 60	0 – 5
		VB	20 – 39	61 – 80	0 – 5

Table 1 European Cements available today (4)

The use of additives and admixtures in concrete has been shown to be highly beneficial in improving the quality and durability when the correct procedures are followed. However, some European countries are far more advanced than others in implementing these improved procedures.

Eco-Cement

Eco-Cement was a term used at the turn of the century for more environmentally friendly cement and has caught on since then. The first commercial scale Eco-Cement plant was commissioned in 2001 in Japan by Taiheiyo Cement. The Principle of Eco-Cement is that the cement kiln can serve as an incinerator for waste materials, with any residue becoming part of the cement. Taiheyo has developed processes for removing chlorides and heavy metals from incinerator fly ash. The cement plant consumes sizeable quantities of refuse-derived fuel (from municipal solid waste) and can use sewage sludge. All wash waters are cleaned and recycled. There are no particulate emissions. Dioxin emissions are within those legally specified by the Japanese authorities. Any trace of dioxin trapped in the precipitators is recycled to the cement kilns, where it is decomposed in the high temperature zone (1350℃).

Many other companies followed suit and much publicity is given today to the so called Eco-Cement generation. These include just to mention two examples:

1) Using cement kiln dust and granular blast furnace slag developed in China
2) Tec-Eco in Australia which used the strategy of replacing the calcium with magnesium which allowed much lower furnace temperatures to be used. This cement proved to be more resistant to salt, acid and chlorine corrosion

Holcim (contribution by Dr. Markus Tschudin)

Holcim has a strong commitment to sustainable development. In 2007, for the third year running, the Dow Jones Sustainability Index acknowledged Holcim as the "leader of the industry". Holcim was honored for its efforts to raise awareness for sustainable development. Awareness for sustainable development will become a core element of the company's culture and the concern of managers at every level. To achieve this goal, precise objectives have been formulated and a concise reporting procedure set up.

Holcim as established several internal standards and complies with the external norms defined by the World Business Council for Sustainable Development. For example, Holcim is actively taking part in the Cement Sustainable Initiative, a global effort by 18 major cement producers that collectively account for 28 % of the world's cement production. The aim is to identify actions and facilitate steps to accelerate progress toward sustainable development in the cement industry.

By the end of 2007 Holcim achieved a reduction of more than 16 % in net CO2 emissions per ton of cement compared with figures in 1990. The target is 20 % by 2010.

Super-sulphated cements are used for structures in contact with sea water or sulphate-containing media and soils They can be used in sewer construction, for example. The ingredients for making super-sulphated cements are 80 – 95 % granulated blast furnace slag ground with 10 – 15 % calcium sulphate in the form of anhydrite or burnt gypsum and 5 % portland cement.

Sulphate-resistant portland cement. Sulphate solutions can react with the hydrated C3A phase or hydrated lime in ordinary portland cement to give a calcium sulphoaluminate phase. The reaction is accompanied by a large change in volume that can lead to weakening, fracture, or dusting. To overcome this problem special grades of cement have been developed with low levels of C3A phase present.

Oil well cements are pumped down oil wells during the drilling operation with the objectives of supporting the steel well liner and sealing off porous material. Since depths of 5000 – 10000 meters are not uncommon, the cements have to perform under extreme conditions of temperature (>150℃) and pressure (100 MPa). In addition, they should also provide fluid for pumping and placing during the duration of the lining operation; therefore, super plasticizer and retarders are usually specified.

Expanding cements are designed with one of two objectives: either to compensate for the shrinkage that occurs during the setting of normal cement (thereby avoiding cracking or unsoundness in general), or in self-stressing reinforced concrete where the expansion of the matrix transmits a tensile stress to the reinforcing steel bars or mesh. Such materials are very useful in pavement slabs, bridge decks and liquid storage tanks. It has been estimated, that 1 % of concrete structures are made with expanding cement. The material is about 20 % more expensive than ordinary portland cement.

Chemically, most expanding cements comprise sulphate ingredients that lead to the formation of calcium alumino-sulphate hydrate phases during settling at a controlled rate. The expansion should occur while the cement has some strength, but is still sufficiently plastic to avoid cracking. Ideally, the expansion should cease after only a few days. The material needs to be wet-cured. The addition of stabilizers, such as ground slag or silica fume, is a common approach to control or limit the expansion beyond a certain point.

5. New innovative cements in the nuclear power industry

Nuclear Power industry in general

Nuclear energy production is over 50 years old. After a rapid increase in the 60s and 70s, stagnation set in due to the continued low prices for fossil fuels, to the accidents at Three Mile Island and Chernobyl and also to the increasing costs of power plants. In recent years, however, these concerns have been allayed, the global hunger for primary energy has grown and the necessity for reducing CO2 production has been recognized. The result is that nuclear power production is on the verge of experiencing a global renaissance. On 1 January 2008, 439 nuclear power plants operated in 30 countries worldwide, with a total installed capacity of 371 GWe. Recent projections indicate that by 2060 there could be at least 1130 GWe and up to 3500 GWe.

An average size power station of 1000MWe will generate 25 – 30 t spent fuel and 200 – 350 m3 of short lived low and intermediate level wastes per year. When a nuclear plant is decommissioned, it will produce around 10'000 m3 of low level wastes, most of this will be contained in cement and concrete. Since the beginning of the nuclear industry, comprehensive plans have been established for the disposal of radioactive wastes from commercial nuclear power programs. A critical component of the important nuclear fuel cycle is the safe disposal of radioactive wastes. Many national waste management organizations and private companies world wide are performing dedicated research to address these issues. For example, large programs like that of the Department of Energy in the USA have had an annual budget of several hundred million dollars for the last 25 years. Even in small nuclear programs, such as in Switzerland with only 5 nuclear plants, R&D work in waste disposal has already cost over 500 million dollars.

Cements in the nuclear power industry

Cement and concretes have played a significant role in the radioactive waste disposal scenarios. There are a variety of applications for cementitious materials and these depend on the different disposal concepts. A key issue here is that, for many applications, the mechanical and hydraulic performance are not of prime importance as is the case for standard engineering thinking. The reason for this is that the structures will mostly be backfilled. This is certainly true for underground tunnels and caverns proposed for disposal of spent fuel or high-level wastes. However, for surface and shallow disposal of low level waste (where short half lives of the radion nuclide imply that isolation is required for only a few hundred years), the strategy which is considered in some countries is to allow for periodic monitoring of the disposal site, so that backfilling if at all, will only take place at the time of decommissioning.
Some key requirements on the cements and concretes used in the varied applications are given in the following categories:

a) Conditioning cement/mortar (for low level and intermediate level waste)
- chemical compatibility with the waste stream composition
- good incorporation of safety-critical radio nuclide
- low dissolution rate
- resistance to mineralogical alteration which could enhance radio nuclide release rates

b) Backfill mortar (for low level and intermediate level waste)
- good mortar flow properties for emplacement
- high sorption capacity
- sufficient gas permeability
- high calcium content

c) Structural concrete (for surface / shallow disposal)
- low hydraulic conductivity
- reasonable structural strength
- resistance to cracking, shrinkage and degradation

d) Structural concrete (deep disposal for intermediate waste)
- requirements as mentioned for surface / shallow disposal with additional emphasis on pH conditioning of ground-water which could enter the vault

e) Structural concrete (deep disposal for high level waste)
   - minimum chemical interaction with the Engineered-Barrier System, especially if bentonite clay is a key radiological safety barrier

f) Injection grouts
   - similar to requirements mentioned above for category d)

Cement has many favourable characteristics which make it an attractive candidate for a waste binding agent. It is readily available, inexpensive, non-combustible, radiation-resistant, and has good chemical, mechanical and thermal stability at the temperatures reached with low-level and medium-level wastes. Optimally processed cement/waste composites, using well established concrete technology, have low leach rates in ground waters and can be modified relatively easily to suit the specification required by the waste disposal experts.

Long-term stability of concrete is the most significant, and the largest unknown factor in its application in a nuclear waste repository. It is essential for prediction of long-term behavior and assessment of suitability for use in radioactive waste repository environments to understand chemical, mechanical and thermal stability under a wide variety of conditions including elevated pressure, temperature and diverse groundwater compositions.

Concrete durability will depend on the following factors:
- Chemical and electrochemical compatibility with the host rock. This directly influences reactions which could adversely affect the stability of the concrete in the repository site.
- Chemical and physical stability in the in-situ repository environment. The concrete should not be adversely influenced by groundwater, pressure or temperature. Additionally, the concrete should be chemically stable so that its ability to withstand environmental stresses and perform adequately is not altered over very long time periods.

Many concrete structures exposed to highly aggressive media for prolonged periods of time have withstood such exposures successfully without any special protective measures. Dense concrete is one of the essential prerequisites for sulphate resistance even when using cements of low C3A content.

The major constituent of hydrated cement paste is C-S-H which is considered to be thermodynamically metastable with respect to crystalline calcium silicate hydrates of the same composition. With prolonged exposure the metastable constituents will crystallize and porosity will be increased only very slightly at temperatures at or below 100°C.

Under anticipated environmental conditions it is desirable to use a sulphate resistant cement for long-term chemical and thermal stability when incorporating high concentrations of certain radioactive waste species. The addition of waste to cement-water mixtures has been shown to influence set time. A decrease of set time can sometimes be attributed to the heat of hydration of the waste components. Borate wastes and boric acid from reactor coolant can prevent cement paste from setting if used in sufficient quantities. In order to improve the hydration and setting characteristics of these waste forms, lime is added to the borate waste/cement paste. Boric acid also decreases the rate of heat release and the total heat liberated during the curing of concrete, whilst calcium hydroxide has the opposite effect on curing exotherms when used with boric acid.
The C3A content is a very important factor to control the chemical resistance. The C3A content of sulphate resisting cement should not exceed 5.4 %. One method of increasing the sulphate resistance is the substitution of the compound C4AF for C3A. However, too high content of C4AF decreases the chemical resistance of low-C3A contents and Sulfacem appears to have very high content of C4AF.

Under normal conditions the waste forms would be isolated within sealed drums. Leachability becomes a concern under geologic repository situations where the container is breached and water is allowed to come in direct contact with the waste form. Cobalt, cesium, strontium and alpha emitters are the species of greatest concern in radioactive waste solidification matrixes – the first three because they are the most intensive sources of radiation in the short term, the last because their radioactivity is very long lived. Leachability varies with types of cement and sludge. Long cure times and irradiation tend to decrease leachability while prolonged exposure to high temperatures and increased leachant renewal frequency tend to increase leachability. Leachability of cesium is generally greater than that of cobalt from similar waste forms.

The abilities of bentonite clay to swell to provide an excellent hydraulic barrier and to retard radionuclide transport by sorption are key processes determining long-term safety in many geological repository concepts. Accordingly, in nuclear waste disposal programs there are concerns about high pH plumes emanating from cements and altering the physical and chemical properties in the bentonite buffers. A lot of work has been done on this particular subject, for example at the University in Aberdeen. The concern is associated with OH which affects mineral stability and sorptive capacities. Studies on natural analogues, as in Jordan where highly alkaline springs occur in the vicinity of clay deposits, have disclosed that the "alkali plume" hydroxide could migrate. In particular low pH cement/grouts have been developed pushing the cement chemistry into a new field of research and therefore dissolution modeling needs to become much more sophisticated (5). In fact, the necessity in waste disposal for long-term predictions of cement behavior has led to rapid advances in computer modeling of the evolution of the chemical and physical properties of cements over thousands of years.

Summary

In general, some of the major requirements on cements and concretes considered for nuclear waste disposal are:

Cement as a waste solidification matrix:

- A sulphate-resisting cement should be used to reduce substantially chemical attack by groundwater.
- The sulphate-resisting cements should have a relatively high C2S content and low alkali content.
- The C3A in the cement should be as low as possible in order to achieve maximum durability of the concrete.
- The water-cement ratio should be as low as possible and preferably 0.40 or less.
- The amount of chlorides and sulphates in the mix should be reduced to a minimum.

Cements for structural purposes

- Low alkali or low pH cements should be employed; these are blended Portland cements consisting of varied combinations of the three products silica fume, fly ash and blast furnace slag. These blended cements satisfy acceptable durability performance requirements such as; positive strength developments, low shrinkage, permeability, resistance to leaching. But more importantly they offer the possibility of greatly reduced interaction with bentonite clay which, in concepts for high level wastes and spent fuel, is a key safety barrier reliant on chemical and physical properties that can be disrupted by potential alteration in high pH pore fluids. The lowered heat of hydration and low shrinkage means that they are preferred for construction of massive concrete plugs for tunnel and shaft sealing as they reduce potential thermal effects (spalling, cracking) in the host rock and help ensure good seal performance.

- Other types of cement which have also been considered are: .
    - Calcium aluminate cements
    - Phosphate cements
    - Magnesia cements

Research programs in cement for nuclear waste disposal concentrated at first on the mechanisms of durability and leaching. These solutions were then provided by looking at availability of raw materials and how best to use these for tailor made solutions. In this case the necessity was to understand the mechanism and the invention is subtle modifications of existing strategies well established in the modern concrete industry. (We should not however forget to pay our due respects to the ancient Greeks and Romans.) More recent work on cements and concretes in the area of radioactive waste disposal has focussed on understanding their interactions with the engineered safety barriers in repositories and in developing sophisticated computerised models of their behaviour over very long periods of time.

6. Concluding remarks

The four examples given in this paper have discussed the developments provoked by demands initiated by changing environments.

The asbestos cement industry has converted its image from the boring gray asbestos cement product to a new generation of products with extravagant colors and products with greater impact resistance.
In the concrete industry the addition of fibres and other additives have allowed architects to design elegant/bold structures which are not only esthetically pleasing but also provide more secure structures especially in earthquake prone areas.

The cement industry has been pressurized into developing more “CO2” friendly cements resulting in the development of a large variety of innovative cements with improved flow and sulfate resistant properties.

The nuclear power industry has devoted much effort into the understanding of the durability and leaching properties of cements. This has made it possible to develop cements which have a predicted life of more than 10’000 years, based on mathematical models.

The creative and inventive spirit of mankind will always be inspired by changes related to progress.

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