Cement and Concrete Research 41 (2011) 642–650

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Sustainable cement production—present and future

M. Schneider [a,*], M. Romer [b], M. Tschudin [b], H. Bolio [c]

[a] VDZ, Düsseldorf, Germany
[b] Holcim Group Support Ltd, Holderbank, Switzerland
[c] CEMEX, Monterrey, Mexico

ARTICLE INFO

Article history:
Received 23 March 2011
Accepted 28 March 2011

Keywords:
Cement manufacture (E)
Alternative fuels and raw materials
Grinding (A)
Clinker substitution
CO_2

ABSTRACT

Cement will remain the key material to satisfy global housing and modern infrastructure needs. As a consequence, the cement industry worldwide is facing growing challenges in conserving material and energy resources, as well as reducing its CO_2 emissions. According to the International Energy Agency, the main levers for cement producers are the increase in energy efficiency and the use of alternative materials, be it as fuel or raw materials. Accordingly, the use of alternative fuels has already increased significantly in recent years, but potential for further increases still exists. In cement, the reduction of the clinker factor remains a key priority: tremendous progress has already been made. Nevertheless, appropriate materials are limited in their regional availability. New materials might be able to play a role as cement constituents in the future. It remains to be seen to what extent they could substitute Portland cement clinker to a significant degree.

Contents

1. Introduction

Cement production has undergone a tremendous development from its beginnings some 2000 years ago. While the use of cement in concrete has a very long history, the industrial production of cements started in the middle of the 19th century, first with shaft kilns, which were later on replaced by rotary kilns as standard equipment worldwide. Today's annual global cement production has reached 2.8 billion tonnes, and is expected to increase to some 4 billion tonnes per year. Major growth is foreseen in countries such as China and India as well as in regions like the Middle East and Northern Africa (Fig. 1) [20].

At the same time, the cement industry is facing challenges such as cost increases in energy supply, requirements to reduce CO_2 emissions, and the supply of raw materials in sufficient qualities and amounts. The World Business Council for Sustainable Development and its Cement Sustainability Initiative, comprising cement producers worldwide, has initiated the project "Getting the Numbers Right" which for the first time

* Corresponding author. Tel.: +49 211 45 78 200; fax: +49 211 45 78 296.
E-mail address: sch@vdz-online.de (M. Schneider).

0008-8846/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2011.03.019

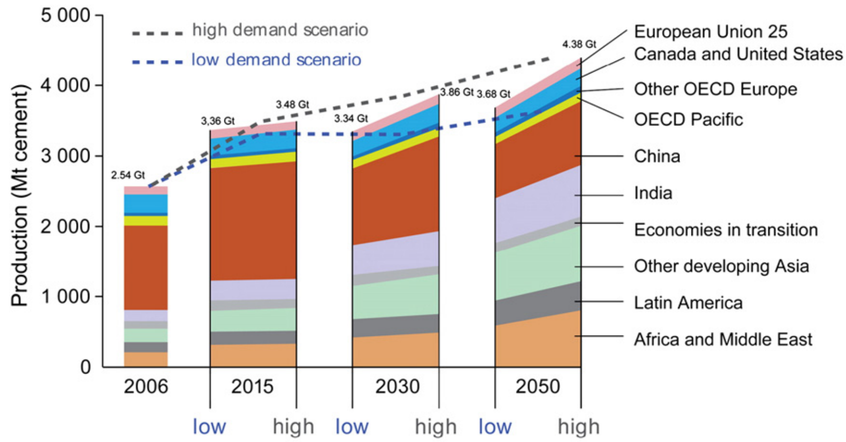

Fig. 1. Global cement production ([39]).

provides a good database for most of the global cement industry with respect to CO_2 and energy performance [37].

2. Clinker production

2.1. Energy efficiency in clinker production

Energy demand in clinker production has been significantly reduced over the last few decades. Best available techniques (BAT) levels for new plants and major upgrades are 2900 to 3300 MJ/t clinker, based on dry process kilns with multistage-preheaters and precalciners [11]. However, the factors involved to further reduce this demand are plant-specific. The moisture content of the raw materials or given by-pass rates determine the heat consumption [2,22] (Fig. 2). The main driver to reduce energy consumption on a global average is kiln size, which is, however, in most cases, not applicable for existing installations. Cement plant capacities will remain in the typical range of between 1.5 and 2.5 million t/a, resulting in typical single clinker production lines between 4000 and 7000 t/d. Very large cement and clinker lines of 10,000 or even 12,000 t/d will generally be the exception, and will be located on large rivers for domestic distribution or on the coast for international distribution [25].

In this context, waste heat recovery may play a more important role. While in China and Japan boilers for electricity generation are widely integrated to cement kilns, a growing potential might be raised in other parts of the world. Rising electricity prices in combination with decreasing investment costs will result in the further expansion of this technology in general [30]. 30–45 kWh/t of clinker is becoming feasible for recovered energy from bigger kilns. The waste heat utilization industry itself is developing technologies to widen the potential for energy recovery. Depending on the volume and temperature level of waste heat, a range of specific technologies can be applied. An interesting case for the cement industry is the low temperature waste heat recovery made possible by using the Organic Rankine cycle, which allows the generation of electrical power even with smaller volumes of lower temperature flue gas.

2.2. Alternative fuels

The use of alternative fuels and raw materials (AFR) for cement clinker production is certainly of high importance for the cement manufacturer but also for society as a whole. Alternative fuel utilization began in the mid 1980s. Starting in calciner lines, up to almost 100% alternative fuel firing at the precalciner stage was very quickly achieved. Alternative fuels are mainly used tires, animal residues, sewage sludges, waste oil and lumpy materials. The last are solid recovered fuels retrieved from industry waste streams, and to a growing extent also from municipal sources. These refuse-derived fuels are pre-treated light fractions processed by mechanical or air separation. Waste-derived fuels consist of shredded paper, plastics,

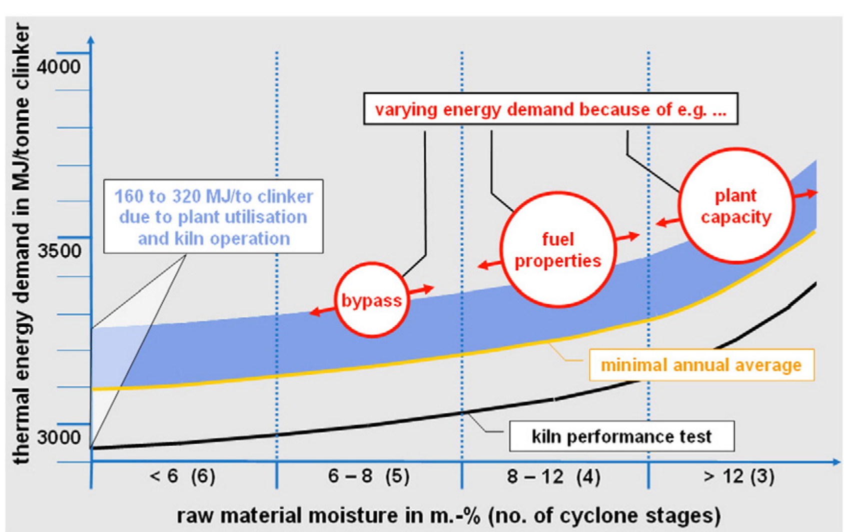

Fig. 2. Factors affecting the specific fuel energy requirement of cement clinker kilns ([2], p.56).

foils, textiles and rubber and also contain metal or mineral impurities. Alternative fuel utilization in cement kilns is still progressing. While in some kilns up to 100% substitution rates have been achieved, in others, local waste markets and permitting conditions do not allow for higher rates of AFR. In any case, AFR utilization requires the adaptation of the combustion process. Modern multi-channel burners designed for the use of alternative fuels and thermograph systems allow control of the flame shape to optimize the burning behavior of the fuels and the burning conditions for the clinker [35]. Finding an ideal burner position is beneficial for the burning process and clinker quality. Oxygen enrichment of primary or secondary air is proving to be promising for advanced alternative fuel combustion.

In a conventional preheater kiln (without precalciner), it is only possible to burn fuels in the kiln inlet with substitution rates of up to 25 to 30%. This means that 70 to 75% has to be fired in the main firing. In precalciner kilns usually up to 65% of the total fuel energy input is fired into the calciner and a minimum of 35% through the main kiln burner. As a consequence, in precalciner kilns, fluctuations in fuel quality, which can significantly depend on the type of fuel (Fig. 3), have less impact on the kiln performance. On the other hand, changes or fluctuations in the main kiln firing have a significant effect on kiln operation and clinker quality. Therefore – if alternative fuels are used – most operators first increase the alternative fuel substitution in the precalciner. After this, they start to increase the proportion of alternative fuels in the sintering zone firing.

While the use of alternative fuels for the production of Portland cement clinker can substitute fossil fuels, it can have an influence on the clinker properties. The burning behavior of most alternative fuels differs significantly from the behavior of fossil fuels due to higher particle sizes, material densities and transport characteristics. This can change the temperature profile of the kiln including the sintering temperature, the length of the sintering zone and the cooling conditions. All of these changes can affect different clinker characteristics like the burning grade of the clinker, the porosity of the granules, the crystal size of the clinker phases or their reactivity.

The amount and composition of the ashes introduced by alternative fuels mostly differ from those of fossil fuel ashes, partly introducing unusual components into the kiln. A prominent example is phosphorous, mainly contained in meat and bone meal or sewage sludge. Phosphorous oxide ($P_2O_5 = P$) is mainly incorporated in crystals of a solid solution of belite (C_2S) and C_3P with the crystal structure of β-, α- or α'-belite, depending on the C_3P-content. Belite with a certain amount of C_3P-component does not react with free lime at sintering conditions in the kiln, causing clusters of belite and free lime (Fig. 4, [3]).

Additionally, ion substitution reactions ($2\,Si^{4+} \leftrightarrow Al^{3+} + P^{5+}$) lead to a further increase of the belite content and a decrease of the C_3A content in the clinker. The influence of phosphorous can have effects on the performance of cements produced with the clinker, e.g. lower early strength or longer setting times [28].

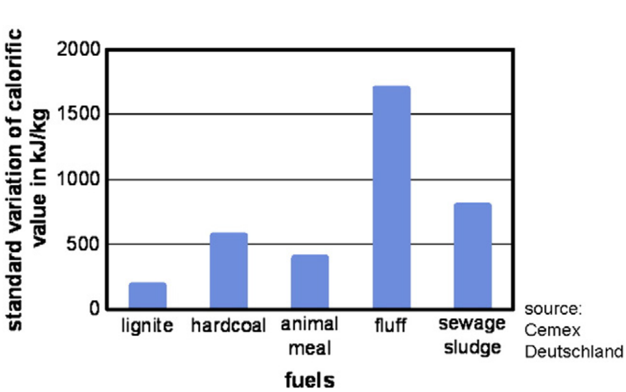

Fig. 3. Standard variation of calorific values of various fuels ([35], p.44).

An adequate tool for the prevention of negative effects is limiting the phosphorous content in the clinker. The limit has to be individually adjusted to each cement plant and clinker. With the close control of the phosphate level of the respective alternative fuels, the maximum proportion of the fuel can easily be calculated. Generally, the production process and the materials have to be monitored more closely when high ratios of alternative fuels are used. With adequate comprehensive production control, the manufacturing of high-performance Portland cement clinker is possible even with significant substitution rates of alternative fuels.

Process energy for clinker burning will also in the future most certainly depend on waste-derived fuels and fossil fuels. Renewable energy might come from selected waste streams—on a more visionary basis, methanol produced from hydrogen and CO_2 might be an interesting option. While hydrogen could come from renewable electricity sources and CO_2 from capturing installations, the total energy balance remains an open question but deserves a closer look. ECRA, the European Cement Research Academy, will conduct a first study work on this technology [10].

2.3. Alternative raw materials

Raw materials for clinker production are for good reasons primarily based on limestone, clay or its natural mixture, marl. In many cases, alternative raw materials are used mostly as corrective materials. Typical examples are given in Table 1 [33]. With respect to resource efficiency along the value chain, concrete recycling is already in an advanced state. Separating concrete from reinforcement is common practice in order to recycle the material, e.g. to be used as aggregates in new concretes [18]. Only the use of crushed concrete sand in concrete itself remains a challenge. Research has shown, however, that concrete crusher sand can serve as an alternative material in cement clinker manufacture. By definition, concrete crusher sand has a grading of 0 to 2 mm and is obtained when recycled aggregates are generated from crushed concrete. Its use as a raw material in cement clinker production allows the complete and high-grade recycling of concrete. In addition, uncarbonated hardened cement paste in the concrete crusher sand may additionally result in CO_2 emission reduction from clinker production.

Chemical analyses of concrete crusher sands typically show the high silicon content largely derived from the sand portion of the recycled concrete. The chemical composition of the concrete crusher sands clearly indicates that these materials can primarily be utilized as a substitute for sand, and can account for an average of 3% of a typical raw material mix [17]. Crusher sands with a higher calcium oxide proportion can additionally be substituted for calcium agents. In any case, crusher sands can only be used if the raw material composition

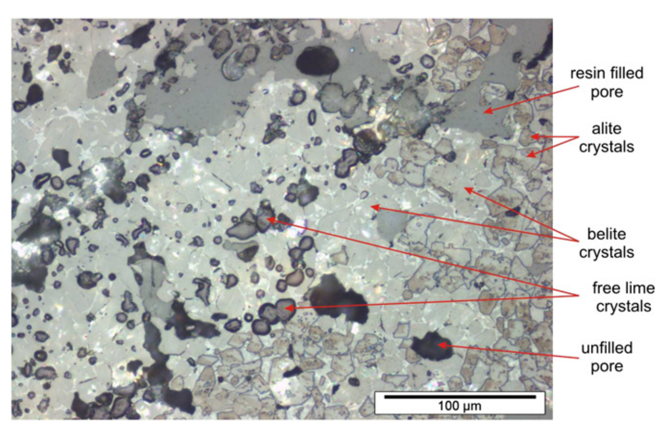

Fig. 4. Belite enriched in P_2O_5 (light gray), interspersed with fine grained free lime (dark gray) ([3]).

Table 1
Raw materials for clinker production ([33], p.8).

Group	Material—examples
Ca	Limestone/marl/chalk
	Others, such as:
	–Lime sludge from drinking water and sewage treatment
	–Hydrated lime
	–Foam concrete granulates
	–Calcium fluoride
Si	Sand
	Used foundry sand
Si–Al	Clay
	Bentonite/kaolinite
Fe	Iron ore
	Other input materials from the iron and steel industries, such as:
	–Roasted pyrite
	–Contaminated ore
	–Iron oxide/fly ash blends
	–Dusts from steel plants
	–Mill scale
Si–Al–Ca	Granulated blast furnace slag
	Fly ash
	Oil shale
	Trass
	Others, such as:
	–Paper residuals
	–Ashes from incineration processes
	–Mineral residuals, e.g. soil contaminated by oil
Al	Al Input materials from the metal industry, such as:
	–Residues from reprocessing salt slag
	–Aluminum hydroxide
S	Natural gypsum
	Natural anhydrite
	Gypsum from flue gas desulfurization

from the local quarry allows for it and the overall composition of the raw mix corresponds with the requirement of the clinker quality.

A future challenge of the cement industry is to use more alternative raw materials originating as byproducts from other industries or directly from other waste streams. One example could be bottom ash from municipal solid waste incinerators. The cement industry has a good tradition of implementing such new materials into its raw material portfolio, and has maintained a focus on OH&S aspects as well as on environment factors, which are of course considered in each individual case.

Another topic of alternative material use in cement production is related to gypsum. Besides the natural deposits, gypsum results as a byproduct from various industrial processes e.g. desulfurization plants from electrical power production. Normally, such synthetic gypsum contains traces of other materials, which might require adaptations in the manufacturing processes. Again, OH&S as well as environmental requirements have to be met in any individual case.

2.4. Grinding efficiency

Grinding efficiency is important for all comminution processes in a cement plant, i.e. raw material, coal and cement grinding. While the requirements are basically the same in all cases, cement grinding has a special additional focus, which is workability of the final product and its strength development. Both parameters not only depend on the particle size but to a large degree on the size distribution. From a technology point of view, grinding remains the biggest source of energy consumption in cement production. While total electrical energy consumption for cement production is about 100 kWh/t of cement, roughly two thirds are used for particle size reduction [31,32] (Fig. 5).

The overall efficiency of comminution is between 1% and 5%, certainly unsatisfactory. It is known that single particle comminution can be up to one order of magnitude more efficient [19]. On the other hand, technical requirements for through-put in mass production put severe technical limits on efficiency improvement.

Ball mills have been used for over 100 years for milling processes in cement production. This mill type has prevailed because of its reliability and the favorable properties of the cement ground with ball mills. Primary ball mills were operated as open-circuit mills, later, separators were added to produce improved cement qualities in a closed-circuit. The fundamental disadvantage of the ball mill is the relatively high specific grinding energy demand. In addition to the ball mill, high-pressure grinding systems such as vertical roller mills (VRM) or high-pressure grinding rolls (HPGR) are in use today for cement grinding. The specific energy demand of these grinding systems is comparatively low, but the cement from high-pressure mills shows slightly different properties in terms of its particle size distribution (PSD).

The PSD of cement and/or its components has an important influence on water demand, the setting behavior, and the strength development of cement in mortar and concrete. The PSD of the product depends significantly on the mill system used for cement grinding and therefore especially affects the choice of cement mills.

The cement grinding process in the ball mill generates a relatively broad PSD. Typical slopes are in the range of about 0.8 to about 1.0 on the RRSB granulometric diagram if the ball mill is operated in a closed circuit with a separator. The cement fineness can be adjusted by the selected fresh material feed, the rotational speed of the separator, and the separation air volume flow. In open circuit ball mill grinding plants, slopes of about 0.8 to 0.9 can be achieved, and varying the PSD is possible only in relatively narrow ranges (e.g. by modification of grinding media composition). The required fineness of cement can only be adjusted by the selected fresh material feed. In the case of high pressure comminution with vertical roller mills (VRM) or high-pressure grinding rolls (HPGR), the achievable PSD is much narrower. With such mills, slopes in the range of about 0.95 to 1.1 (VRM) or 1.1 to 1.25 (HPGR) are achievable.

For rheological reasons, most of the required mixing water is used for the moistening of the particles and the filling of the gap volume between the particles. To achieve the workability of the cement, sufficient water must be added so that the particles can move against each other. The required amount of water is particularly influenced by the PSD. Consequently, in most cases, the water demand of cements from high pressure comminution is higher, since these cements have narrower PSD and thus there is a larger gap volume to be filled.

The strength of cements with the same specific surface area increases with narrowing of the PSD. This is caused by an increase of completely hydrated fines as a result of the decreasing average particle size (position parameter). This position parameter represents the fine particle fraction, which is responsible for the strength behavior of the cement.

In addition to energy demand, reliability in operation, and water demand of the finished product, the demand for drying energy when grinding granulated slag can also affect the choice of the grinding system. The differences in dehydration of gypsum in the various mills

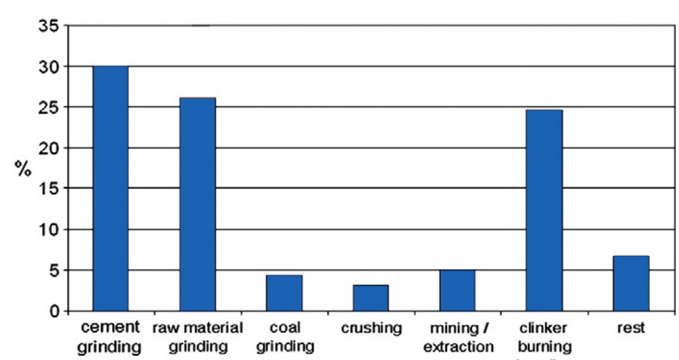

Fig. 5. The use of electrical energy in cement production.

are known and taken into account when choosing the right kind of sulfates.

It still remains an open question if more efficient grinding systems can be expected in the future. Certainly existing technologies will be re-evaluated and cross-experience from other industries might give some new insights.

Grinding a material always produces a range of particle sizes. Not all the particle sizes of a material are of equal relevance for the physical and chemical aspects of cement application. In relation to the hydration processes, each type of material would theoretically have its ideal particle size allowing the optimal chemical transformation at the right time during cement hydration. In reality, there are always significant proportions of particles that are too small or too big.

The grinding system (mill, grinding media, and dwell time) and the mechanical resistance of the materials determine comminution. Softer materials like natural pozzolans and limestone tend to form large proportions of very fine particles, whereas hard materials like blast furnace slag tend to result in coarser fractions. By intergrinding the cement constituents, a range of materials are combined and ground simultaneously. The possibility of optimizing the PSD of each individual constituent is therefore limited. The separator can also not overcome this and only acts on aerodynamic properties.

It is widely accepted that grinding selected main cement constituents separately and subsequently blending them allows better control of the cement characteristics and can also lead to better valorization of the different materials. In addition, the specific energy consumption of grinding/blending in relation to the product performance is better than in intergrinding. Separate grinding allows the reduction of clinker content in cements with several constituents while performance is kept constant. Of course, such a process requires more equipment in the plant and the additional handling of intermediate products.

With respect to future developments, completely new approaches have been tested and will certainly be further developed. For example, ultrasonic comminution transfers the energy needed for crushing to the material by acoustic pulses. This approach was introduced in 2003 [15,27]. Two counter-rotating disks with special aerodynamic surfaces generate ultrasonic pulses, which due to their small pulse duration exert pressure waves on the particles which are pulverized very efficiently. The results from first tests with granulated blast furnace slag of different origins were promising, but future research remains necessary. The scaling up to industrial dimensions in particular is an open question. The system has been tested for slag grinding in model scale only [13].

Completely open are developments such as plasma comminution. Plasma comminution is performed in a liquid by using shock waves. The application is still limited to semiconductor materials.

In conclusion, it remains an open question how grinding efficiency can be improved while ensuring sufficient throughput for mass production. Certainly, fracture mechanics has not given sufficient understanding with respect to clinker and the other cement constituents. A more comprehensive approach might be necessary to reveal a deeper understanding and consequently better adaptation of today's grinding systems.

Besides optimizing the grinding system and cement composition, the addition of chemical substances during the grinding process offers further potential to improve the process and product performance. Such additives are promoted by a growing number of manufacturers/suppliers and the business of cement additives is growing worldwide. Depending on the situation, so called grinding aids offer benefits in specific grinding energy and can increase the mill throughput by 10% or more. Such substances show primarily a physical surface action and reduce the tendency to form particle aggregates. By this, coating of the grinding media is reduced and the efficiency of the separator improved.

Cement additives may also contain substances which have an impact on the cement performance in application. Such solutions may directly affect the water demand of cement by a physical dispersing action which leads to better workability. Other products affect chemical reactions of cement hydration and may lead to faster setting or strength improvements in early and/or late age. The use of air-entraining cement additives is normally used in masonry cements, where special application requirements are more easily achieved with high levels of entrained air in the fresh mortar mix.

2.5. Carbon Capture and Storage (CCS)

According to different abatement scenarios and the International Energy Agency's recently published roadmap, the cement industry is expected to contribute to CO_2 mitigation globally by a set of different measures among which CCS plays a key role. After 2020, a commercial application of CCS technologies is anticipated to be available at least in the OECD countries, but to a significant extent also in countries like China and India. It is obvious that any pilot or even demonstration plant can only be initiated on the basis of sound facts and figures on the technical and economical feasibility.

Against this background, ECRA, the European Cement Research Academy, has decided to look at the capture of carbon dioxide as a prerequisite for a safe geological storage of CO_2 [7]. ECRA's goal is to examine the technical and economical feasibility of this technology as a potential application in the cement industry. ECRA puts a strong emphasis on the global perspective of its research and also its sustainability aspect. This implies that not only CO_2 emissions as such, but also the huge energy demand for operating CCS plants will be taken into account.

Besides technical aspects, the economic framework will be decisive for future applications of carbon capture in the cement industry. At the moment, the costs for CO_2 capture are estimated to amount to 20 to 50 €/t CO_2. This does not include additional costs for transport and storage of CO_2. Furthermore it does not include costs for the potential retrofit of existing cement technology including necessary switches in fuels and raw materials. The wide range represents the very different values given in the literature for the individual technologies. Based on avoided CO_2 emissions, the cost estimates range from 24 to 75 €/t CO_2. These costs are higher since more CO_2 emissions occur in plants with CO_2 capture due to their reduced overall efficiency than in a reference plant without CO_2 capture.

All presently available capture technologies are far from being applicable to the cement industry due to technical and economic reasons. However, some capture technologies seem to be more appropriate for the potential application at cement kilns than others [8,38].

Oxy-fuel technology relies on oxygen instead of ambient air for combustion, i.e. the nitrogen is removed from the air in a separation plant, prior to being applied to the kiln. Consequently, the concentration of carbon dioxide in flue gas is increased significantly and for CO_2-capture only a comparatively simple carbon dioxide purification is required, if any. To introduce oxy-fuel technology with flue gas recirculation into an existing cement plant is extremely challenging. To prevent air intrusion, the complete plant has to be sealed or has to be operated with excess pressure. An air separation plant has to be established on the cement plant premises and the equipment for flue gas recirculation has to be included into the existing plant units. The different flue gas enthalpies and flows require a different design of all plant units. Hence the implementation of oxy-fuel technology with flue gas recirculation seems to be predominantly an option for new plants.

Post-combustion capture does not require fundamental changes in the clinker burning process. Therefore this technology would be available not only for new kilns, but also for retrofits at existing cement kilns. The most promising post-combustion technology is chemical absorption because operational experiences exist in several industries, and high abatement efficiencies seem to be achievable. Membrane technology also seems to be a candidate for future application at cement kilns. Other post-combustion measures, e.g. physical absorption or mineral adsorption seem to be less feasible from today's point of view, because of a lack of selectivity or huge mass streams of mineral adsorbents.

Up to now, no full-scale trials with post-combustion capture have been carried out in the cement industry. In other industrial sectors, several commercially available post-combustion capture technologies exist, limited however to comparatively small gas volumes. First tests in a cement plant are planned for 2012 and 2013.

A different approach has been chosen by the Calera process in which CO_2 is mineralized in an aqueous precipitation process. CO_2 reacts with calcium or magnesium in e.g. brines resulting in carbonates which can be used as building material. Calera supposedly exhibits a CO_2 capture efficiency of 70–90% with a good input conversion. It remains open to what degree these carbonates as the final product show cementitious properties. The inventors claim the product to be carbon negative. First results are expected to be delivered. To what degree Calera is able to reduce significant amounts of CO_2 is open at this time [5].

A technology which is currently used on an experimental level is related to the photosynthesis of algae. The basic principal consists of running flue gas from cement kilns through a reactor which contains water and where algae grow and build up hydrocarbon. These algae can be harvested and reused as fuel for the kiln.

The advantages of such a biological CO_2 capturing technology are obvious, namely CO_2 abatement and the production of biomass at the same time. However, current research has shown the limitations of these reactors. Chemically, the “driving force” is solar energy, by which CO_2 must be digested and converted into hydro-carbons. Even under favorable conditions, extremely large reactor surfaces would be required to capture significant amounts of the CO_2 emission of a single kiln. In addition, the algae need to be dried and processed before being used as fuel. It will be very interesting to follow current research on this subject, but for the time being, the expectations for industrial scale application seem to be very limited.

3. Cement products

While cement production in its beginnings only focused on ordinary Portland cement, later cements with several main constituents were produced by replacing parts of the clinker content by supplementary cementitious materials.

As such, fly ash from coal power plants, granulated slag from iron production as well as natural pozzolans were used in increasing amounts. Also limestone can substitute some clinker in cement. The substitution of clinker in cement is the most effective way to reduce the specific CO_2 emission per ton of cement, because only clinker is related to substantial fuel consumption and the calcination of limestone. Fig. 6 illustrates how the proportions of OPC declined over time in relation to the cements with other major constituents. Holcim achieved in 2010 an average specific CO_2 emission per ton of cement which was 20% lower compared to 1990.

3.1. Cements with several main constituents

The reduction of specific CO_2 was not the only driver for the fast development in the production of cements with several main constituents; the use of granulated blast furnace slag, fly ash from coal power plants and natural pozzolans also offer additional benefits in cement performance. The nature of these mineral constituents varies considerably, and therefore the substitution of clinker is always limited up to a certain degree. Slag is latently hydraulic and is often used in proportions of more than 50% of the cement. Pozzolanic materials like fly ash and natural or synthetic pozzolans can be used to levels of up to 40%. Limestone is not strongly involved in chemical reactions during cement hydration but has a positive impact on the physical characteristics of cement. Also, in the case of fly ash, the particle shape plays an important role. Due to its spherical shape, it has a positive impact on the rheological property of cement applications.

The so called clinker factor (CF) is the proportion of clinker in cement. It can be derived for every cement product, but it is mainly used as an indicator of the average clinker substitution of a producer, an area or worldwide. In 2003, the world average CF was 0.85 [16]. The continent with minimum CF was South America (0.75), while North America was the region with the highest CF of 0.92. The clinker factor in an area is affected by the type and volume availability of clinker substitutes, the cement standards, and also by the cement market itself. In 2010, the world CF was 0.77 and the long term prediction of the “Cement Technology Roadmap 2009” is 0.71.

3.2. Challenges in the application of cements with several main constituents

In practice, the substitution of clinker in cements affects the characteristics of strength development over time. Most important is the fact that the strength development is slower compared to a purely clinker-based cement of the same fineness. Because the vast majority of cement applications require a certain strength of the finished product after a couple of hours or a few days, the industry is using different strategies to overcome this problem.

The reactivity of clinker depends on the clinker phase assemblage and the reactivity of the individual phases. Maximum clinker reactivity requires full process control and optimized conditions from raw materials through fuels down to clinker storage. Another way to

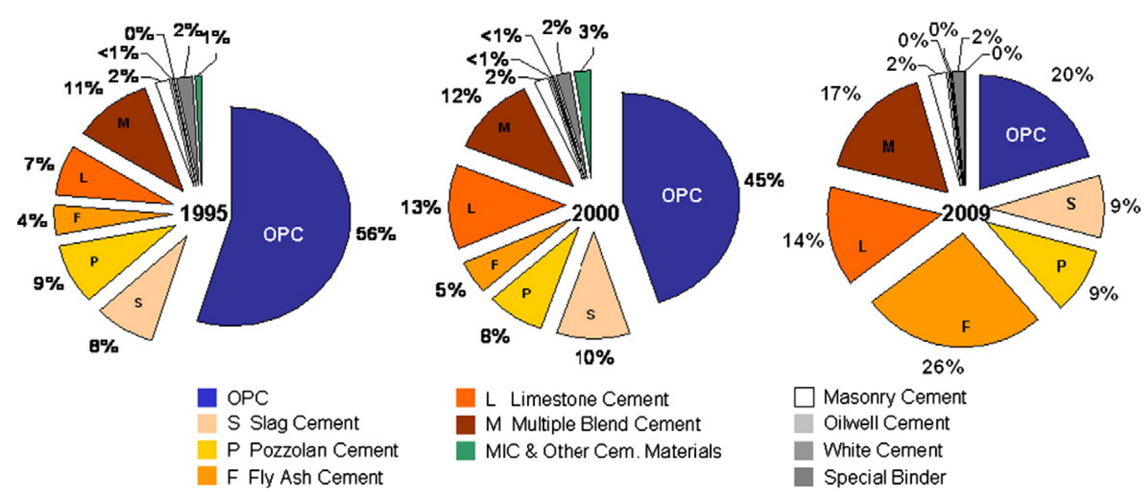

Fig. 6. Cement types produced by Holcim 1995–2009.

improve the clinker phase composition in clinker is the concept of mineralized clinker. This technology uses fluoride-containing materials and makes it possible to reach higher lime saturation and therefore maximum contents of the alite phase. Other means to compensate for clinker substitution consist of grinding cement constituents finer or adding chemical activators like NaOH or Na_2SO_4 to the cement.

Early strength is of course not the only specification in cement application. Nowadays, life cycle cost is a key requirement, especially in infrastructure projects. In terms of cement and concrete this is strongly related to the durability of the final applications. In this respect, cements with several main constituents offer a large potential. Their slower hydration is also related to lower levels of heat release and therefore to less internal tension in structural elements. Most important is the fact that most cements with several main constituents develop a dense microstructure and are therefore more resistant against diffusion-driven deterioration mechanisms, especially chloride ingress. Nevertheless, in specific aggressive conditions, cements with several constituents might be more susceptible than OPC to chemical attack. But even under such conditions, the dense microstructure may outweigh the chemical shortcoming and lead to overall superior durability. Nowadays it is quite common that large infrastructure projects require long term guarantees to fulfill their life cycle cost target. The challenge here is related to the difficulty in predicting the long-term behavior of cement applications based on accelerated laboratory testing.

Admixtures play an important role in modern concrete production. New developments in this field have taken into account the developments on the cement side, e.g. towards more cements with several constituents. Even for complex concrete systems, tailor made solutions are available. The requirements, however, remain to adapt admixtures and cement properties to provide optimum solutions for an increasing variety of applications.

From the point of view of concrete, the clinker content in cement can be optimized when put into the context of additional parameters, i.e. cement content in concrete, cement composition (constituents other than clinker), concrete strength class, and the equivalent water/cement ratio. The reasons for this are well-established from the point of view of concrete technology: the granulometric optimization of the main cement constituents, particularly clinker, a reduction in the effective water/cement ratio, and the use of effective plasticizers or superplasticizers.

An analysis in Fig. 7 [23] of common concretes produced in the laboratory shows that compressive strengths in the range of 40 ± 5 MPa allow for cement compositions exhibiting a broad range of clinker ratios. Mix designs typically used for concrete compressive strength classes C25/30 and C30/37 in the ready-mixed concrete sector contain an average of 290 and 320 kg/m³ of cement, respectively [4]. The use of a CEM III/A 42.5 N blast-furnace cement containing approx. 50 mass% of blast-furnace slag in such concretes results in clinker content between 130 and 150 kg/m³ when considering further additions and sulfate carriers.

An estimate of the theoretical minimum clinker content in concrete can be derived from these first test to be in the range of 2 kg/($m^3 \times$ MPa). This could be achieved by adding a high proportion of limestone and with a low water/cement ratio of 0.32. One of the major challenges will be to identify those laboratory-scale options that can actually be transformed into robust practical solutions for the industrial production of cement and concrete. Similar results have been reported in: [21].

3.3. New clinker substitutes

Among constituents which might not have realized their full potential as cement constituents, calcined clays could play an important role. It is known that these materials exhibit pozzolanic properties. However, the calcination process is pretty much determined by the origin and the composition of these clays. The availability of clays can be regionally very limited. However, geologic formations containing high amounts of clay minerals occur in many parts of the world. Materials rich in clay exhibit pozzolanic properties after calcination. The reactivity is mainly determined by the mineralogical composition, the calcination conditions and the grain size distribution of the calcined material [14]. The calcination temperature typically lies between 600 and 850 °C. The main factors influencing the reactivity of these materials and the properties of cements containing calcined clays are currently subjects of investigations at VDZ's Research Institute.

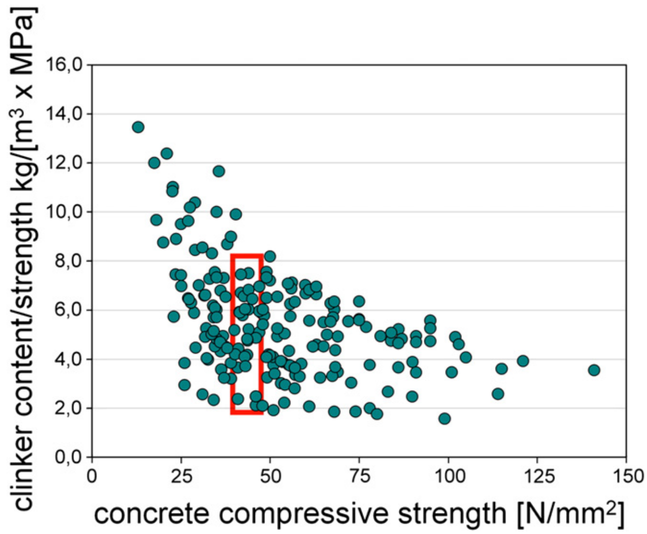

Fig. 7. Correlation between the compressive strength related clinker content and compressive strength (clinker ratio); highlighted area: concretes with compressive strengths of 40 +/− 5 MPa ([23], p.86).

Alternative pozzolanic or latent hydraulic materials might be derived from waste. Vitrified waste materials which exhibit adequate composition could be promising latent hydraulic materials. Some of these waste materials, such as lignite ashes, in some countries show sufficient amounts of calcium; others with a low calcium content might be favorable to produce more pozzolanic materials. Research in this field is ongoing [36].

3.4. Standardization

In the global context of cost reduction and CO_2 constraints, cement producers are striving to lower the clinker content in their cements. Limits are given by the regional and global availability of appropriate materials. Taking granulated blast furnace slag and fly ashes as an example, the total mass produced in 2008 and 2007 worldwide amounts to about 1 billion tonnes per year [12]. Thus it is clear that other well-tried and proven materials must be taken into account. Among these a special focus is on cements with high limestone content. This is basically an extension of current cement standards as they have been developed worldwide and certainly provides opportunities for the future. As an example, research is being performed in the context of the European standard with the main focus on strength development and – even more importantly – on the durability of the concrete produced. Fig. 8 shows the range of current cement types standardized in Europe today and the extension which is currently under research.

From a worldwide perspective, many standards are in place to handle cements with several main constituents. The concepts differ substantially. Many countries developed national terms which further determine the possible cement compositions and also the type and extent of cements allowed to be used in concrete. In regard to GBFS and FA, there is not much activity in cement, whereas in Europe the standardization of those materials for use in concrete is currently addressed. In relation to cement standards, more activity is related to limestone. While limestone has been used for decades as a minor

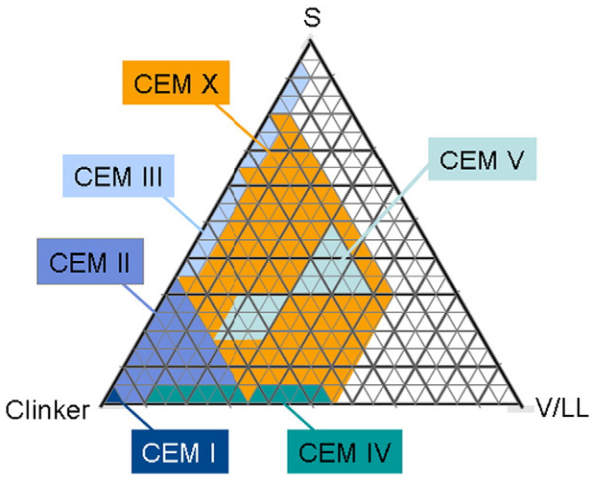

Fig. 8. Cements according EN 197-1 and its potential extensions by means of well tried and proven.

constituent, its use as main constituent is much more recent. ASTM C 150 adapted to the use of 5% limestone in 2004 [1]. In Canada, the CSA A3001 standard introduced a new cement class named Portland–Limestone cements in 2008, a maximum limestone content of 15% is specified [6]. Australia and New Zealand also allow the use of 15% limestone in certain cements.

In any case, the production of cements with the extended use of well tried and proven constituents certainly requires excellent quality assurance mechanisms as they have been successfully implemented in the cement industry. In addition, the inherent characteristics of cement production guarantee large volume flows and good homogenization resulting in a constant product quality of the final product.

4. New types of binders and material concepts

All future cements will certainly have to be based on materials which are globally available in sufficient amounts. CaO, SiO_2 as well as Fe_2O_3 and Al_2O_3 are certainly key materials in this respect, magnesium oxide also seems to be available, even if the deposits might not be as close to the surface as today's quarries of the cement industry. Based on calcium, silicon, aluminum and iron, new cements could be foreseen, starting from Portland cement all the way to pure aluminosilicates which contain no lime at all. Some of the binder systems or their basic concepts have been known for decades and have gained more attention recently, while others are based on new concepts.

Geopolymer is a name used for a large group of binders which solidify after the activation of a reactive solid in a highly alkaline environment. The setting and strength development can mainly be ascribed to polycondensation reactions which form three dimensional networks of amorphous inorganic aluminosilicates. Geopolymers can be produced on the basis of natural sources of aluminosilicates, e.g. kaolin, or on the basis of waste materials like fly ash. The characteristics of geopolymer binders strongly depend on the source material and the activation conditions.

Possible advantages of these materials can be a high early and/or final strength, a high resistance against chemical attack, the good passivation of reinforcement, a very dense microstructure and heat resistance. However, the prices of the activators, their energy intensiveness (with associated CO_2 emissions) and the availability of the raw materials limit the use of geopolymer binders and their potential to replace Portland cement clinker-based binders. Additionally, there are still open questions with regard to durability issues.

Celitement is the name of a group of binders based – like Portland cement – on the formation of calcium silicate hydrates. The binder itself consists of preformed calcium silicate hydrate phases [29]. The production process is based on Ca- and Si-rich raw materials (e.g. lime and sand). The raw materials are processed in two stages.

In the first stage, calcium silicate hydrates (CSH) are formed under hydrothermal conditions at a maximum temperature of 200 °C. In the second stage the calcium/silicon ratio of the CSH phases is decreased by reactive grinding with silicates. If limestone is the Ca-source, the calcination process has to be considered as an additional step. The calcium/silicon ratio of the product is lower than in Portland cement clinker, consequently the CO_2 emissions due to calcination of the calcium source are lower. However, the process has not yet been upscaled to a test plant or a full sized production plant. Additionally, data on durability is not yet available.

Novacem is reported as a cement based on magnesium oxide and hydrated magnesium carbonates [26]. According to the inventors of this binder, the raw material is based on magnesium silicates which are globally available in large quantities. The materials are digested and subsequently partly carbonated in an autoclave process under elevated levels of temperature and pressure (i.e. 180 °C/150 bar). The resulting magnesium carbonates und hydroxides are calcined at approx. 700 °C to form magnesium oxide as a part of the binder. The final Novacem cement composition is a blend of magnesium oxide and hydrated magnesium carbonates. According to the inventor, the addition of the special magnesium carbonates provides mechanical strength to the cement system by modifying the cement hydration chemistry and leads to net sinks of CO_2, allowing the cement to achieve a carbon negative footprint.

During hardening, Novacem absorbs carbon dioxide from ambient air. The company intends to run a pilot plant. Scientific publications on the production process or on the mechanisms of the strength development and on the performance or the durability of the binder are expected to be published as the research progresses.

Calcium sulfoaluminate (CSA) cements are binders mainly based in the phases yeelimite (C_4A_3S'), belite, C_4AF and gypsum in varying ratios. The solidification of these binders is mainly based on the formation of ettringite and CSH phases. A clinker containing yeelimite is produced at temperatures which are about 100 to 150 °C lower than the sintering temperatures of Portland cement clinker. Due to the lower temperatures and the lower content of calcium, the specific CO_2 emissions of CSA cements are lower than those of Portland cement clinker. However, the global availability of aluminum and sulfur sources suitable for the production of CSA cements is limited. Therefore, this group of binders can only play a subordinate role as a replacement for Portland cement clinker.

5. Education and know-how development

Sustainable cement production relies on well educated and well trained employees, be it in cement plants or along the value chain as far as the construction companies using the product. The challenge of reducing energy and raw material consumption and at the same time complying with quality, performance and cost requirements in the context of the huge demand for cement as a construction material in the future will only be met with highly efficient training programs. Academic education platforms as provided by the Nanocem [24] network or courses for plant-engineers and foremen provided by ECRA [9] or VDZ [34] will play an even more important role in the time to come. Customized training platforms based on e-learning tools can tailor education programs to the specific needs of individual companies and employees. These platforms even allow for the implementation of tests, e.g. in safety at work issues, which facilitates training and its documentation quite substantially.

Cement production has always further developed its processes and improved its performance in the context of sustainability. The challenge however remains, to transform large amounts of natural materials, fuels and alternative resources into affordable and durable buildings and infrastructures. To cope with this challenge, education and R&D will remain key factors in the cement industry, which offers various opportunities for fundamental and applied R&D work. Only with expertise and know-how will the cement industry be able to further reduce the environmental footprint of its operations and its products in their final application.

References

[1] ASTM C 150, Standard Specification for Portland Cement, 2004.
[2] K. Bauer, V. Hoenig, Energy efficiency of cement plants, Cement International 8 (3) (2010) 148–152.
[3] M. Böhm, R. Pierkes, Evaluation of Portland cement clinker with optical microscopy: case studies, in: B. Middendorf, et al., (Eds.), 12th Euroseminar on Microscopy Applied to Building Materials, Dortmund 15–19 September 2009, 2009.
[4] Bundesverband der Deutschen Transportbetonindustrie, Ökobilanzielle Baustoffprofile von Transportbetonen der Druckfestigkeitsklassen C20/25, C25/30 und C30/37: Technischer Bericht TB-BTe 2135/2007. Duisburg, 2007.
[5] T. Carter, Converting carbon emissions to profitable products [on-line], Warsaw, Cement Sustainability Initiative Forum. http://www.wbcsdcement.org/pdf/CSI Forum2010/06%20CSI%20Carter%20100914.pdf [Accessed 18 March 2011].
[6] CSA A3001, Cementitious Materials for Use in Concrete, 2008.
[7] European Cement Research Academy, [on-line], Carbon Capture Technology: ECRA's approach towards CCS; Communication Bulletin, 2009. http://www.ecra-online.org/fileadmin/redaktion/files/pdf/ECRA_CCS_Communication_Bulletin.pdf, [Accessed 18 March 2011].
[8] European Cement Research Academy, [on-line], ECRA CCS Project: Report about phase II; Technical Report TR-ECRA-106/2009, 2009. http://www.ecra-online.org/fileadmin/redaktion/files/pdf/ECRA__Technical_Report_CCS_Phase_II.pdf, [Accessed 18 March 2011].
[9] European Cement Research Academy, [on-line], Programme 2011: Seminars, Training Course and Conference, 2011. http://www.ecra-online.org/fileadmin/redaktion/files/pdf/Programme/ECRA_Programme_2011_final.pdf, [Accessed 18 March 2011].
[10] European Cement Research Academy, 2011. (Internal communication, February 2011).
[11] European Commission, Reference Document on Best Available Techniques in the Cement, Lime and Magnesium Oxide Manufacturing Industries, 2010.
[12] European Coal Combustion Products Association, ECOBA, 2007 and FehS—Institut für Baustoff-Forschung, 2008. (Personal communication, 2007 and 2008).
[13] FEhS—Institut für Baustoff-Forschung, FEhS Report 15 (1) (2008).
[14] R. Fernández, F. Martirena, K. Scrivener, The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite, Cement and Concrete Research 41 (1) (2011) 113–122.
[15] Fraunhofer-Patentstelle für die Deutsche Forschung, [on-line], Schall verpulvert Feststoffe, 2003. http://www.fraunhofer.de/archiv/presseinfos/pflege.zv.fhg.de/german/press/pi/pi2003/04/md_t1.html, [Accessed 18 March 2011].
[16] J. Harder, Development of clinker substitutes in the cement industry, Zement-Kalk-Gips 59 (2) (2006) 58–64.
[17] B. Hauer, H. Klein, Recycling of concrete crusher sand in cement clinker production, in: S. Jacobsen, et al., (Eds.), International Symposium on Sustainability in the Cement and Concrete Industry, Lillehammer 16–19 September 2007, 2007, pp. 106–120.
[18] C. Hendriks, H.S. Pietersen, A.F. Fraay, Recycling of building and demolition waste: an integrated approach, in: R.K. Dhir (Ed.), Sustainable Construction: Use of Recycled Concrete/Aggregate, London 1998, Telford, London, 1998, pp. 419–431.
[19] K. Höffl, Zerkleinerungs- und Klassiermaschinen, Springer, Berlin, 1986.
[20] International Energy Agency World Business Council for Sustainable Development, Cement Technology Roadmap 2009: Carbon Emissions Reductions up to 2050, 2009.
[21] V.M. John, B. Daminelli, Cement use optimization, [on-line], Sao Paulo, Cement Sustainability Initiative Forum, 2009. http://www.wbcsdcement.org/pdf/CSI Forum2009/CSI%20Forum%20vmjohn%20Learning%20by%20Sharing.pdf, [Accessed 18 March 2011].
[22] H. Klein, V. Hoenig, Model calculations of the fuel energy requirement for the clinker burning process, Cement International 4 (3) (2006) 44–63.
[23] C. Müller, S. Palm, Cement grades with a low Portland cement clinker ratio for the concretes of the future, in: Bundesverband Deutsche Beton- und Fertigteilindustrie (Ed.), Sustainable Innovation: Proceedings 55th BetonTage, Neu-Ulm 10–11 February 2011. 86–89, 2011.
[24] Nanocem the Industrial–Academic Research Network on Cement Concrete, [on-line]., Marie Curie Research Training Network NANOCEM, 2008. http://www.nanocem.org/index.php?id=133, [Accessed 18 March 2011].
[25] R. Nobis, Burning Technology, Cement International 7 (5) (2009) 52–71.
[26] Novacem Limited, [on-line], Novacem Carbon Negative Cement: Presentation for SCI 25 November 2010, 2010. http://novacem.com/wp-content/uploads/2010/12/20101125-Technical-update.pdf, [Accessed 18 March 2011].
[27] Patent specification, Verfahren und Vorrichtung zur Desintegration und tribochemischen Aktivierung von anorganischen Stoffen. DE 102 59 456 B4, 2005.
[28] S. Puntke, M. Schneider, Effects of phosphate on clinker mineralogy and cement properties, Cement International 6 (5) (2008) 80–93.
[29] P. Stemmermann, U. Schweike, K. Garbev, G. Beuchle, H. Möller, Celitement: a sustainable prospect for the cement industry, Cement International 8 (5) (2010) 52–66.
[30] J. Theulen, Waste heat power generation at Heidelberg cement, in: Verein Deutscher Zementwerke (Ed.), Process Technology of Cement Manufacturing: 6th International VDZ Congress, Düsseldorf 30 September-2 October 2009. Düsseldorf: Verl. Bau und Technik, 174–175, 2009.
[31] K.G. Tsakalakis, G.A. Stamboltzis, Correlation of the Blaine value and the d80 size of the cement particle size distribution, Zement-Kalk-Gips 61 (3) (2008) 60–68.
[32] Verein Deutscher Zementwerke, 2008. (Personal communication, 2008).
[33] Verein Deutscher Zementwerke (Ed.), Environmental Data of the German Cement Industry 2009, 2010.
[34] Verein Deutscher Zementwerke, VDZ online courses[on-line], http://www.elearning-vdz.de/w3l/jsp/startseite/index.jsp?navID=110_512127[Accessed 18 March 2011].
[35] R. Wirthwein, B. Emberger, Burners for alternative fuels utilisation: optimisation of kiln firing systems for advanced alternative fuel co-firing, Cement International 8 (4) (2010) 42–46.
[36] Wolter, A., 2010. (Personal communication, 2010).
[37] World Business Council for Sustainable Development, The cement sustainability initiative: getting the numbers right, [on-line], Cement Industry Energy and CO_2 Performance, 2008. http://www.wbcsdcement.org/pdf/csi-gnr-report-with%20label.pdf, [Accessed 18 March 2011].
[38] European Cement Research Academy, [on-line], Carbon Capture Technology: Options and Potentials for the Cement Industry; Technical Report TR 044/2007, 2007. http://www.cement.org/bookstore/download.asp?mediatypeid=1&id=15360&itemid=SN3022, [Accessed 18 March 2011].
[39] International Energy Agency, [on-line], Cement roadmap targets, 2009. http://www.iea.org/papers/2009/Cement_Roadmap_targets_viewing.pdf, [Accessed 18 March 2011].