Opportunities for use of bauxite residue in Supplementary Cementious Materials

WORLD ALUMINIUM

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Current IAI membership represents over 60 % of global bauxite, alumina and aluminium production. Since its foundation in 1972 (as the International Primary Aluminium Institute), the members of the IAI have been companies engaged in the production of bauxite, alumina, aluminium, the recycling of aluminium, or fabrication of aluminium or as joint venture partners in such.

The global objectives of the Institute are:

Governance	People	Places	GHGs	Waste	Products
To conduct business ethically, with sound systems of corporate governance	To protect, nurture and develop the workforce and the communities in which we operate	To protect, nurture and sustainably develop the places in which we operate	To deliver beneficial services...while bringing a net reduction in greenhouse gas emissions...[1]	To reduce waste and to manage it effectively and safely	To deliver aluminium products that meet the needs of society and improve individuals' quality of life...[2]

[1] To deliver beneficial services to society through the use of aluminium products, while bringing a net reduction in greenhouse gas emissions across their full lifecycle

[2] To deliver aluminium products that meet the needs of society and improve individuals' quality of life while minimizing environmental impact and optimizing sustainable end of life strategies, including recycling and other material and energy recovery and reutilization measures

In 2016 the International Aluminium Institute undertook a review of opportunities for bauxite residue in all aspects of cement production and usage. This paper addresses the background to using bauxite residue in supplementary cementitious materials, separate papers cover possible usage in the production of Portland cement clinker and calcium sulfoaluminate/special/sulfobelite cements.

Summary

Work on the use of bauxite residue in cement has been pursued for over 80 years with a number of successful technical studies, several large-scale initiatives and industrial usage in Portland Cement clinker production reinforcing the prospects of large scale utilisation of bauxite residue in cementious materials. The driving force behind the usage in the production of both Portland cement and calcium sulfoaluminate /special cements is because the iron and aluminium contents of the bauxite residue.

Meanwhile, and possibly having an even greater environmental impact in the long term, is the potential to use bauxite residue in supplementary cementious materials. Considerable work has been undertaken on a laboratory/pilot scale exploring opportunities for bauxite residue as a filler in blended cements, sometimes for their pozzolanic activity but also to improve the mechanical properties in blended cement by other mechanisms such as optimising packing density or rheological characteristics. It has been observed at laboratory scale by several groups of researchers that bauxite residue as produced or after calcination, pure or mixed with other additives, may successfully replace clinker in blended cements at dosages between 10 and 20 wt%. If used as produced, this would have a significant impact on the cement industry CO_2 emissions as the clinker production is responsible for 85 % of the total emissions in an integrated cement plant. Usage in clinker or blended cement productions will most likely in locations where there is a shortage of alternative conventional raw materials such as natural clays, bauxite and iron ore for the former and fly ash, blast furnace slag and ground limestone for the latter. In these situations, the use of bauxite residue would help the cement industry reach two of their most important strategic targets: resource efficiency, by replacing non-renewable iron and alumina sources, and CO_2 emissions by minimising clinker production, the main CO_2 origin in the cement manufacturing process.

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1. Background

Bauxite residue (sometimes called red mud) is an inevitable secondary product that is generated in the extraction of alumina (aluminium oxide) from bauxite by the Bayer process. Virtually all aluminium metal is made by the electrolytic smelting of alumina and over 95% of alumina is manufactured by the Bayer process. There is no economic alternative route existing or likely to emerge within the next 50 years so the generation of bauxite residue will continue at a high level for many decades. Production of bauxite residue in 2017 is estimated to be over 160 million tonnes per year. The International Aluminium Institute is keen to encourage the cement industry to investigate, and wherever possible exploit, all the possible approaches to use bauxite residue in clinker production or the manufacture of supplementary cementious materials.

This paper serves to give some guidance to cement companies, universities and research institutes on some of the relevant background to encourage them to do further work in, and ultimately large scale utilisation of, bauxite residue in supplementary cementious materials which would lead to significant environmental benefits to both the aluminium and cement industries.

2. Cement – basic background

A cement may be defined as a binder or a substance that sets and hardens and can bind other materials together. Cements used in construction can be characterised as being either **hydraulic** or **non-hydraulic**, depending upon the ability of the cement to set in the presence of water.

Non-hydraulic cement will normally not set in wet conditions or underwater and sets as it dries and reacts with carbon dioxide in the air, however, hemihydrate (Plaster of Paris) hardens by precipitation of dihydrate after mixing with water. It is more susceptible to attack by aggressive chemicals after setting.

Hydraulic cements set and harden due to a chemical reaction between the dry ingredients and water. The chemical reaction results in mineral hydrates that have low water solubility so are durable in water and reasonably resistant to chemical attack. This allows setting in wet conditions or underwater and further protects the hardened material from chemical attack. They are normally termed Portland Cement, sometimes Ordinary Portland Cement (OPC) and have been used for many centuries and were widely spread across the Roman Empire and initially made from volcanic ash (activated aluminium silicates) and lime (calcium oxide).

The most important uses of cement are as a component in the production of mortar in masonry, and in concrete, a combination of cement and an aggregate to form a strong building material.

Non-hydraulic cement, such as slaked lime (calcium hydroxide mixed with water), hardens by carbonation in the presence of carbon dioxide which is naturally present in the air. These are manufactured by first producing calcium oxide by the calcination of calcium carbonate at temperatures above 825 °C for about 10 hours at atmospheric pressure:

$$CaCO_3 \rightarrow CaO + CO_2$$

The calcium oxide is then slaked mixing it with water to form calcium hydroxide:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
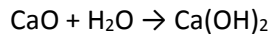
Once the water in excess from the slaked lime is completely evaporated the carbonation starts:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
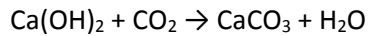
This reaction takes a significant amount of time because the partial pressure of carbon dioxide in the air is low. The carbonation reaction requires the dry cement to be exposed to air, for this reason the slaked lime is a non-hydraulic cement and cannot be used under water.

Conversely, the chemistry ruling the action of the **hydraulic cement** is hydration. Hydraulic cements (such as Portland cement) are made of a mixture of silicates and oxides, the four main components being:

Belite ($2CaO \cdot SiO_2$ or dicalcium silicate or C_2S);

Alite ($3CaO \cdot SiO_2$ or C_3S or tricalcium silicate);

Tricalcium aluminate ($3CaO \cdot Al_2O_3$ or C_3A) (historically, and still occasionally, called 'celite');

Brownmillerite or ferrite or alumino-ferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ or C_4AF).

Clinker usually contains some other phases, such as alkaline sulfate and calcium oxide. The silicates are responsible for the mechanical properties of the cement, the tricalcium aluminate and the brownmillerite are essential to allow the formation of the liquid phase during the kiln sintering.

The belite content for ordinary cement clinkers is 15-30 %. It is Ca_2SiO_4 modified by introducing in the foreign ion structure and usually completely or mostly present as β-modification. Belite reacts with water slowly, thus weakly affecting hardness during the first 28 days, but significantly increases hardness later. After a year, the hardness due to alite alone and belite alone under comparable conditions are approximately the same.

Alite is the most important constituent in all conventional cement clinkers; its content is 50—70 %. It is a tricalcium silicate: Ca_3SiO_5, the composition and structure of which are modified through location in the foreign ions lattice, particularly Mg^{2+}, Al^{3+} and Fe^{3+}. Alite reacts with water relatively quickly also in ordinary cements. Of all phases, alite plays the most important role in hardness development. This phase contribution is especially important in establishing the 28-day hardness.

The ferritic phase of an ordinary cement clinker is 5—15 %. It is a tetracalcium alumino-ferrite, (4CaO·Al$_2$O$_3$·Fe$_2$O$_3$ or C4AF), the composition of which changes drastically with changing Al/Fe ratio and location in the structure of foreign ions. The rate at which the ferritic phase reacts with water can vary due to differences in the composition or other characteristics, but, as a rule, it is initially high and is intermediate between speeds for alite and belite at later stages.

The aluminate phase content for most ordinary clinkers is 5—10 %. It is a tricalcium aluminate (composition — 3CaO·Al$_2$O$_3$), significantly changed in composition and sometimes also in structure due to the presence of foreign ions, particularly Si^{4+}, Fe^{3+}, Na$^+$ and К$^+$. The aluminate phase reacts quickly with water and can cause undesirable fast setting, if setting controlling agents such as gypsum are not added.

Cement is manufactured through a closely controlled chemical combination of calcium, silicon, aluminium, iron and other ingredients. The products of the chemical reaction aggregate together at their sintering temperature, above 1,450 °C.

Aluminium oxide and iron oxide are present only as a flux to reduce the sintering temperature and contribute little to the cement strength. The most common raw materials used to manufacture cement include limestone, shells, chalk or marl which are combined with smaller quantities of shale, clay, slate, blast furnace slag, silica sand, and iron ore. Production plants are normally located adjacent to the source of the principal raw material, limestone.

The most common way to manufacture Portland cement is through a dry method although the raw materials are sometimes wet milled before being fed into the kiln. The principal raw materials, mainly limestone, are crushed, combined with other ingredients such as iron ore or fly ash and ground and fed to a rotary kiln which can be up to 4 m in diameter and 100 m long. The finely ground raw material or the slurry is fed into the higher end with the flame at the lower end: fuels such as powdered coal, oil, municipal waste, old tyres, sewage waste or gas are burnt to give a temperature about 1,500 °C. A schematic diagram showing the cement making process is shown in Figure 3, Appendix 1.

As the material moves through the kiln, certain elements are driven off in the form of gases. The remaining elements unite to form a new substance called clinker which comes out of the kiln as grey balls, about the size of marbles. Clinker is discharged red-hot from the lower end of the kiln and generally is brought down to handling temperature in various types of coolers.

After the clinker is cooled, it is ground and mixed with small amounts of gypsum (calcium sulfate dihydrate) and limestone to give cement. The production of cement is one of the largest producers of carbon dioxide, creating 8-10 % of worldwide man-made emissions of this gas, of which approximately 55 % is from the chemical process and 45 % from burning fuel. The carbon dioxide produced for the manufacture of one tonne of clinker (world average) is 842 kg and for one tonne of cement is 589 kg. The industry is keen to reduce the amount of carbon dioxide generated by both

the use of the most appropriate fuel and modifying the process – bauxite residue can play a role in the latter.

The aluminium and iron content of bauxite residue provide valuable benefits to the cement in terms of strength and setting characteristics of the cement. As a general rule, the iron oxide content in the bauxite residue used should be greater than 50 %.

Further background on the different types of cement and Bouge calculations is given in Appendix 1 including some options for reducing carbon dioxide generation.

Some information on global production volumes of cement is given in Appendix 2.

Information on standards for cements in different countries is given in Appendix 3.

Appendix 4 provides information on the main industrial cement and concrete associations.

Appendix 5 summaries the work being undertaken as part of the EU MSCA ETN project on Red Mud Valorisation which is part of Horizon 2020.

Appendix 6 lists some of the key Organisations involved in cement/bauxite residue research.

A brief review of the opportunities for bauxite residue in geopolymers is contained in Appendix 7.

Appendix 8 contains a bibliography of some of the most important papers on the topic.

3. Key beneficial characteristics of bauxite residue

3.1 Chemical and mineralogical

A first step in considering the use of bauxite residue in cementious materials is to consider the chemical compounds present in the bauxite residue, the levels present and the physical characteristics of the material. The variation in composition is extremely wide as shown in Table 1; certain oxides such as iron, aluminium, calcium and silicon are beneficial in using the material in cement whilst others such as sodium are detrimental. Successful cement production relies on careful control of calcium, silicon, aluminium and iron and obtaining the proportions of the necessary phases. The ratio of these elements in the bauxite residue, and the form they are found, will play a key role in the ability to use the output from a particular refinery. It is important, however, to understand the release of the elements of interest and concern during clinker production or use in supplementary cementitious materials. It is also important for potential users to appreciate the variation in composition possible if an alumina refinery uses bauxites from different sources.

Table 1: Chemical composition, expressed as oxides, commonly found in bauxite residue

Component	Typical range (wt%)
Fe_2O_3	5 - 60
Al_2O_3	5 - 30
TiO_2	0.3 -15
CaO	2 - 14
SiO_2	3 - 50
Na_2O	1 - 10

A wide range of other components may also be present at low levels; these will invariably be as metallic oxides e.g. arsenic, beryllium, cadmium, chromium, copper, gallium, lead, manganese, mercury, nickel, potassium, scandium, thorium, uranium, vanadium, zinc, zirconium and rare earth elements. Non-metallic elements that may occur in the bauxite residue are phosphorus, carbon and sulfur.

The minerals present are complex and comprise some which are present in the bauxite and others that are produced during the autoclaving and the desilication processes. The range of minerals typically found for bauxite residues is shown in Table 2.

Table 2: Typical range of components found in bauxite residues.

Component	Typical range (wt%)
Sodalite ($3Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 0\text{-}2H_2O \cdot 2NaX$ where X could be CO_3^{2-}, Cl^-, OH^-, SO_4^{2-}, or $Al(OH)_4^-$)	4- 40
Haematite (Fe_2O_3)	10 - 30
Al - goethite (($Fe, Al)_2O_3 \cdot nH_2O$)	10 - 30
Magnetite (Fe_3O_4)	0- 8
Silica (SiO_2) crystalline and amorphous	3- 20
Calcium aluminate ($3CaO \cdot Al_2O_3 \cdot 6H_2O$)	2- 20
Boehmite (AlOOH)	0- 20
Titanium Dioxide (TiO_2) anatase and rutile	2- 15
Muscovite ($K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$)	0- 15
Calcite ($CaCO_3$)	2- 20
Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)	0- 5
Gibbsite ($Al(OH)_3$)	0- 5
Perovskite ($CaTiO_3$)	0- 12
Cancrinite ($Na_6[Al_6Si_6O_{24}] \cdot 2CaCO_3$)	0- 50
Diaspore (AlOOH)	0- 5

In addition there are various other minerals sometimes found at low levels including Brookite (an orthorhombic variant of TiO_2), ilmenite ($FeTiO_3$), Carnegieite ($Si_4Al_4Na_4O_{16}$), Dolomite ($CaMg(CO_3)_2$), Hydrogarnet ($Ca_3Al_2(O_4H_4)_3$), various Hydroxycancrinite/Cancrinite ($Na_6Ca_2(Al_6Si_6O_{24})(CO_3)_2 \cdot 2H_2O$), ($(Na,Ca)_8(Al,Si)_{12}O_{24}(CO_3) \cdot 4H_2O$), Cancrinite-$NO_3$ ($Na_{7.92}Si_6Al_6O_{31}.56N1.74$), Cancrisilite-CO3 ($Na_{7.86}(AlSiO_4)_6(CO_3)(H_2O)_{3.3}$), Katoite-Si ($Ca_3Al_2(SiO_4)(OH)_8$), Lawsonite ($CaAl_2Si_2O_7(OH)_2 \cdot H_2O$), Nepheline ($Na_2KAl_4Si_4O_{16}$), Nosean ($Na_8 Al_6 Si_6 O_{24}(SO_4)$), Portlandite ($Ca(OH)_2$), Schaeferite ($Na_{0.7}Ca_{.2.3})(Mg_{1.85}Mn_{0.15})(VO_4)_{2.88}(PO_4)_{0.12}$)), sodium titanate ($Na_2TiO_3$) and zircon ($ZrSiO_4$). How all these phases change, or otherwise, at temperatures used to make cement clinker, up to 1,500 $^{\circ}C$, is crucial.

A wide variety of organic compounds can also be present, these are derived from vegetable and organic matter in the bauxite/overburden or the use of crystal growth modifiers or flocculants and includes carbohydrates, alcohols, phenols, and the sodium salts of polybasic and hydroxyacids such as humic, fulvic, succinic, acetic or oxalic acids. These will almost all be burnt off during cement production and are not thought to be relevant in the use of bauxite residue in cement.

In general sodium is detrimental in cement production. The sodium in bauxite residue may be present in a sparingly soluble form, called the desilication product (DSP) or a very soluble form. The small quantities of some of the soluble sodium compounds resulting from the sodium hydroxide used in the extraction process will remain depending on the dewatering and washing systems used. All Bayer alumina refineries try to maximise the recovery of the valuable caustic soda from the residues in order to reuse it during the extraction process. The residual soluble sodium species, predominantly a mixture of sodium aluminate and sodium carbonate, give rise to an elevated pH for bauxite residue slurries.

Over time the residual sodium species are partially neutralised by carbon dioxide from the air to form sodium carbonate and other metal carbonate species; these species will result in a lower pH for the bauxite residue which renders them less hazardous. The desilication product ($3Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 0\text{-}2H_2O \cdot 2NaX$ where X could be CO_3^{2-}, Cl^-, OH^-, SO_4^{2-}, or $Al(OH)_4^-$) arises from the reaction between sodium aluminate and soluble sodium silicates.

The other factors to consider are the physical characteristics such as particle size distribution and some variable parameters such as moisture content. The particle size will have only a small effect on reactivity in clinker production or the generation of supplementary materials since the raw materials are ball milled at the start of the process. The moisture content is important in dry processes, see above; additionally, it will affect the handling characteristics and transport costs which are very critical.

The feed bauxite used will have a major impact on the particle size distribution of the residue; the coarse fraction (greater than 100 μm) which is generally high in quartz is separated at some alumina refineries from the finer silty muds (typically 80 % less than 10 μm with a substantial fraction less

than 1 μm). The coarse fraction is much easier to wash, has much better draining behaviour so has a lower residual caustic content.

In the use of bauxite residue in blended cements or supplementary cementitious materials the most important parameter may be the capacity of bauxite residue to improve packing density or improve adherence after curing conditions.

4. Laboratory investigations involving use of bauxite residue as a pozzolanic material or as a filler in cement blends

Bauxite residue, in some cases after treatment, can improve the packing characteristics or rheological behaviour and can play a valuable role in mortars or concrete as a pozzolanic additive. There have been many studies demonstrating the possible benefit and some of the most significant ones are discussed below.

4.1 San Ciprian study

A programme of work was undertaken at the University of Aveiro, Portugal for Alcoa on incorporating bauxite residue from San Ciprian into cement mortars. Portland cement was progressively replaced in the mix and addition levels of bauxite residue between 7 to 50 % (dry basis) were used in the trials and pozzolanic activity and rheological properties were measured. The composition of the residue was 18.76 % Al_2O_3, 51.8 % Fe_2O_3, 5.54 % SiO_2, 11.18 % TiO_2, 3.27 % CaO, 6.84 % Na_2O; the particle size ranged from 0.1 to 7 μm (median 0.78 μm) and the surface area was 20 m^2/g.

The workability of the mixes was significantly changed by the addition of bauxite residue. As the bauxite residue particles were finer and had a higher surface area than the cement particles they replaced, they reduced the amount of water available to lubricate the mix so the workability was in most cases reduced. This could be compensated for by the use of more water and/or the use of plasticisers, however, the former leads to a weaker cement and the latter increases costs. Addition levels of up to 7.1 % bauxite residue gave similar compressive strengths to the reference material. The effect on hydration rate was low whilst the pozzolanic activity was low.

A drawback of the study was that it concentrated mainly on rheology and put little focus on strength development. The adverse effect on workability was significant, however, relatively high levels of cement were replaced by the bauxite residue and up to 7.1 % could be tolerated.

4.2 NALCO study

This study, undertaken by KIT College of Engineering in Kolhapur, India. The bauxite residue used was neutralised using hydrochloric acid, concretes were made up to different grades (M30, M40 and M50) with the amount of cement in the concrete mix progressively replaced in 5 % increments up to 25 % on a weight basis. Setting times and 7-day, 28-day and 56-day compressive strengths were then

determined.

There was some increase in setting time above a 10 % addition. In all cases the compressive strengths initially fell as the neutralised bauxite residue was added but in some of the concrete mixes (the strongest ones with the highest cement content) the strength actually increased. There was some scatter in the data but on balance it would appear that a 15 % addition of bauxite residue could not only be tolerated but actually gave a concrete with a higher 28-day compressive strength. These benefits were maintained after 56 days. Some limited information on costings was provided and a 15 % addition of bauxite residue was reported to give a 7.5 to 8.2 % economy in costs.

Whilst the results were technically promising the costings to be explored in more detail including how the cost of neutralising the bauxite residue was calculated and the slightly adverse effect of setting time.

4.3 Shandong study

A project was undertaken at the University of Science and Technology, Beijing on bauxite residue from Chalco's Shandong alumina plant. The bauxite residue, with a composition of 6.31 % Al_2O_3, 12.38 % Fe_2O_3, 38 % SiO_2, 3.32 % TiO_2, 35.09 % CaO, 2.71 % Na_2O, was dried, ground and calcined at temperatures between 400 to 900 °C. The resulting materials were mixed with cement clinker and gypsum in the ratio 50:45:5, and 3, 7 and 28-day compressive strengths measured. The optimum compressive strength was seen after calcination at 600 °C. The work was very detailed with respect to the development of different micro-structures and phases.

4.4 MALCO study

Bauxite residue from the MALCO alumina plant in India has been used to make concrete. The solids content of their residue is 65 to 70 %, pH 11 to 12 with a composition of Al_2O_3 20-22 %, Fe_2O_3 40-45 %, SiO_2 12-15 %, TiO_2 1.8-2.0 %, CaO 1.0-2.0 %, Na_2O 4-5 %.

Some details have been published of experimental work undertaken at Anna University, India whereby different levels of bauxite residue from the MALCO plant were mixed with hydrated lime and incorporated into concrete mixes. The target cement was OPC grade 53 that conformed to IS269:1976 with a composition of CaO 63 %, SiO_2 22 %, Al_2O_3 6 %, Fe_2O_3 3 %, MgO 2.5 %, plus LOI 1.5 %, alkalis 0.5 %. The dried bauxite residue composition was:

Al_2O_3	14.1 %,
SiO_2	11.5 %
Fe_2O_3	48.5 %
TiO_2	5.42 %
CaO	3.96 %
V_2O_5	0.116 %

Na$_2$O	7.5 %
MnO	0.17 %
P$_2$O$_5$	0.297 %
K$_2$O	0.058 %
LOI	7.25 %

The work describes how varying percentages of the cement in the mix were replaced by neutralised bauxite residue together with 5 % hydrated lime (all by weight). For M3 grade, as the amount of bauxite residue increased, the slump value rose from 25 mm to 29 mm, the compaction factor from 0.85 to 0.9. When no hydrated lime was added, the 28-day compressive strength rose from 33.3 N/mm^2 to 38 N/mm ^{2} whilst when 5 % hydrated lime was added, the maximum 28-day compressive strength was found when an addition of 15 % bauxite residue was added. The 28-day tensile strength is at a maximum with a 10 % addition of bauxite residue, with or without the addition of hydrated lime. The ultimate flexural strength and deflection strength were at a maximum with a 15 % addition of neutralised bauxite residue, with or without the addition of hydrated lime.

Based on their results, they claim that at a 15 % addition of neutralised bauxite residue, the concrete will be nearly 7.5 % more economic with benefits in some properties including a 21 % improvement in 28-day compressive strength. However, it has been noted (RS) that a 10-15 % replacement is not particularly interesting for cement producers, they are now looking at blends that have 30 % or more replacement to abate their CO$_2$ emissions further. Otherwise bauxite residue producers would need to pay a gate fee to encourage them.

4.5 UNESC study

A project was undertaken at the UNESC (the University of the Extreme South of Santa Catarina) in Criciuma on incorporating calcined bauxite residue from Alunorte into mortar mixes and assessing its pozzolanic activity. Samples of bauxite residue from Alunorte were dried, milled to less than 74 µm and then mixed with local clays with different alumina to silica ratios, and fired using different conditions and at temperatures up to 1,300 ^{o}C. This cost would be particularly negative. Mixtures of 100 % bauxite residue, 80:20 mixes of bauxite residue and different types of industrially used clays. The mixes where then annealed at 1,200 ^{o}C and re-milled. 35 % of the cement in a mortar mix was then replaced with the different fired bauxite residue clay mixes and their pozzolanic activity assessed to NBR 5752:1952 by measuring their compression strength testing after 28 days.

The higher the firing temperature, the greater the pozzolanic activity; with the exception of one formulation, the pozzolanic activity values were all greater than the standard, >75 %, judged to be acceptable to NBR 12653. A firing temperature of 1,200 ^{o}C must be maintained for at least 50 minutes.

In the paper prepared for ICSOBA, the alkalinity values, however, for all samples and formulations were greater than the acceptable standard of <1.5 %. However, subsequent investigations suggests that an acceptable material could be made using a 70:30 mix of bauxite residue and clay. A PCT patent application, WO/2014/176656 (PCT/BR2014/000140) was filed in April 2014 covering aspects of this work.

4.6 Votorantim study

Companhia Brasileira de Aluminio (CBA) generate about 600,000 t/y of bauxite residue and have been looking at ways of utilising the residue. Within 20 km of the alumina plant, Votorantim have two cement plants with a combined production capacity of 6 million t/y. A study to use the bauxite residue as a pozzolanic material has been undertaken. The composition of the bauxite residue is 23.3 % Al_2O_3, 25.3 % Fe_2O_3, 19.3 % SiO_2, 3.3 % CaO, 3.4 % TiO_2, 8.0 % Na_2O, 0.42 % K_2O, 0.21 % MgO and 0.61 % P_2O_5. The silica is mainly present as cristobalite (16 %) and quartz (3.3 %). The absence of kaolin and high soda means that the residue cannot be converted directly into a pozzolanic material simply by heating and the chemical composition needs to be adjusted. In a study to produce pozzolanic material, limestone and aluminous clay are added and the material calcined to 1,150 $^{\circ}$C. Given the Na_2O content, probably a glass-like material is produced. Mixtures standard cement with 15 % and 30 % of the pozzolanic materials produced gave cements to standards CPIV-32 ENV197 (CP IV/A) and CP II-Z-32 (CP II/A-Q) respectively. The strength tests matched standard materials after 60 days. The pozzolanic materials made from the bauxite residue matched the colour of cement clinker; note that red coloured pozzolans cannot be used in OPC.

The pozzolans produced from bauxite residue have the advantage of lower energy consumption and lower CO_2 emissions. A patent has been filed covering the work PCT/BR2014/000208.

Votorantim/CBA are promoting the benefits of using bauxite residue in pozzolanic materials and at the 7th International Congress on Aluminium in June 2016 described the promising trials in the Votorantim Cimentos Pozzolan plant in Nobres, Brazil. In this trial 2,000 tonnes of bauxite residue were successfully used.

4.7 Belgaum experience

Work was undertaken at Pune University using bauxite residue from Hindalco's Belgaum plant as an additive to concrete; no activation treatment is reported to have been employed. Addition levels of between 5 and 40 % were used in a M30 concrete formulation. 28-day compressive and tensile strengths were then tested. It was reported that a level of 25 % of the cement could be replaced by bauxite residue without loss of strength. Workability of the mix, however, was poor but could be corrected by superplasticisers. The mix was only recommended for non-structural work and would of course be coloured red. [N.B. Interpretation of the results was that all additions of bauxite residue led to a lower 28-day compressive strength.]

The chemical composition of the bauxite residue was: Al_2O_3 21.6 %, Fe_2O_3 38.3 %, SiO_2 11.4 %, CaO 1.47 % and Na_2O 6.87 %.

Table 3: Summary of major studies on using bauxite residue in supplementary cementious materials

Study	Main points	Comments / Questions
San Ciprian	Up to 7 % residue in mortar gave similar compressive strengths in mortars, but workability was degraded	Study concentrated on rheology with little focus on strength development
NALCO	Up to 15 % HCl-neutralised residue in cement could be beneficial (stronger) and economic (8 % cheaper)	Economics need to be checked, especially cost of HCl neutralisation and processing. The presence of chlorides would make the application in reinforced concrete impossible (risk on chloride induced rebar corrosion)
Shandong	Calcined residue added to 50 % makes good clinker	Not many operations would see calcination of residue as an economic alternative to storage
MALCO	Up to 15 % neutralised residue is beneficial (21 % stronger) and "nearly 7.5 % more economic"	How was it neutralised? Do the economics stack up?
UNESC	70:30 mix of calcined residue and clay gives a mortar of acceptable strength and leachability	The residue must be dried, milled, blended with clay and fired at 1,300 °C and annealed at 1,200 °C
Votorantim	Residue is mixed with clay and lime and calcined. Then, "the pozzolans … have …lower energy consumption and … CO_2 emissions"	Requires drying, blending and calcination
Belgaum	Can use 25 % residue to make red cement for non-structural applications	Strength is an issue; 'superplasticisers' needed for workability. Obviously, a restriction on colour.
Cockburn Cement comments	No longer have ability to produce clinker or calcine bauxite residue to make a pozzolanic material	Concern about alkalis and chlorides levels. Bauxite residue not an approved pozzolan nor mineral additive

5. Limitations

When considering the widespread industrial implementation of using bauxite residue in cement products it is important to consider the potential limitations. The materials that bauxite residue

would be replacing in any application are readily and cheaply available so any negative feature or minor impediment is a potential barrier to change. Assessing both the actual risk, and the perceived risk to the stakeholders for any particular application is crucial. Some important risk factors to consider are discussed below.

5.1 Moisture level

A high moisture level will add to transport costs and will be an issue as energy has to be expended in driving it off when drying or firing, so it is advantageous for the bauxite residue to have as high a solids content as possible. The use of plate and frame press filters are being increasingly adopted; these can reduce the moisture level to 26/27 % or even lower so will help to reduce this cost penalty. The levels achieved at AoG using a plate and frame filter seem to be acceptable as do the level achieved at Nikolaev using air drying.

5.2 Hazardous rating of bauxite residue in some jurisdictions

There have been many discussions, particularly in the EU, concerning the hazardous nature of bauxite residue in particular in respect of its pH. If classified as a hazardous waste, this will add considerably to the cost of all aspects of handling, storage and transport. Based on a number of standard test criteria, material with a pH value above 12.5 is often considered hazardous. Implementation of an improved filtering operation, should reduce the pH to a level that avoids skin and eye irritation criteria being exceeded.

5.3 Transport costs

The logistics cost is very substantially increased if the material is classified as hazardous since special procedures must be implemented during transportation. Whilst the high alkalinity does not impose a problem with corrosion of steel, it can cause pitting of aluminium which is a part of the UN transport code. Use of neutralised products would minimise this issue.

5.4 Alkalinity/high sodium

The high pH is a problem from both a health and safety aspect and potentially adverse effects in cement production. During drying or firing, the high sodium may adversely after the refractory lining and in blended cement formulations a reaction or leaching may be an issue. High soluble alkali levels give high early strength development but are known to decrease the compressive strength on the longer term. Another issue of concern is the effect on subsequent hydration of the final products.

The nature of the sodium present also needs to be considered. As discussed earlier, whether the sodium is present in a highly soluble form or as a sparingly soluble sodium form will be important. The highly soluble residual sodium present will lead to an elevated pH and could lead to a hazardous rating which will affect transport costs.

Both high sodium levels and high pH will be reduced when press filters are used. Accelerating carbonation by the use of carbon dioxide, intensive farming or acid neutralisation as a first stage could also be considered to reduce the pH.

The high temperatures in the cement kiln will decompose all sodalite and cancrinite products present as new thermodynamic equilibria are established. Sodium can be built into mainly the aluminate (C$_3$A) phase and causes a shift in polymorphs from cubic to orthorhombic, it has been claimed that the orthorhombic form is more reactive than the cubic one. Additionally, other clinker phases take in alkalis in minor amounts in solid solution.

5.5 Heavy metals

The presence of chromium has been raised as an issue in the use of bauxite residue in

Portland cement clinker production in Greece and the Ukraine, and is addressed in more detail below. The leaching of metals, especially heavy metals, into the environment is a particular issue for any material that is used in building products although there is no reference noted relating to studies on the leaching characteristics of cements made using bauxite residue.

5.6 Chromium

With regard to chromium and health and safety aspects, the water-soluble compounds of chromium in cement are most relevant, specifically compounds of the form chromium (VI). Chromium in the cement can originate from: raw materials; fuel; magnesia-chrome kiln refractory brick; wear metal from raw mill grinding process, if chromium alloys are used; and additions such as gypsum, pozzolans, ground granulated blast furnace slag, mineral components, and cement kiln dust.

5.7 Radioactivity

Most bauxites will contain low levels of radioactive elements, termed NORM (naturally occurring radioactivity material) in particular ^{238}U and ^{232}Th, and this is normally doubled in the bauxite residue. The radioactivity in the bauxite residue is sometimes referred to as TENORM (technologically enhanced naturally occurring radioactivity material).

In general, two approaches are used to assess the risk from radioactivity: measurement of the elements that could lead to radioactivity, namely analysing for Ac, At, Bi, Pa, Pb, Po, Ra, Th, Tl, U and then calculating a radioactivity value; or by direct measurement. The EU Radiation Protection Guideline 112 has a recommended range of 0.3 – 1 mSv/y for building materials; the particular limit being determined by the expected exposure.

There is limited data published but some information that has been reported on a range of bauxite residue shows that thorium was only present in significant levels in bauxite residue from Venezuelan bauxite but still remains below acceptable limits. The uranium content is over 10 mg/kg in Jamaican and Venezuelan bauxites but the total radioactivity calculated will still remain below legislative limits in bauxite residue. Some of the uranium does dissolve in the Bayer process but it subsequently re-precipitates and is associated with the coarser bauxite residue fraction. Meanwhile thorium is not affected by the extraction process and is most often associated with the fine bauxite residue fraction. Data for Australian derived bauxite residue shows a level of 0.005 – 0.2 Bq/g for the sand fraction and 0.15 – 0.6 Bq/g for the mud fraction due to ^{238}U and 0.3 – 0.8 Bq/g for the sand fraction

and 1– 1.9 Bq/g for the mud fraction due to ^{232}Th and 0.07 – 0.23 Bq/g due to K^{40} in mud fraction. In 2008 the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) issued safety guidelines relating to the management of naturally occurring radioactive materials and reviewed bauxite residue generated in Australia amongst the materials investigated.

They concluded that: "the chemical concentrations for Th and U in bauxite mud residue, and the corresponding ^{232}Th and ^{238}U activity concentrations, can be expected to increase by as much as a factor of 2-3 relative to the bauxite concentrations, depending on the mineralogy of the ore as well as the level of the bauxite. The indicative activity concentrations for ^{232}Th taken across the Australian operations varies from levels substantially less than 0.5 Bq/g to values in the vicinity of 1.5 Bq/g. The corresponding indicative range for ^{238}U has an upper limit of approximately 0.6 Bq/g. The indicative range of ^{232}Th activity concentrations signifies that, while the mud residue for some operations slightly exceed the exemption limit of 1 Bq/1 specified in the ARPANSA Code of Practice and Safety Guide for Radiation Protection and Radioactive Waste Management in Mining and Mineral Processing (issued in 2005), operators may seek an exemption from the appropriate regulator(s) on a graded basis." "For this reason, consideration of an exemption application for such operations would require an assessment of above-background doses for workers against the 1 mSv/a criterion, as well as the demonstration of protection optimisation. Activity concentrations for sand residue from the operations are substantially less than the corresponding bauxite levels, and therefore the sand residue materials can be expected to gain a regulatory exemption according to activity."

Data published by KU Leuven on bauxite residue from Distomon shows ^{238}U and 199 +/- 32 Bq/kg, ^{226}Ra 379 +/- 43 Bq/kg, ^{228}Ra 419 +/- 31 Bq/kg, ^{226}Th 472+/- 23 Bq/kg, ^{228}Th 472+/- 23 Bq/kg and ^{40}K 21+/- 11 Bq/kg.

The IAEA (International Atomic Energy Authority) Basic Safety Guide for marketable materials sets a limit of 1 Bq/g per radionuclide; for uranium this is equivalent to 81 mg/kg. From the published data for bauxite residue, this level does not representative a problem for bauxite residues although it should be noted that the level measured for ^{238}U and ^{232}Th on bauxite residue from the closed Jamaican alumina plant at Maggotty was 0.97 and 0.32 Bq/g[6]. The values generally present in local soil for ^{238}U and ^{232}Th were 0.22 and 0.037 Bq/g respectively.

A thorough understanding of the radioactivity issues are most important when any application is considered. Public perception and concerns must be addressed as despite the data shown above, the radioactivity levels measured have stopped a number of interesting applications proceeding. Examples include the manufacture of bricks for domestic buildings in Jamaica, the use of construction materials in applications other than roof tiles in Hungary and the manufacture of ceramic insulating fibre for domestic situations. An "Activity Index" assessment has been proposed to consider each application on its merits looking at the level of radioactivity in the bauxite residue, the amount of bauxite residue in the product and the time and degree of expected exposure. As only a small quantity of bauxite residue is used in clinker production, the impact of radioactivity levels in the final product will be low. The issue, however, cannot be ignored. Use in supplementary

cementious materials, where bauxite residue use will be higher, requires a deeper consideration; although this should not prove a block, the issue must be addressed.

5.8 Chlorides

Alkali and chloride levels could have a significant impact on cement and where it could be utilised – stressed concrete has strict limits in these areas and the potential for alkali silica reaction would also preclude use except with benign aggregates.

Table 4: Summary of limiting factors

| Issue	Information	Comments
Moisture	Affects transport and energy costs Press filtration to 25 to 28 % moisture content beneficial	Readily achievable
Hazard ratings	pH below 12.5 should avoid Hazardous Material classification	Pre-neutralisation would avoid this problem
Transport cost	Substantially increased if classified "Hazardous"	Focus on local synergies – look for alumina and cement plants close together. Possibly up to 1,200 km
Alkalinity/ Na	Potential health and safety issues with high pH Possibly refractory issues, cement rings formation. Influence on viscosity in clinker production	Press filtration, and neutralisation with acid (note chlorides not acceptable), CO_2, land farming beneficial
Heavy metals	Leaching from cements made from residue needs to be reviewed further, especially chromium	
Chromium	Many sources Oxidised to Cr(VI) in the kiln Can be reduced by various metal sulfates Sodium increases solubility of chromates	
Radioactivity	U and Th contents a concern, especially for domestic construction products.	

6. Growth opportunities

Data in Appendix 2 shows cement production in 2015 from various the US Geological Survey, CEMBUREA (the European Cement Association) and Statista. CEMBUREAU data indicates a 2015 production cement production level of 4,600 million tonnes per year of which China accounts for over half the production and Asia in total comprises over 83 % of the total cement production. Regional production is shown in Figure 1 below.

Figure 1: Worldwide cement production 2015

World cement production 2015, by region and main countries, %
4.6 billion tonnes

Source: CEMBUREAU
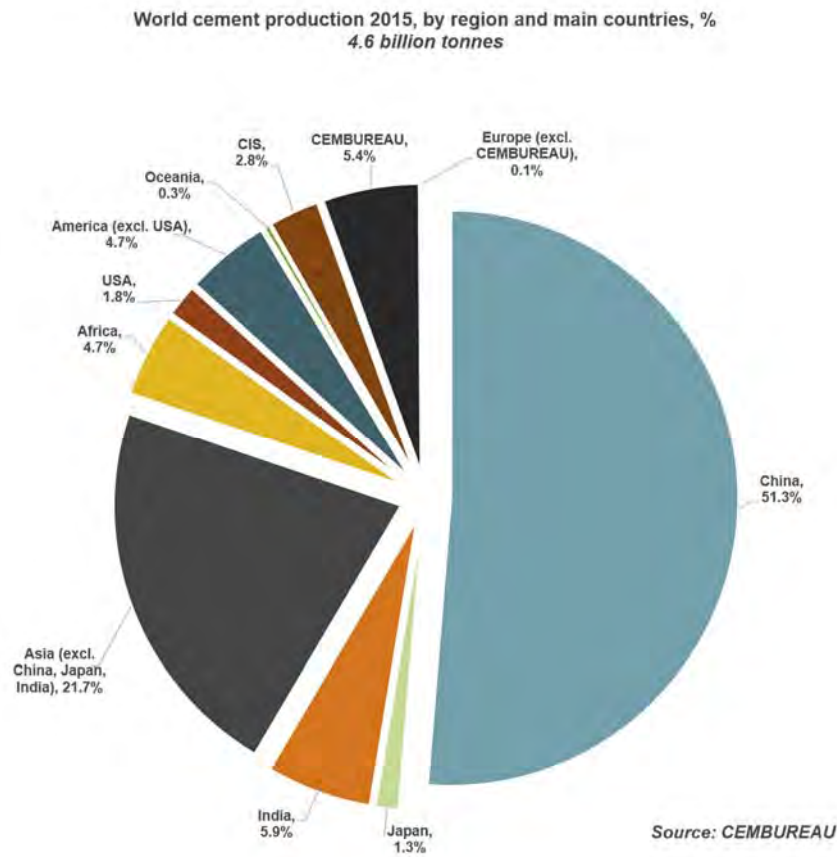
The data below, Figure 2, shows the projected growth in the production of cement globally.

Figure 2: Cement production and predicted growth by region
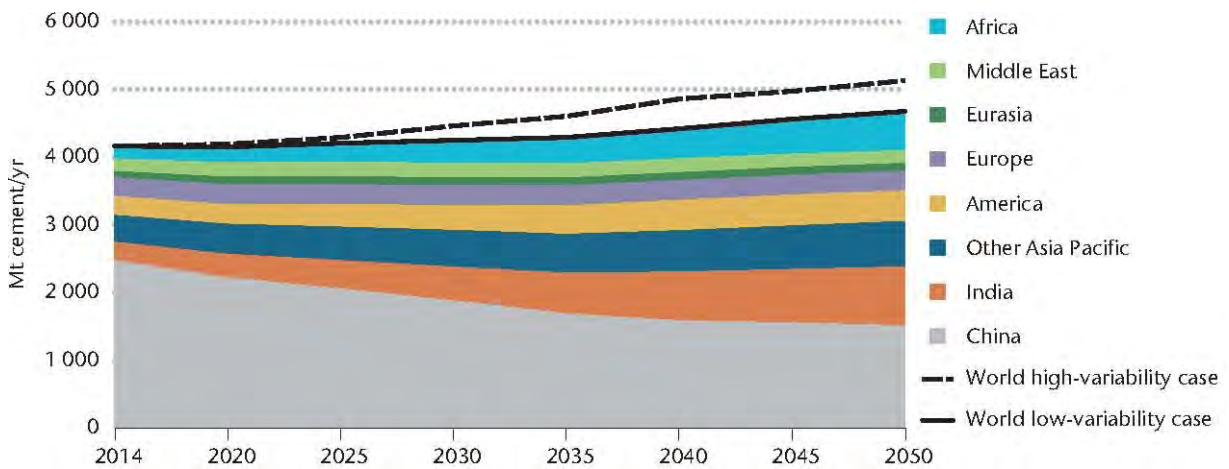
Sources: Base year cement production data from van Oss, H. G. (2016), *2014 Minerals Yearbook: Cement*, United States Geological Survey data release.

Some pertinent clinker production levels different regions/countries are:

European production 250 million tonnes, Oceania Production 7 million tonnes, USA production 216 million tonnes and India 270 million tonnes. Table 5 shows the potential requirements for bauxite residue in different regions using a conservative level of 2.5 % utilisation. In Oceania, with a cement production level of 7 million tonnes and assuming a utilisation rate of 2.5 %, less than two hundred thousand tonnes of bauxite residue would be required.

Table 5: Potential bauxite residue usage in cement by region

Region*	Cement production (million t/y)	Potential at 2.5 % utilisation rate (million t/y)	Bauxite residue generation (million t/y)
Africa	216	5.4	1
America (excluding USA)	216	5.4	25
China	2,360	60	80
Europe	250	6.3	4
India	270	6.8	9.5
Oceania	7	0.18	30
USA	83	2.1	7
World	4,600	115	155

*Not all regions included and data from different sources so indicative only.

7. Summary

The usage of bauxite residue in Portland Cement clinker production is carried out at plants in China, Ukraine, India, Russia, Cyprus, Georgia, Moldova and Greece providing significant environmental benefits. The potential to use bauxite residue in supplementary cementious materials offers the cement industry even greater environmental benefits in the long term.

Considerable work has been undertaken on a laboratory/pilot scale exploring opportunities for bauxite residue as a filler in blended cements, sometimes for their pozzolanic activity but also to improve the mechanical properties in blended cement by other mechanisms such as optimising packing density or rheological characteristics. It has been observed at laboratory scale by several groups of researchers that bauxite residue as produced or after calcination, pure or mixed with other additives, may successfully replace clinker in blended cements at dosages between 10 and 20 wt%. If used as produced, this would have a significant impact on the cement industry CO_2 emissions as the clinker production is responsible for 85 % of the total emissions in an integrated cement plant. Usage in clinker or blended cement productions will most likely in locations where there is a shortage of alternative conventional raw materials such as natural clays, bauxite and iron ore for the former and fly ash, blast furnace slag and ground limestone for the latter. In these situations, the use of bauxite residue would help the cement industry reach two of their most important strategic

targets: resource efficiency, by replacing non-renewable iron and alumina sources, and CO_2 emissions by minimising clinker production, the main CO_2 origin in the cement manufacturing process.

Issue	Comments
Sodium/alkalinity	Soda level is not a barrier to implementation *per se* except in low-alkali cements, but it sets the upper limit to the blend: • of up to 2.5 % seems to be acceptable without pre-treatment, • of a higher percentage would be needed in individual cases to make a real impact (say 20 % if 10 % of world concrete production was involved), • of research on how to get up to say 25 % is worthwhile
Chromium	Of particular concern to clinker manufacturers and given the amounts of residue potentially that could be used in blends, this seems to be a due diligence and context issue –important to discuss it with potential users at an early stage
Other contaminants	Leachability is a key issue that must be covered up front Chlorides not acceptable (HCl neutralisation unacceptable)
Radioactivity	Not likely to be a problem for low levels of additions, but important to have a defined position
Carbon Dioxide	Need for clarification including consideration for any additional calcination of bauxite residue prior to use
Standards	Important that cements with bauxite residue in them meet the applicable standards

Appendix 1 – Background to types of cement and Bouge calculation

Nomenclature

The oxides used in cement chemistry are frequently abbreviated as follows:

$A = Al_2O_3$, $F = Fe_2O_3$, $S = SiO_2$, $C = CaO$, $H = H_2O$.

So alite (tri-calcium silicate) = C_3S, belite (di-calcium silicate) = C_2S, calcium aluminate = C_3A, ferrite (calcium aluminate ferrite) = $C_2(AF)$.

Portland cement

Portland cement is by far the most common type of cement in general use around the world. This cement is made by heating limestone (calcium carbonate) with small quantities of other materials (such as clay) to 1,500 °C in rotary kilns to liberate the carbon dioxide to form calcium oxide, or quicklime, which is then blended with the other materials that have been included in the mix. The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder to make 'Portland Cement', the most commonly used type of cement (often referred to as OPC).

See Figure 3 below for a schematic representation of the cement manufacturing process.

Portland cement blends

Portland cement blends are often available as inter-ground mixtures from cement producers, but similar formulations are often also mixed from the ground components at the concrete mixing plant.
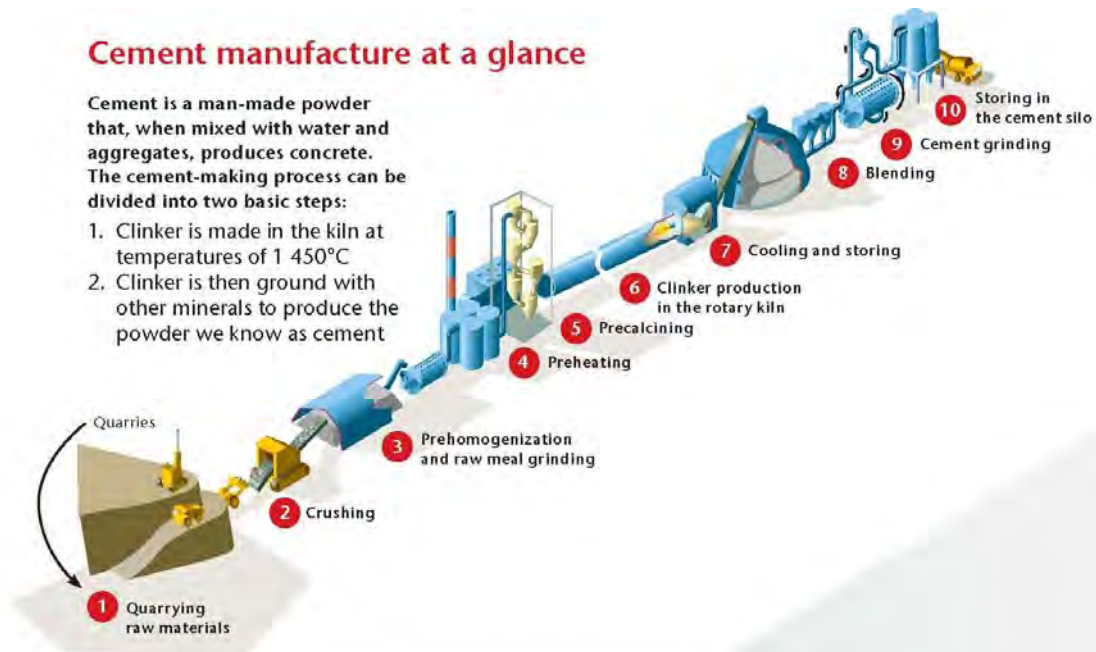
Portland blast-furnace slag cement, or Blast furnace cement (ASTM C595 and EN 197-1 nomenclature respectively), contains up to 95 % ground granulated blast furnace slag, with the rest Portland clinker and a little gypsum. All compositions produce high ultimate strength, but as slag content is increased, early strength is reduced, while sulfate resistance increases and heat evolution diminishes. Used as an economic alternative to Portland sulfate-resisting and low-heat cements.

Portland-fly ash cement contains up to 40 % fly ash under ASTM standards (ASTM C595), or 35 % under EN standards (EN 197-1). The fly ash is pozzolanic, so that ultimate strength is maintained. Because fly ash addition allows a lower concrete water content, early strength can also be maintained. Where good quality cheap fly ash is available, this can be an economic alternative to Portland cement.

Figure 3: Schematic representation of cement manufacturing process.
Source: Cement Technology Roadmap 2009, World Business Council for Sustainable Development, International Energy Agency

Portland pozzolan cement includes fly ash cement, since fly ash is a pozzolan, but also includes cements made from other natural or artificial pozzolans. In countries where volcanic ashes are available (e.g. Italy, Chile, Mexico, and the Philippines) these cements are often the most common form in use. The maximum replacement ratios are generally defined as for Portland-fly ash cement.

Portland silica fume cement. Addition of silica fume can yield exceptionally high strengths, and cements containing 5–20 % silica fume are occasionally produced, with 10 % being the maximum allowed addition under EN 197-1. However, silica fume is more usually added to Portland cement at the concrete mixer.

Masonry cements are used for preparing bricklaying mortars and stuccos, and must not be used in concrete. They are usually complex proprietary formulations containing Portland clinker and a number of other ingredients that may include limestone, hydrated lime, air entrainers, retarders, waterproofers and colouring agents. They are formulated to yield workable mortars that allow rapid and consistent masonry work. Subtle variations of Masonry cement in the US are Plastic Cements and Stucco Cements. These are designed to produce controlled bond with masonry blocks.

Expansive cements contain, in addition to Portland clinker, expansive clinkers (usually sulfoaluminate clinkers), and are designed to offset the effects of drying shrinkage that is normally encountered with hydraulic cements. This allows large floor slabs (up to 60 m square) to be prepared without contraction joints.

White blended cements may be made using white clinker (containing little or no iron) and white supplementary materials such as high-purity metakaolin.

Coloured cements are used for decorative purposes. In some standards, the addition of pigments to produce "coloured Portland cement" is allowed. In other standards (e.g. ASTM), pigments are not allowed constituents of Portland cement, and coloured cements are sold as "blended hydraulic cements".

Very finely ground cements are made from mixtures of cement with sand or with slag or other pozzolan type minerals that are extremely finely ground together. Such cements can have the same physical characteristics as normal cement but with 50 % less cement particularly due to their increased surface area for the chemical reaction. Even with intensive grinding they can use up to 50 % less energy to fabricate than Portland cements.

Pozzolan-lime cements. Mixtures of ground pozzolan and lime are the cements used by the Romans, and can be found in Roman structures still standing. They develop strength slowly, but their ultimate strength can be very high. The hydration products that produce strength are essentially the same as those produced by Portland cement.

Slag-lime cements. Ground granulated blast furnace slag is not hydraulic on its own, but is

"activated" by addition of alkalis, most economically using lime. They are similar to pozzolan lime cements in their properties. Only granulated slag (i.e. water-quenched, glassy slag) is effective as a cement component.

Supersulfated cements contain about 80 % ground granulated blast furnace slag, 15 % gypsum or anhydrite and a little Portland clinker or lime as an activator. They produce strength by formation of ettringite, with strength growth similar to a slow Portland cement. They exhibit good resistance to aggressive agents, including sulfate. Calcium aluminate cements are hydraulic cements made primarily from limestone and bauxite. The active ingredients are monocalcium aluminate $CaAl_2O_4$ ($CaO \cdot Al_2O_3$ or CA in Cement chemist notation, CCN) and mayenite $Ca_{12}Al_{14}O_{33}$ (12 $CaO \cdot 7Al_2O_3$, or $C_{12}A_7$ in CCN). Strength forms by hydration to calcium aluminate hydrates. They are well-adapted for use in refractory (high-temperature resistant) concretes, e.g. for furnace linings.

Calcium sulfoaluminate cements are made from clinkers that include ye'elimite ye'elimite ($Ca_4(AlO_2)_6SO_4$ or C_4A_3S in CCN) as a primary phase. They are used in expansive cements, in ultra-high early strength cements, and in "low-energy" cements. Hydration produces ettringite, and specialized physical properties (such as expansion or rapid reaction) are obtained by adjustment of the availability of calcium and sulfate ions. Their use as a low-energy alternative to Portland cement has been pioneered in China, where several million tonnes per year are produced. Energy requirements are lower because of the lower kiln temperatures required for reaction, and the lower amount of limestone (which must be endothermically decarbonated) in the mix. In addition, the lower limestone content and lower fuel consumption leads to a CO_2 emission around half that associated with Portland clinker. However, SO_2 emissions are usually significantly higher.

Work on reduction of carbon dioxide emissions
There is a growing interest in reducing carbon emissions related to concrete from both the academic and industrial sectors, especially with carbon tax implications. Several approaches to reducing emissions have been suggested.

One reason why the carbon emissions are so high is because cement must be heated to very high temperatures for clinker to form. A major culprit of this is alite (Ca_3SiO_5), a mineral in concrete that cures within hours of pouring and is therefore responsible for much of its initial strength. However, alite also must be heated to 1,500 °C in the clinker-forming process. Some research suggests that alite can be replaced by a different mineral, such as belite (Ca_2SiO_4). Belite is also a mineral already used in concrete. It has a roasting temperature of 1,200 °C, which is significantly lower than that of alite. Furthermore, belite is stronger once concrete cures. However, belite takes on the order of days or months to set completely, which leaves concrete weak for an unacceptably long period of time. Current research is focusing on finding possible impurity additives, like magnesium, that might speed up the curing process. It is also worthwhile to consider that belite takes more energy to grind, which may make its full life impact similar to or even higher than alite.

Another approach has been the partial replacement of conventional clinker with such alternatives as

fly ash, bottom ash, and slag, all of which are by-products of other industries that would otherwise end up in landfills.

Portland cement clinker: the Bogue calculation

The Bogue calculation is used to calculate the approximate proportions of the four main minerals in Portland cement clinker.

The standard Bogue calculation refers to cement clinker, rather than cement, but it can be adjusted for use with cement. Although the result is only approximate, the calculation is an extremely useful and widely-used calculation in the cement industry.

The calculation assumes that the four main clinker minerals are pure minerals with compositions:

Alite: C_3S, or tricalcium silicate

Belite: C_2S, or dicalcium silicate

Aluminate phase: C_3A, or tricalcium aluminate

Ferrite phase: C_4AF, or tetracalcium alumino-ferrite

It is important to remember that these assumed compositions are only approximations to the actual compositions of the minerals.

Clinker is made by combining lime and silica and also lime with alumina and iron. If some of the lime remains un-combined, (which it almost certainly will) *we need to subtract this from the total lime content before we do the calculation* in order to get the best estimate of the proportions of the four main clinker minerals present. For this reason, a clinker analysis normally gives a figure for un-combined free lime.

(NB: If it is desired only to calculate the potential mineral proportions in a clinker, the correction for un-combined free lime can be ignored; the calculation will then give the clinker mineral proportions assuming that all the lime has combined).

The calculation is simple in principle:

Firstly, according to the assumed mineral compositions, ferrite phase is the only mineral to contain iron. The iron content of the clinker therefore fixes the ferrite content.

Secondly, the aluminate content is fixed by the total alumina content of the clinker, minus the alumina in the ferrite phase. This can now be calculated, since the amount of ferrite phase has been calculated.

Thirdly, it is assumed that all the silica is present as belite and the next calculation determines how much lime is needed to form belite from the total silica content of the clinker. There will be a surplus of lime.

Fourthly, the lime surplus is allocated to the belite, converting some of it to alite.

In practice, the above process of allocating the oxides can be reduced to the following equations, in which the oxides represent the weight percentages of the oxides in the clinker:

BOGUE CALCULATION

Clinker analysis (wt%)										
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI	IR	**Total**
21.5	5.2	2.8	66.6	1.0	0.6	0.2	1.0	1.5	0.5	**98.9**
Free lime = 1.0 % CaO										

Worked example of a Bogue calculation:

Using the above analysis, the calculation is as follows:

Combined CaO = (66.6 % - 1.0 % free lime) = 65.6 %

CaO=65.6 %; SiO_2=21.5 %; Al_2O_3=5.2 % and Fe_2O_3=2.8 %

The Bogue calculation is therefore:

$C_3S = 4.0710CaO - 7.6024SiO_2 - 1.4297Fe_2O_3 - 6.7187Al_2O_3$

$C_2S = 8.6024SiO_2 + 1.1Fe_2O3 + 5.0683Al_2O_3 - 3.0710CaO$

$C_3A = 2.6504Al_2O_3 - 1.6920Fe_2O_3$

$C_4AF = 3.0432Fe_2O_3$

Therefore:

$C_3S = (4.0710 \times 65.6) - (7.6024 \times 21.5) - (1.4297 \times 2.8) - (6.718 \times 5.2)$

$C_2S = (8.6024 \times 21.5) + (1.0785 \times 2.8) + (5.0683 \times 5.2) - (3.0710 \times 65.6)$

$C_3A = (2.6504 \times 5.2) - (1.6920 \times 2.8)$

$C_4AF = 3.0432 \times 2.8$

So:

$C_3S = 64.7 \%$

$C_2S = 12.9 \%$

$C_3A = 9.0 \%$

$C_4AF = 8.5 \%$

It should be stressed that the Bogue calculation does not give the 'true' amounts of the four main clinker phases present, although this is sometimes forgotten. The results of the Bogue calculation differ from the 'true' amounts (often called the phase proportions) principally because the actual mineral compositions differ - often only slightly, but occasionally more so and particularly in the case of the ferrite phase, from the pure phase compositions assumed in the calculation.

To adjust the calculation for use with Portland cement, it is necessary to consider first what other materials may be present in the cement. If the cement is a mixture of clinker and gypsum only, the calcium bound with the gypsum can be allowed for approximately by deducting ($0.7 \times SO_3$) from the total CaO. Note that this does not allow for any clinker sulfate present as potassium or sodium sulfate and a small error will therefore be introduced.

A similar adjustment can be carried out for limestone; the limestone content can be estimated by determining the CO_2 content of the cement and calculating the corresponding CaO. If either slag or fly ash is present, in principle the formula could be adjusted to take it into account, but the slag or ash composition would need to be known accurately and in practice this is not an adjustment normally made.

Appendix 2 – Annual cement production and producers

A number of sources of information were obtained on global cement production: the US

Geological Survey, CEMBUREA (the European Cement Association); Statistica.

The largest 20 cement producers by volume are also shown in Table 6.

US Geological Survey

In 2014, the world production of hydraulic cement was 4,180 million tonnes. The top three producers were China with 2,500 million tonnes, India with 280, and the USA with 83.3 million tonnes for a combined total of over half the world total by the world's three most populated states.

Data from USGS data:

http://minerals.usgs.gov/minerals/pubs/commodity/cement/mcs-2015-cemen.pdf

For the world clinker capacity in 2014, the situation was similar with the top three countries (China, India, and USA) accounting for over half the world total capacity.

Over 2011 and 2012, global consumption continued to climb, rising to 3,585 million tonnes in 2011 and 3,736 million tonnes in 2012, while annual growth rates eased to 8.3 % and 4.2 %, respectively.

China, representing an increasing share of world cement consumption, by 2014, Chinese demand was recorded at 2,500 million tonnes, representing nearly 60% of world consumption. Annual growth rates, which reached 16 % in 2010, appear to have softened, slowing to 3–4 % over 2013-2014, as China's economy targets a more sustainable growth rate. Outside of China, worldwide consumption climbed by 4.4 % to 1,462 million tonnes in 2010, 5 % to 1,535 million tonnes in 2011, and 2.7 % to 1,576 million tonnes in 2012.

Iran is now the third largest cement producer in the world and has increased its output by over 10 % from 2008 to 2011; annual production is now 75 million tonnes very similar to that of Turkey. Due to climbing energy costs in Pakistan and other major cement-producing countries, Iran is a unique position as a trading partner, utilizing its own surplus petroleum to power clinker plants. Now a top producer in the Middle-East, Iran is further increasing its dominant position in local markets and abroad.

Growth in production in North America was very strong at 8.2 % between 2013 and 2014 whilst Europe production levels showed a slight decline.

The performance in the rest of the world, which includes many emerging economies in Asia, Africa and Latin America and representing some 1,020 million tonnes cement demand in 2010, was

positive and more than offset the declines in North America and Europe. Annual consumption
growth was recorded at 7.4 % in 2010, moderating to 5.1 % and 4.3 % in 2011 and 2012,
respectively.

As at year-end 2012, the global cement industry consisted of 5,673 cement production facilities,
including both integrated and grinding, of which 3,900 were located in China and 1,773 in the rest of
the world.

Total cement capacity worldwide was recorded at 5,245 million tonnes in 2012, with 2,950 million
tonnes located in China and 2,295 million tonnes in the rest of the world.

CEMBUREAU

Data from indicates a 2015 production cement level of 4,600 million tonnes per year and the Figure
below shows the production by region. China accounts for over half the production and Asia in total
comprises over 83 % of total production.
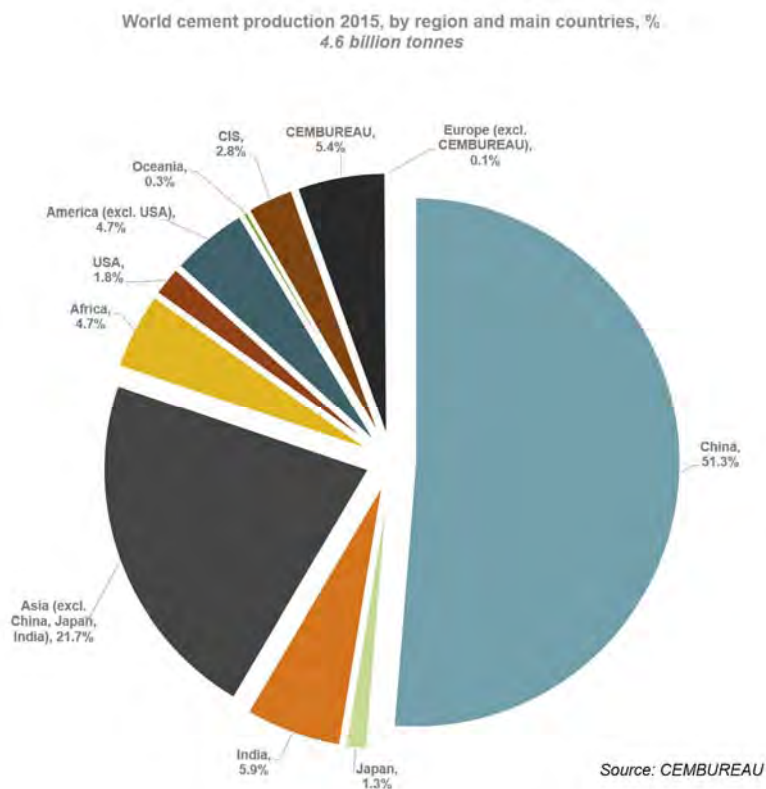
Figure 1: Worldwide cement production 2015

The figure below from CEMBUREAU shows the growth in production between 2001 and now.
Particularly noteworthy is the growth in Asia, Africa and the CIS; production in Europe has declined.
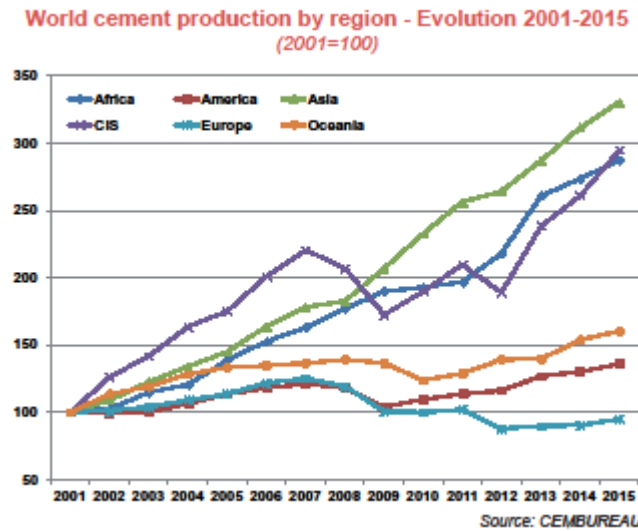
Figure 4: Cement production by region 2001 – 2015

Statista

Data from Statista:

http://www.statista.com/statistics/373845/global-cement-production-forecast/

Indicates global production of cement in 2014 at 4,100 million tonnes and forecasts a value of 4,400 million tonnes by 2020.

Table 6: Major cement producers, Largest cement producers – 2013

Rank	Company/Group	Country	Capacity (Mt/y)	No. of plants
1	Lafarge	France	225	166
2	Holcim	Switzerland	217	149
3	CNBM	China	200	69
4	Anhui Conch	China	180	34
5	HeidelbergCement	Germany	118	71
6	Jidong	China	100	100
7	Cemex	Mexico	96	61
8	China Resources	China	89	16
9	Sinoma	China	87	24
10	Shanshui	China	84	13
11	Italcementi	Italy	74	55

12	Taiwan Cement	Taiwan	70	-
13	Votorantim*	Brazil	57	37
14	CRH**	Ireland	56	11
15	UltraTech	India	53	12
16	Huaxin	China	52	51
17	Buzzi	Italy	45	39
18	Eurocement	Russia	40	16
19	Tianrui	China	35	11
20	Jaypee***	India	34	16

Lafarge and Holcim merged in 2015 to form LarfargeHolcim.

Appendix 3 – Cement standards

EU Standards

EN 197-1:2011 Cement. Composition, specifications and conformity criteria for common cements

This European Standard defines and gives the specifications of 27 distinct common cements, 7 sulfate resisting common cements as well as 3 distinct low early strength blast furnace cements and 2 sulfate resisting low early strength blast furnace cements and their constituents. The table below shows the 27 products in the family of common cements according to EN 197-1:2000. The values in the table refer to the sum of the main and minor additional constituents. The proportion of silica fume is limited to 10 %.

EN 197-1:2000

Table 1- The 27 products in the family of common cements

Main types	Notation of the 27 products (types of common cement)		Composition [proportion by mass[1]]										Minor additional constituents
			Main constituents										
			Clinker	Blastfurnace slag	Silica fume	Pozzolana natural	natural calcined	Fly ash siliceous	calcareous	Burnt shale	Limestone*		
			K	S	D[2]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland-limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	21-35	0-5
	Portland-composite cement[3]	CEM II/A-M	80-94	<--- 6-20 --->										0-5
		CEM II/B-M	65-79	<--- 21-35 --->										0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement[3]	CEM IV/A	65-89	-	<-------------- 11-35 -------------->					-	-	-	0-5
		CEM IV/B	45-64	-	<-------------- 36-55 -------------->					-	-	-	0-5
CEM V	Composite cement[3]	CEM V/A	40-64	18-30	-	<---------- 18-30 ---------->				-	-	-	0-5
		CEM V/B	20-38	31-50	-	<---------- 31-50 ---------->				-	-	-	0-5

1) The values in the table refer to the sum of the main and minor additional constituents.   2) The proportion of silica fume is limited to 10%.

3) In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B
    and in Composite cements CEM V/A and CEM V/B the main constituents besides clinker shall be declared by designation of the cement.

* L : total organic carbon (TOC) shall not exceed 0.5% by mass; LL: TOC shall not exceed 0.20% by mass.

The definition of each cement includes the proportions in which the constituents are to be combined to produce these distinct products in a range of nine strength classes.

The definition also includes requirements which the constituents must meet. It also includes mechanical, physical, and chemical requirements. Furthermore, this standard states the conformity criteria and the related rules. Necessary durability requirements are also given.

Contents for BS EN 197-1:2011 includes:

- Scope
- Normative references
- Terms and definitions
- Cement
- Constituents
- General

- Main constituents

- Portland cement clinker (K)

- Granulated blast furnace slag (S)

- Pozzolanic materials (P, Q)

- Fly ashes (V, W)

- Burnt shale (T)

- Limestone (L, LL)
- Silica fume (D)

- Minor additional constituents

- Calcium sulfate
- Additives
- Composition and notation
- Composition and notation of common cements

- Composition and notation of sulfate resisting common cements (SR-Cements)

- Composition and notation of low early strength common cements
- Mechanical, physical, chemical and durability requirements

- Mechanical requirements

- Standard strength

- Early strength
- Physical requirements

- Initial setting time

- Soundness

- Heat of hydration

- Chemical requirements

- Durability requirements

- General

- Sulfate resistance

- Standard designation
- Conformity criteria
- General requirements

- Conformity criteria for mechanical, physical and chemical properties and evaluation procedure
- General

- Statistical conformity criteria

- Single result conformity criteria
- Conformity criteria for cement composition

- Conformity criteria for properties of the cement constituents.

Brazilian standards

Standard cement CPIV-32 ENV197 (CP IV/A) cement (30 % pozzolan)

CP II-Z-32 (CP II/A-Q) cement (15 % pozzolan).

India

Here are the IS codes which cater to the need of civil engineering relating to cement and concrete. These IS codes include the Standardization in the field of all types of cement, pozzolan, testing sand, concrete, aggregates, instruments for cement and concrete testing, cement plant machinery and ferrocement concrete, reinforced concrete and pre-stressed concrete, test methods for concrete, concrete production and execution of concrete structures, performance requirements for structural concrete, non-traditional reinforcing materials for concrete structures and cement and lime.

IS 269:1989 – Specification for ordinary Portland cement, 33 grade.

IS 383:1970 – Specification for coarse and fine aggregates from natural sources for concrete.

IS 455:1989 Specification for Portland slag cement.

IS 456:2000 Code of practice for plain and reinforced concrete.

IS 457:1957 Code of practice for general construction of plain and reinforced concrete for dams and other massive structures.

IS 516:1959 Method of test for strength of concrete.

IS 650:1991 Specification for standard sand for testing of cement.

IS 1199:1959 Methods of sampling and analysis of concrete.

IS 1343:1980 Code of practice for prestressed concrete.

IS 1344:1981 Specification for calcined clay pozzolana.
IS 1489(Part 1):1991 Specification for Portland pozzolana cement Part 1 Flyash based.

IS 1489(Part 2):1991 Specification for Portland-pozzolana cement: Part 2 Calcined clay based.

IS 1727:1967 Methods of test for pozzolanic materials.

IS 2386(Part 1):1963 Methods of test for aggregates for concrete: Part 1 Particle size and shape.

IS 2386(Part 2):1963 Methods of test for aggregates for concrete: Part 2 Estimation of deleterious materials and organic impurities.

IS 2386(Part 3):1963 Methods of test for aggregates for concrete: Part 3 Specific gravity, density, voids, absorption and bulking.
IS 2386(Part 4):1963 Methods of test for aggregates for concrete: Part 4 Mechanical properties.

IS 2386(Part 5):1963 Methods of test for aggregates for concrete: Part 5 Soundness.

IS 2386(Part 6):1963 Methods of test for aggregates for concrete: Part 6 Measuring mortar making properties of fine aggregates.

IS 2386(Part 7):1963 Methods of test for aggregates for concrete: Part 7 Alkali aggregate reactivity.

IS 2386(Part 8):1963 Methods of test for aggregates for concrete: Part 8 Petrographic examination.

IS 2430:1986 Methods for sampling of aggregates for concrete.

IS 2645:2003 Integral waterproofing compounds for cement mortar and concrete – Specification.

IS 2770(Part 1):1967 Methods of testing bond in reinforced concrete: Part 1 Pull-out test.

IS 3085:1965 Method of test for permeability of cement mortar and concrete.

IS 3370(Part 1):2009 Code of practice for concrete structures for storage of liquids: Part 1 General requirements.

USA

Main ASTM standards

Chemical Reactions

Designation	Title
C227 - 10	Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)
C441 / C441M - 11	Standard Test Method for Effectiveness of Pozzolans or Ground Blast-Furnace Slag in Preventing Excessive Expansion of Concrete Due to the Alkali-Silica Reaction
C586 - 11	Standard Test Method for Potential Alkali Reactivity of Carbonate Rocks as Concrete Aggregates (Rock-Cylinder Method)
C1105 - 08a(2016)	Standard Test Method for Length Change of Concrete Due to Alkali-Carbonate Rock Reaction
C1260 - 14	Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)

Designation	Title
C1293 - 08b(2015)	Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction
C1567 - 13	Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)

Chemical Tests

Designation	Title
C25 - 11e2	Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
C400 - 98(2013)	Standard Test Methods for Quicklime and Hydrated Lime for Neutralization of Waste Acid
C1271 - 99(2012)	Standard Test Method for X-ray Spectrometric Analysis of Lime and Limestone
C1301 - 95(2014)	Standard Test Method for Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) and Atomic Absorption (AA)
C1318 - 15a	Standard Test Method for Determination of Total Neutralizing Capability and Dissolved Calcium and Magnesium Oxide in Lime for Flue Gas Desulfurization (FGD)

Compositional Analysis

Designation	Title
C114 - 15	Standard Test Methods for Chemical Analysis of Hydraulic Cement
C1356 - 07(2012)	Standard Test Method for Quantitative Determination of Phases in Portland Cement Clinker by Microscopical Point-Count Procedure
C1365 - 06(2011)	Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis

Designation	Title
C114 - 15	Standard Test Methods for Chemical Analysis of Hydraulic Cement
C1356 - 07(2012)	Standard Test Method for Quantitative Determination of Phases in Portland Cement Clinker by Microscopical Point-Count Procedure
C1365 - 06(2011)	Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis

Appendix 4 – Industry Associations

Australia

Cement, Concrete and Aggregates Australia (CCAA):
http://www.ccaa.com.au/iMIS_Prod/CCAA/Home/CCAA/Public_Content/Home.aspx?hke_y=5d15d9c7-40ce-440b-adfd-4c02257c39e6

Our members operate cement manufacturing and distribution facilities, concrete batching plants, hard rock quarries and sand and gravel extraction operations throughout the nation. CCAA membership is made up of the majority of material producers and suppliers, and ranges from large global companies, to SMEs and family operated businesses.

We represent our members' interests through advocacy to government and the wider community; assistance to building and construction industry professionals; development of market applications; and a source of technical and reference information.

The role of CCAA is to support the maintenance of the overall industry operation by:

- Building an understanding of industry and its role with stakeholders Maintain existing and develop new markets for members' products

- Advocate for and influence the application and use of members' products

- Influence development of codes and standards to support the use of member's products

- Demonstrate the industry's sustainability credentials

- Encourage collaboration and networking across the industry Supply and share information to support the industry

The Concrete Institute of Australia: https://www.concreteinstitute.com.au/Home.asp**x**

The Concrete Institute of Australia is an independent, not for profit organisation made up of many members who share a common interest in staying at the forefront of concrete technology, design and construction in Australia.

Brazil

Brazilian Portland Cement Association (Associação Brasileira de Cimento Portland) was founded in 1936 in order to promote studies on the cement and their applications.
http://ietd.iipnetwork.org/content/brazilian-portland-cement-association

It is a non-profit, maintained by the Brazilian cement industry, which makes up their membership. ABCP is active in different areas such as (ABCP 2011):

- Promotion of courses and training seminars and technical events;

- Partnership with dozens of universities, colleges and research institutions of the country; Publication of books, journals and technical documents;

- Support the generation of Brazilian technical standards

Europe

European Cement Association (CEMBUREAU): http://ietd.iipnetwork.org/content/european-cement-association

The European Cement Association, CEMBUREAU, is the representative organization of the cement industry in Europe acting as spokesperson for the cement industry before the European Union institutions and other public authorities, and communicates the industry's views on all issues and policy developments. Currently, its Full Members are the national cement industry associations and cement companies of the European Union (with the exception of Cyprus, Malta and Slovakia) plus Norway, Switzerland and Turkey. CEMBUREAU plays a role in the world-wide promotion of cement and the ready-mix and precast concrete industries in co-operation with Member Associations and other relevant organisations. The Association regularly co-hosts conferences on specific issues aimed at improving the market perception of the concrete industry and promoting the use of generic cement and concrete products. In addition, the Association regularly commissions studies to evaluate specific issues of importance to the industry.

CEMBUREAU has been involved in the promotion of energy efficiency and the use of alternative fuels in the cement industry. For instance, CEMBUREAU has published a report on the co-processing of alternative fuels and raw materials in the European cement industry (CEMBUREAU 2009). In another report by CEMBUREAU, it discusses the environmental benefits of using alternative fuels in cement production (CEMBUREAU 1999).

Nanocem: http://www.nanocem.org/

Nanocem is a consortium of European academic and industrial partners, all interested in fundamental research of cement and concrete. Working together, we combine passion with pragmatism, cooperation with independence and long term vision with hands on experience. We don't develop products directly. But the combined academic and industrial knowledge that we produce drives the development of new and improved materials and products that are adapted to modern needs, whilst minimising the environmental impact of the construction cycle. Nanocem was founded in 2004, and has grown to a network of 24 academic and 11 industry partners. There are some 120 academic researchers in the team who, between them, are in the process of managing some 60 PhD and post-doctoral research projects in related areas. Nanocem is now recognised as the world reference for quality research in cementitious materials.

India

The Indian Concrete Institute: http://www.indianconcreteinstitute.org/about-us.html

The Indian Concrete Institute (ICI) is one of the leading professional bodies in India, catering to the professional needs of individuals and organisations involved in concrete. Being a non-profit Organisation, it is dedicated to the cause of Disseminating Knowledge on Concrete, to Promote Concrete Technology and Construction and to address the Research Needs of Concrete.

The Genesis of ICI dates back to the year 1982, when SERC Chennai and Anna University jointly conducted an International Seminar on Modern Concrete Construction Practices. The overwhelming response to the seminar prompted the Organisers to start the Indian Concrete Institute. Thus, the ICI was born in 1982 with around 500 members from 5 regional Centres. Since then, there is no looking back and ICI has grown in leaps and bounds. Today ICI is a strong professional body having more than 11,000 enrolled members, from 30 regional Centres in all major cities, spread across the entire length and breadth of the country. Of these, more than 250 are Organisational Members. All segments of cement and concrete industries are widely represented in the membership.

To meet the objectives of ICI, the regional centres conduct varieties of programs like Seminars, Workshops, Conferences, Exhibitions, etc. throughout the year. These are at both National and International level. These events prove to be a unique platform, for all the stakeholders in the concrete industry, wherein Practicing Engineers, Manufacturers, Academics, Consultants and Researchers make their global participation, to discuss the issues, to share their views and experience on the concrete related matters. Thus, ICI derives the synergy amongst the various categories of people associated with concrete.

Any professional Body is recognized by the technical documents it creates. Today, at ICI, several Technical Committees are striving hard to bring out technical documents, to frame guidelines, to

standardize, to fix norms for various speciality, concretes and construction practices, to create unified code and to bring out Hand Books etc. The outcome of these committees has placed ICI high in the concrete arena.

ICI works in close coordination with various Central and State Government Bodies like CPWD, PWDs, Municipal Corporation etc., for the adoption of Latest Technologies and practices in Infrastructure Building. ICI members represent in several Codal Committees of BIS.

ICI is an active participant in Asian Concrete Federation (ACF), which is a cluster of nine Asian Countries. ICI has signed MOU with other concrete institutes like Singapore Concrete Institute, Concrete Institute of Australia, Korea Concrete Institute, American Concrete Institute and RILEM for exchange of technological Information, technical documents and to organize programmes, jointly.

A professional body has got its responsibilities towards society. So also, ICI is committed to the society for its wellbeing. ICI is focused towards advocating the concept of sustainability in construction practices. Many of the ICI events are focused on achieving sustainability through innovative materials and techniques. Response to such programmes from Government Bodies is overwhelming.

ICI embraces budding civil engineers thro ICI Students Chapters. There are more than 120 students' chapters, all over the country and this number is on the increase. The very objective of these students' chapters is to bridge the gap between their theoretical knowledge and what is being practiced in the field. Their involvement in ICI activities help them shape themselves to face the challenges in the field, when they come out of the Institutions and enhance their Employability Quotient. ICI also conducts value-added courses in concrete for the benefit of Practicing Engineers and Students.

ICI identifies, recognizes and rewards the experts in the field of concrete for their contributions to the development of concrete technology and Concrete Construction. Sixteen such awards are presented every year at the time of AGM. ICI brings out several publications, proceedings of all the important events for the benefit of members and others. Work is on to bring out a journal of international standard, through one of the world renowned Publisher.

Cement Manufacturers' Association: http://www.iipnetwork.org/cement-manufacturer%E2%80%99s-association-india

Cement Manufacturers' Association (CMA) is made up of both the private and public sector cement companies and members and has offices in New Delhi, Noida, Mumbai and Hyderabad. Its main objectives include promoting the growth of the cement industry, protecting the consumer interests, identifying newer applications of cement usage and establishing contacts with similar bodies abroad for exchange of information, data, publications etc. -

USA

The Portland Cement Association (PCA) is a powerful and vocal advocate for sustainability, jobs creation, economic growth, infrastructure investment, and overall innovation and excellence in construction throughout the U.S.
 http://www.cement.org/about-pca

Headquartered in Skokie, Illinois with offices in Washington, DC, PCA represents America's cement manufacturers. The association takes an active role in industry advocacy for increased infrastructure investment, jobs creation, passage of a new highway bill in the United States, and the establishment of fair and reasonable emissions guidelines that protect the environment while helping to get the economy back on track.

More than mere advocacy, the industry and PCA have taken strong initiatives that will not only help improve the state of the industry, but will also improve the state of the world around us. Among some of these key initiatives are:

- The creation of the Concrete Sustainability Hub at the Massachusetts Institute of Technology with a goal of quantifying and enhancing the sustainable nature of concrete.

- The development and promotion of a sample ordinance, called High Performance Building Requirements for Sustainability (HPBRS), which seeks to establish a new paradigm for sustainability in high-performance buildings.

- The launch of a campaign – Think Harder. Concrete – to build awareness that there is a new reality in the paving industry whereby state and local officials can save taxpayers millions of dollars by turning to concrete rather than asphalt as the lowest-cost and most durable and sustainable material for road and highway construction.

- Support and recognition of excellence in construction and sustainability through a number of industry awards, including Energy & Environment Awards, Concrete
- Bridge Awards, Safety Performance Awards, Safety Innovation Awards, and others.

- Continued leadership in education and training through a wide range of seminars, webinars, training programs, and participation in important new social networking vehicles.

Appendix 5 – EU MSCA ETN for Zero-Waste Valorisation of Bauxite Residue

European Training Network for Zero-Waste Valorisation of Bauxite Residue (Red Mud)

To tackle its (critical) raw material dependency, Europe needs comprehensive strategies based on sustainable primary mining, substitution and recycling. Freshly produced flows and stocks of landfilled industrial residues such as mine tailings, non-ferrous slag and bauxite residue (BR) can provide major amounts of critical metals and, concurrently, minerals for low-carbon building materials. The European Training Network for Zero-Waste Valorisation of Bauxite Residue (REDMUD) therefore targets the vast streams of new and stockpiled BR in the EU-28. BR contains several critical metals, is associated with a substantial management cost, whereas spills have led to major environmental incidents, including the Ajka disaster in Hungary. To date, zero-waste valorisation of BR is not occurring yet. The creation of a zero-waste BR valorisation industry in Europe urgently requires skilled scientists and engineers, who can tackle the barriers to develop fully closed-loop environmentally-friendly recovery flow sheets. REDMUD trains 15 researchers in the S/T of bauxite residue valorisation, with emphasis on the recovery of Fe, Al, Ti and rare earths (incl. Sc) while valorising the residuals into building materials. An intersectoral and interdisciplinary collaboration of EU-leading institutes and scientists has been established, which covers the full value chain, from BR to recovered metals and new building materials. Research challenges include the development of efficient extraction of Fe, Al, Ti and rare earths (incl. Sc) from distinct (NORM classified) BRs and the preparation of new building materials with higher than usual Fe content. By training the researchers in pyro-, hydro- and ionometallurgy, electrolysis, rare-earth extraction and separation technology, inorganic polymer and cement chemistry, Life Cycle Assessment (LCA), NORM aspects and characterisation, they become the much needed scientists and engineers for the growing European critical raw materials industry.
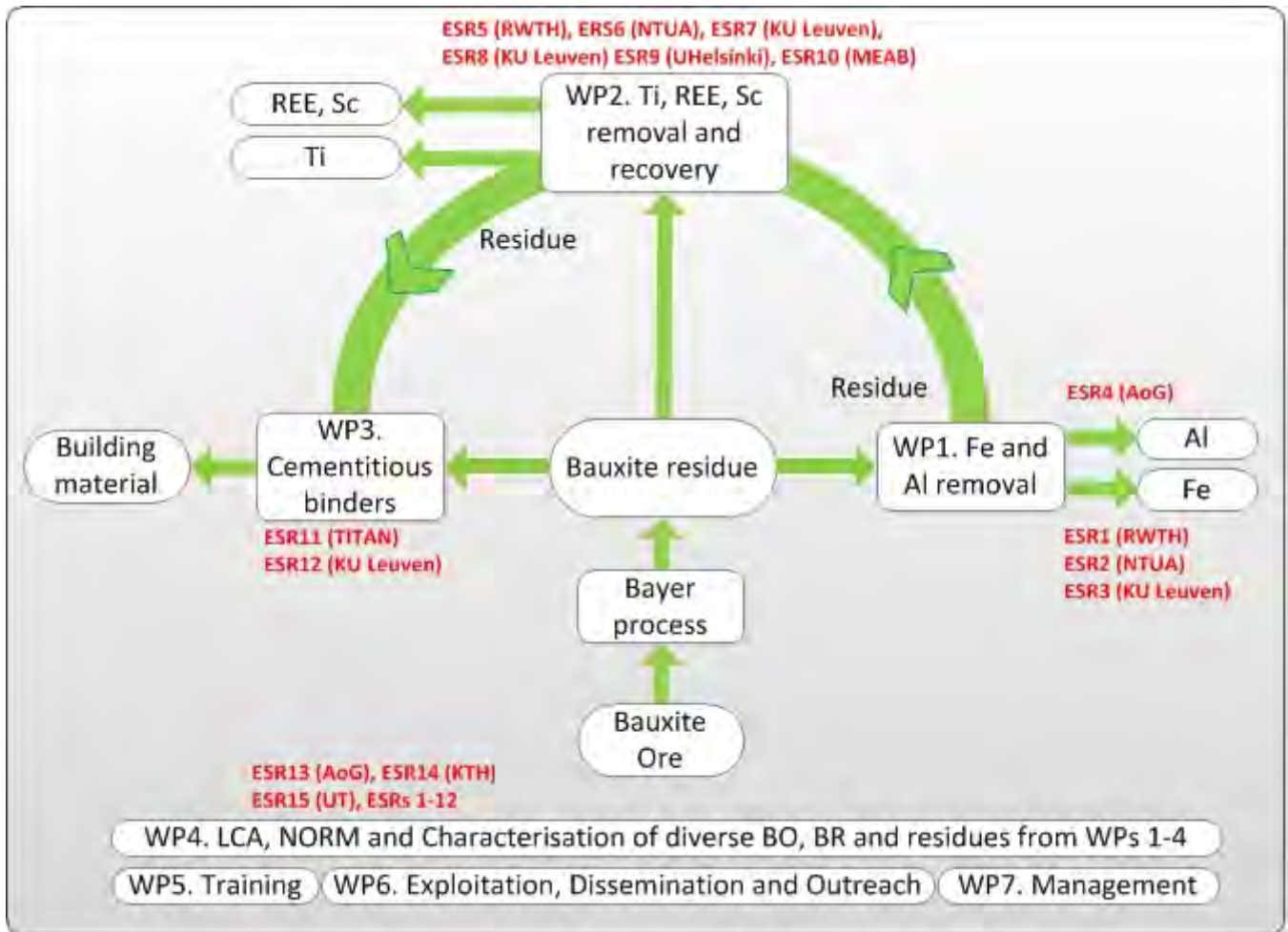
Key data
Partners: KU Leuven, UHelsinki, RWTH Aachen, KTH, NTUA, UTartu, MEAB, Aluminium of Greece, Titan
Partner Organisations: UPatras, UAveiro, Bay Zoltan, Tasman Metals
Funding: 3.7 M EURO

http://etn.redmud.org/

Appendix 6 - Organisations involved in cement/bauxite residue research

Universities/Institutes known to have worked on Bauxite residue and cement

Anna University, Department of Civil Engineering, K. S Rangasamy College of Technology, Tiruchengode, India. M. P. Sureshkumar.

Banaras Hindu University, Department of Mechanical Engineering, Varanasi, India. P. M. Prasad.

Catholic University of Leuven, Belgium. Yiannis Pontikes.

Civil Engineering Department, Sao Paulo, Brazil. Rafael Pileggi.

CSIRO, Australia. C. Klauber.

KIT College of Engineering in Kohlapur, India.

Lucideon (formerly CERAM Research), Stoke on Trent, UK.

Materials Engineering Department, Federal University of Sao Carlos, Brazil. Jose Rodrigues.

National Technical University of Athens, Department of Mining and Metallurgical Engineering, Greece. P. E. Tsakiridis.

S. B. Patil College of Engineering, Indapur/Pune University, India. Ramesh Rathod et al.

The Centre for Cement and Concrete Research, University of Sheffield, UK.

Civil Engineering Department, Sherbrook University, Quebec, Canada.

University of Science and Technology, Beijing, China. Xiaoming Liu.

VAMI, St Petersburg, Russia.

VITO, Mol, Belgium. R. Snellings.

Appendix 7 – Geopolymers

A geopolymer is an Al- and Si-rich cementitious, amorphous binder, which is formed by polymerisation of an alkali-activated solid aluminosilicate precursor. They comprise chains or a 3D framework of linked AlO_4^{5-} and SiO_4^{4-}.

They have been of interest for over 40 years as alternative binders because their excellent properties, such as high compressive strength, resistance to acidic attack, thermal stability and their lower carbon dioxide footprint. The more general term inorganic polymer defines a larger group which do not display the tetrahedral coordination of Al and Si and the aluminosilicate chemistry.

A substantial quantity of work is being done in incorporating bauxite residue in solid blends with a highly reactive precursor material and has been reviewed by Hertel et al and published in August 2016. A brief summary of what has been done is included here for completeness and an indication of what is possible in this related area.

"Compressive strengths of 20.5 MPa were, for instance, reached in metakaolin-based inorganic polymers with additions of 15 wt% bauxite residue. A new type of composite geopolymers with the maximum compressive strengths of 20.5 MPa was described using bauxite residue in combination with rice husk (BR/rice husk weight ratio 0.5) and NaOH solution for the synthesis. In view of the highly amorphous character and hence the high reactivity of the silica source, rice husk ash, the addition of sodium silicate was not necessary. Mixed ground-granulated blast furnace slag (GGBFS) in varying proportions with calcined bauxite residue (800 °C), reaching, for instance, 50 MPa after 28 days in a 50–50 wt% mix. Foamed bauxite residue-based geopolymers were synthesised using up to 25 wt% bauxite residue in combination with waste glass in the solid mix and the filtrate of red mud slurry and NaOH solution, respectively, as liquid component. All of these inorganic polymers are characterised by a significant decrease in compressive strength with an increasing content of bauxite residue.

A second group of studies revolves around thermally treated bauxite residue. In the work of Ke et al., one-part binders were developed after calcination of (dry) bauxite residue with 5–15 wt% Na_2O at 800 °C, probably in air. This alkali treatment resulted in the formation of hydraulic phases, disordered peralkaline aluminosilicate, C_3A, and aL-C_2S. Maximum strengths up to 10 MPa were achieved after 7 days with 10 wt% NaOH addition which dramatically decreased after 3 weeks of curing. In another work, Hairi et al. used raw and calcined bauxite residue as the main component for inorganic polymer, with varying contents of amorphous silica fume (6–26 wt%) and alumina (0–20 wt%) in the solid mix and a sodium silicate solution as an activator. The highest compressive strength of 58 MPa was reported for a mix of 83 wt% of thermally pretreated (500 °C) bauxite residue combined with 17 wt% silica fume and a sodium silicate activating solution at a solution-to-solid ratio of 0.5."

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Appendix 9 - Glossary of terms used in the cement industry

Aggregates: materials used in construction, including sand, gravel and crushed stone.

Alternative fossil fuels: products from fossil fuel origin used as a source of thermal energy and not classified as traditional fossil fuel. This is mainly fossil waste such as plastics, solvents, waste oil, end-of-life tyres, etc.

Blended cement: Portland cement mixed with clinker substitutes.

Carbon leakage: an increase in CO_2 emissions in one country as a result of an emissions reduction in a second country, e.g., if that second country has a stricter climate policy

Cement: a building material made by grinding clinker together with various mineral components such as gypsum, limestone, blast furnace slag, coal fly ash and natural volcanic material. It acts as the binding agent when mixed with sand, gravel or crushed stone and water to make concrete. While cement qualities are defined by national standards, there is no worldwide, harmonised definition or standard for cement but is often defined to include all hydraulic binders that are delivered to the final customer, i.e., including all types of Portland, composite and blended cements, plus ground granulated slag and fly ash delivered to the concrete mixers, but excluding clinker.

Cementitious products: total of all cements and clinker produced by a cement company, excluding the clinker purchased from another company and used to make cement. Cement is equal to cementitious product when the net balance of clinker sold and purchased is zero.

Clinker: intermediate product in cement manufacturing and the main substance in cement. Clinker is the result of calcination of limestone in the kiln and subsequent reactions resulting from calcination process.

Fly ash: exhaust-borne particulates generated and captured at coal-fired power plants.

Geopolymer cement: cement manufactured with chains or networks of mineral molecules producing 80–90 % less CO_2 than OPC; see www.geopolymer.org.

Gross CO_2 emissions: all direct CO_2 emissions (excluding on-site electricity production) excluding CO_2 emissions from biomass which are considered climate neutral.

Net CO_2 emissions: gross CO_2 emissions minus emissions from alternative fossil fuels.

Ordinary Portland Cement (OPC): most common type of cement, consisting of over 90 % ground clinker and about 5 % gypsum.

Pozzolan: a material that, when combined with calcium hydroxide, exhibits cementitious properties.

Precalciner kiln: a rotary kiln equipped so that most of the limestone calcination is accomplished in a separate apparatus ahead of the rotary kiln, more energy-efficient than having all the calcination take place in the kiln itself