

Opportunities for using bauxite residue in Portland cement clinker production



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The global objectives of the Institute are:

 <p>Governance To conduct business ethically, with sound systems of corporate governance</p>	 <p>People To protect, nurture and develop the workforce and the communities in which we operate</p>	 <p>Places To protect, nurture and sustainably develop the places in which we operate</p>	 <p>GHGs To deliver beneficial services...while bringing a net reduction in greenhouse gas emissions...¹</p>	 <p>Waste To reduce waste and to manage it effectively and safely</p>	 <p>Products To deliver aluminium products that meet the needs of society and improve individuals' quality of life...²</p>
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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 the production of Portland cement clinker, separate papers cover possible usage in calcium sulfoaluminate/special/sulfoaluminates cements and in supplementary cementitious materials.

Summary

The prospects for using bauxite residue in Portland cement has been explored for over 80 years with many promising technical studies and several successful large scale commercial initiatives. The iron and aluminium compounds contained in the bauxite residue provide valuable additions in the production of Portland cement at a low cost.

The best estimates are that between 1,000,000 to 1,500,000 tonnes of bauxite residue are currently used annually in the production of Portland Cement clinker. The cement plants currently utilising the bauxite residue in clinker production are based in China, Ukraine, India, Russia, Georgia, Moldova, Cyprus and Greece.

From the evidence from the cement plants that are already using bauxite residue on an industrial scale, it is clear that bauxite residue can satisfactorily be used in cement clinker manufacture with only slight changes to their operating process. With the appropriate bauxite residue, typically a usage rate of 3 to 5 % can be accommodated. From the industrial experience to date, key aspects seem to be:

- a relatively low moisture content - approximately 30 % moisture has been used in several plants and this can readily be achieved by bauxite residue producers, some alumina refineries have used a plate and frame filter press to produce a satisfactory product whilst others have achieved a satisfactory level by air drying the bauxite residue;
- a moderately low sodium content, a value of < 2.5 % Na₂O has been indicated as satisfactory but it will depend on the composition of the other raw materials;
- the appropriate aluminium oxide to iron oxide ratio (an iron oxide to alumina ratio of 0.8:1.2 in the raw mix was found to give the best results in one study although some plants will use the bauxite residue to supplement the iron level whilst others use it for the alumina content);
- and the reasonable proximity of a cement plant (a distance of up to 1,200 km has been found to be acceptable in one case).

There is believed to be scope for many more clinker producers to use bauxite residue leading to improvements in the environmental footprints of both the aluminium and cement industries.

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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 cementitious materials.

This paper serves to give some guidance to cement producers on some of the relevant background specifically relating to use of bauxite residue in Portland cement clinker.

2. Cement – basic background

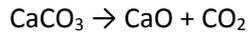
A cement may be defined as a binder or a substance that sets and hardens and can bind other materials together. Cements used in construction can be characterised as being either **hydraulic** or **non-hydraulic**, depending upon the ability of the cement to set in the presence of water.

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.

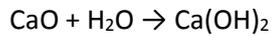
Hydraulic cements set and harden due to a chemical reaction between the dry ingredients and water. The chemical reaction results in mineral hydrates that have low water solubility so are durable in water and reasonably resistant to chemical attack. This allows setting in wet conditions or underwater 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.

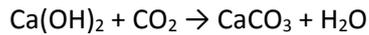
Non-hydraulic cement, such as slaked lime (calcium hydroxide mixed with water), hardens by carbonation in the presence of carbon dioxide which is naturally present in the air. These are manufactured by first producing calcium oxide by the calcination of calcium carbonate at temperatures above 825 °C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



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



Once the water in excess from the slaked lime is completely evaporated the carbonation starts:



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 ($2\text{CaO}\cdot\text{SiO}_2$ or dicalcium silicate or C_2S);

Alite ($3\text{CaO}\cdot\text{SiO}_2$ or C_3S or tricalcium silicate);

Tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$ or C_3A) (historically, and still occasionally, called 'celite');

Brownmillerite or ferrite or alumino-ferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ 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, ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ or C_4AF), 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 use of iron rich residue is widely used in the raw meal used in clinker production but normally limited to low concentrations, in Portland Cement clinker they give optimum liquid formation to achieve suitable clinkering conditions. The C_4AF is the least reactive clinker in Portland Cement but shows hydraulic activity when hydrated separately.

The aluminate phase content for most ordinary clinkers is 5—10 %. It is a tricalcium aluminate (composition — $3\text{CaO}\cdot\text{Al}_2\text{O}_3$), significantly changed in composition and sometimes also in structure due to the presence of foreign ions, particularly Si^{4+} , Fe^{3+} , Na^+ and K^+ . 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 %.

During clinker production, each manufacturer utilizes their own composition dictated by the pedalferric aluminium in the raw materials will use bauxite residue with an alumina content of about 10 % whilst those who have a deficiency in aluminium in their raw materials, would prefer a bauxite residue with an alumina content of 18 % or more.

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. Overview of the use of bauxite residue in cement

The chemical composition of Portland cement typically comprises about 2-6 % Al_2O_3 , 1-6 % Fe_2O_3 , 15-25 % SiO_2 , 55-75 % CaO , up to 5 % MgO , up to 1.5 % $\text{Na}_2\text{O} + \text{K}_2\text{O}$, 1.5-3.5 % SO_3 ; meanwhile Al_2O_3 , Fe_2O_3 , SiO_2 and CaO are all present in bauxite residue in varying proportions as discussed below so can provide useful additions at minimal cost.

3.1 Key beneficial characteristics of bauxite residue

A first step in considering the use of bauxite residue in cement 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 ₂ O ₃	5 - 60
Al ₂ O ₃	5 - 30
TiO ₂	0.3 -15
CaO	2 - 14
SiO ₂	3 - 50
Na ₂ O	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.

In addition there are various other minerals sometimes found at low levels including Brookite (an orthorhombic variant of TiO₂), ilmenite (FeTiO₃), Carnegieite (Si₄Al₄Na₄O₁₆), Dolomite (CaMg(CO₃)₂), Hydrogarnet (Ca₃Al₂(O₄H₄)₃), various Hydroxycancrinite/Cancrinite (Na₆Ca₂(Al₆Si₆O₂₄)(CO₃)₂·2H₂O), ((Na,Ca)₈(Al,Si)₁₂O₂₄(CO₃)·4H₂O), Cancrinite-NO₃ (Na_{7.92}Si₆Al₆O_{31.56}N_{1.74}), Cancrisilite-CO₃ (Na_{7.86}(AlSiO₄)₆(CO₃)(H₂O)_{3.3}), Katoite-Si (Ca₃Al₂(SiO₄)(OH)₈), Lawsonite (CaAl₂Si₂O₇(OH)₂·H₂O), Nepheline (Na₂KAl₄Si₄O₁₆), Nosean (Na₈Al₆Si₆O₂₄(SO₄)), Portlandite (Ca(OH)₂), Schaeferite ((Na_{0.7}Ca_{.2.3})(Mg_{1.85}Mn_{0.15})(VO₄)_{2.88}(PO₄)_{0.12}), sodium titanate (Na₂TiO₃) and zircon (ZrSiO₄). How all these phases change, or otherwise, at temperatures used to make cement clinker, up to 1,500 °C, is crucial.

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

Component	Typical range (wt%)
Sodalite ($3\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 0\text{-}2\text{H}_2\text{O}\cdot 2\text{NaX}$ where X could be CO_3^{2-} , Cl^- , OH^- , SO_4^{2-} , or $\text{Al}(\text{OH})_4^-$)	4- 40
Haematite (Fe_2O_3)	10 - 30
Al - goethite ($(\text{Fe}, \text{Al})_2\text{O}_3\cdot n\text{H}_2\text{O}$)	10 - 30
Magnetite (Fe_3O_4)	0- 8
Silica (SiO_2) crystalline and amorphous	3- 20
Calcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$)	2- 20
Boehmite (AlOOH)	0- 20
Titanium Dioxide (TiO_2) anatase and rutile	2- 15
Muscovite ($\text{K}_2\text{O}\cdot 3\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2\cdot 2\text{H}_2\text{O}$)	0- 15
Calcite (CaCO_3)	2- 20
Kaolinite ($\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$)	0- 5
Gibbsite ($\text{Al}(\text{OH})_3$)	0- 5
Perovskite (CaTiO_3)	0- 12
Cancrinite ($\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{CaCO}_3$)	0- 50
Diaspore (AlOOH)	0- 5

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 ($3\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 0\text{-}2\text{H}_2\text{O}\cdot 2\text{NaX}$ where X could be CO_3^{2-} , Cl^- , OH^- , SO_4^{2-} , or $\text{Al}(\text{OH})_4^-$) 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.

4. Industrial successes and experiences

Clinker producing plants in China, Ukraine, India, Russia, Georgia, Moldova, Cyprus and Greece and currently using bauxite residue as a raw material. It is judged that about 500,000 to 1,500,000 tonnes of bauxite residue is currently used annually in the production of clinker. Some specific experience is reviewed below.

The Mykolayiv alumina refinery in the Ukraine has supplied substantial quantities of bauxite residue to cement plants in the Ukraine, Russia, Georgia, Moldova and Belarus up to a distance of 1,200 km. At its maximum usage, this was approximately 250,000 t/y and was to 10 cement plants. The recent economic situation in region, however, meant that usage has fallen and supply is now only to six plants. After satisfactory completion of the necessary REACH certification, it was also planned to supply bauxite residue for cement production in Bulgaria, Poland and Romania. The Mykolayiv alumina refinery blends the residue produced to give the cement plant a consistent feed and although supply problems often occur during the winter months, in January and February because of freezing and in March, November and December because of high rainfall.

The composition of the bauxite residue historically shipped has typically been 15 % Al_2O_3 , 47 % Fe_2O_3 , 3.3 % Na_2O , and 12 % moisture with a range of 6 to 20 % Al_2O_3 , 34 to 55 % Fe_2O_3 , 0.5 to 7.5 % Na_2O , and 7 to 20 % moisture. The values in Table 3 shows the average levels for the first ten months of 2016.

Experience from the Mykolayiv refinery confirms that the bauxite residue they supply does not cause complications in clinker manufacturing process, it does not require additional equipment, the cake is free flowing and no caking or bridging occurs when it is fed in the pyritic slag chain. The increased content, up to 12-20 %, of aluminium oxide in the residue cake provides an increase in alite content in clinker by 1 – 2 %. This normalises the cement phase composition, which is especially important for cement factories utilising as an input product some agrillous raw material with reduced aluminium in its composition.

The alumina modulus in a range of factories grew from 1.1 to 1.2 – 1.3; at that ratio, the content of main clinker minerals – alite and belite – remains at the same level. This is confirmed by X-ray diffraction and mineral-petrographic studies, as well as cement physical and mechanical property testing. It has been established that when heating a raw mixture at the temperature modifying burning process in a rotating kiln, decarbonisation of calcium carbonate (CaCO_3) contained in the initial feed as lime compounds occurs at lower temperature than in a mixture with pyritic slag.

Clinker produced containing these levels of residue has good granulation, reduced fines and activity. Pedalferric cake is a burning mineraliser, its application is justified both energetically and technologically. [Pedalferric - A material in which there is no layer of accumulated calcium carbonate, but in which oxides of iron and aluminium have tended to accumulate (usually acidic and characteristic of humid climates).]

From the Mykolayiv experience, the requirements for their bauxite residue are:

- Iron oxide content greater than 51 %;
- Soda content less than 2 % (if higher, a problem occurs in both the cement and metallurgical industries);
- Silica content less than 3-4 %;
- Moisture less than 25 %;
- Low level of hexavalent chromium.

In the early 2000s, considerable work was undertaken at the University in Patras on using bauxite residue from AoG's alumina plant in Distomon, Greece in cement. Trials using some 3,500 tonnes were successfully carried out and Lafarge publicly announced plans in their 2003 annual environmental report to use some 300,000 tonnes of bauxite residue in their production plant in Milaki by 2004. A level of 180,000 t/y of bauxite residue was expected to be used, principally for the iron content of the bauxite residue, with a target Na_2O level of < 2.5 %. Funds from the EU supported much of the work programme. The project was subsequently put in abeyance, but it is hoped that it will be resurrected when the construction industry in Greece recovers. Historically Distomon disposed of its bauxite residue in the sea but this has stopped so the plant is under strong pressure to find uses for the bauxite residue. AoG use a press filter to achieve a reasonably low moisture content, approximately 26-30 %, which is more advantageous for cement production and minimises transport cost. After exposure to the sunlight for 20-30 days, the moisture level in the bauxite residue drops to 16-18%.

The TITAN cement plant in Patras, Greece which manufactures about 1.25 million t/y of clinker and 1.75 million t/y of cement reportedly made use of approximately 22,000 tonnes of bauxite residue

between 2012 to 2015. A key driver to the use of the bauxite residue is for the alumina content. The composition of the bauxite residue used will depend on the bauxite mix but the average for Distomon for 2015/2016 was 15.2 % Al_2O_3 , 42 % Fe_2O_3 , 6.9 % SiO_2 , 12.5 % CaO , 6.1 % TiO_2 , 2.8 % Na_2O .

Modest scale successful utilisation of bauxite residue in Portland cement clinker production was carried out in the mid-1980s in Jamaica at the Caribbean Cement Limited plant in Kingston in which several tens of thousands of tonnes of bauxite residue from the Aljam alumina plant at Ewarton, some 55 km away. Approximately 4 % of residue was added during clinker production with no technical problems noted. The residue was obtained from the recently introduced dry mud stacking approach adopted at Ewarton and the material stockpiled for a short period to allow it to further dry to a solids content of about 70 %. The operation use was discontinued because of transport issues and a drop in the solids content to 65 %.

Traditionally the alumina plants in the Northern part of China produced a residue very high in calcium and silicon oxides but low in iron oxide whilst those in the south of China have a residue high in iron which makes the recovery of iron the most likely option for them to pursue. A very strong driving force in China has been government imposed legislation requiring that a significant proportion of the bauxite residue is reused. Many years ago, in China some companies used red mud from the sintering process to produce Portland Cement. Due to the high content of $2\text{CaO}\cdot\text{SiO}_2$ in this residue, it is particularly suitable for producing cement. The addition of bauxite residue for producing cement was reported to have three main advantages: firstly, in that it can lower the consumption of other raw materials including limestone and iron powder; secondly, it also can improve the yield of kiln; and thirdly result in lower carbon dioxide emissions.

It should be noted that in China historically a significant proportion of the bauxite residue was generated from sinter or combined Bayer-sinter routes. This is very different in composition to bauxite residue from the traditional Bayer process in that over 50 % of the material is beta $2\text{CaO}\cdot\text{SiO}_2$. For example, a typical composition of the waste from Shandong alumina plant is 42 % CaO , 22 % SiO_2 , 9 % Al_2O_3 , 3.3 % TiO_2 , 1.7 % MgO , and 2.8 % Na_2O . This is a much better feedstock for cement production than conventional bauxite residue from the Bayer process. A cement plant was constructed adjacent to the Shandong alumina plant in 1965 and was expanded in 1985 to a production capacity of 1.1 million t/y. Recent new regulations, however, relating to sodium content has drastically affected the amount used. Additionally, the number of plants using the sinter or Bayer-sinter route is falling rapidly so the bauxite residue generated will change to a more conventional Bayer type product.

In India over 200,000 t/y of bauxite residue from the Belgaum (state of Karnataka) and Lanjigarh (state of Orissa) alumina plants are used in clinker production. All the major alumina producers there are actively working on cement related projects and there are expectations of much greater sales. Belgaum report that the cement producer pay for the transport cost as well as a modest purchase price.

In Jamaica, there was a proposal in 2011 to use some 116,000 t/y of bauxite residue from the Ewarton alumina refinery at a proposed new 150,000 million t/y plant at St Catherine in Jamaica. There was a delay in obtaining environmental approval for the plant and it has not progressed further since that date.

Tests were undertaken in Japan in 2003/2004 to use bauxite residue in cement; bauxite residue from Showa Denko's alumina plant in Yokohama were trialled in a 4,800 t/d cement plant. Some 700 tonnes of residue were used but the tests were plagued with handling problems. Mortars and concrete made using the bauxite residue met the required Japanese standards but the setting times were delayed and the work was not progressed further.

Table 3 shows some of the bauxite residues that have been successfully used in the production of Portland Cement clinker. The data for Mykolayiv relates to a period when they were using imported bauxite so it is not possible to draw any conclusions on the nature of the bauxite feed but it should be noted that for the characteristics of the residues from Distomon and Mykolayiv are quite similar, especially in iron level; as discussed, conditions in China are very different.

Table 3: Comparison of bauxite residues used successfully in cement production.

Component	Distomon [#]	Shandong	Mykolayiv *
	Bauxite residue (%)	Bauxite residue (%)	Bauxite residue (%)
Fe ₂ O ₃	42	Very low	58
Al ₂ O ₃	15.2	9	11
TiO ₂	6.1	3.3	4
CaO	12.5	42	8
SiO ₂	6.9	22	8
Na ₂ O	2.8	2.8	2.3
MgO		1.7	

*Data for Mykolayiv refinery is based on 2016 values.

[#]Data for Distomon refinery is an average for 2015/2016.

5. Laboratory investigations

There are many references in the literature to the use of bauxite residue but the most significant ones are referred to below.

Tsakiridis et al carried out studies at the National Technical University of Athens using bauxite residue from AoG to make Portland cement clinker. The composition of the bauxite residue was 40.8 % Fe₂O₃, 12.6 % CaO, 6.8 % SiO₂, 19.95 % Al₂O₃, 5.8 % TiO₂, 0.2 % MgO, and 2.7 % Na₂O. A composition containing limestone, schist, bauxite and sand was prepared and bauxite residue was added at a level of 3.5 % to one batch replacing some of each of the other ingredients. The

burnability, setting time, strength development, and expansion and water requirements were measured.

The clinkers were mixed and ground with a 5 % gypsum addition and tested. The addition of 3.5 % of bauxite residue did not affect the microstructures or the characteristic mineralogical phases and only slightly affected the setting time and water content for standard consistency. The strength of the mortars made with and without the bauxite residue addition were measured to EN 196-1 at 2, 7, 28 and 90 days. For the 28 and 90-day tests, the compressive strength was slightly higher for the material with the bauxite residue addition than that found for the control. The paper concludes that the addition of 1 % addition of bauxite residue did not affect the sintering process, the hydration process, the setting time, expansion and compressive strength.

Vangelatos working at the University of Patras collected much data on the topic and mixed bauxite residue from AoG in Distomon, Greece that had been dewatered using a filter press to give a moisture content of 28 to 32 % with limestone and sandstone and produced various clinkers by adding 1, 3 and 5 wt % bauxite residue. The results showed that OPC they made displayed good mechanical properties.

Burnability tests showed that less than 1 % free lime can be obtained in all cases for firing at 1,450 °C, except for the mixture with 1 % bauxite residue addition, which requires 1,550 °C. XRD analysis and optical microscopy examination showed that the bauxite residue addition did not affect the mineralogical phases of the clinkers. The characterisation of the Portland cements that were produced indicated that differences in surface area, water requirement and setting time are negligible. Compressive strength results after 28 days of curing varies from 55 to 63 MPa, which ranks the produced cements in CEM I 42.5N category. More specifically, the cements with bauxite residue addition due to their relatively high 2-day strengths (> 20 MPa) can be ranked in CEM I 52.5N category. Addition of bauxite residue increases the amount of water-soluble chromium proportionally to the amount of total chromium to the mixture; however, conversion of total chromium to hexavalent chromium remains practically constant, in the range of 32-35 %. The results indicated that bauxite residue can be used as raw material in the production of OPC up to 5 % according to the chemical composition of the other raw materials.

Work by Lourenco et al at Sao Carlos University, Brazil in conjunction with Alcoa, explored the use of bauxite residue from the Pocos de Caldas alumina plant in clinker production: this material had a composition of 25.4 % Fe₂O₃, 3 % CaO, 17.4 % SiO₂, 23.3 % Al₂O₃, 3.4 % TiO₂, 0.2 % MgO, 2.3 % K₂O, 6.3 % others and 11 % Na₂O. Two different formulations were prepared to provide the necessary clinker chemical formulation: 58 % 3CaO.SiO₂, 15 % 2CaO.SiO₂, 8 % 3CaO.Al₂O₃ and 8 % 4CaO.Al₂O₃.Fe₂O₃. The bauxite residue contents were 12.05 % and 6.45 %. The mixtures were ball milled and then heated to 1,450 °C, shock cooled and reground. Calcium sulfate hemi-hydrate 5% was added to regulate setting time etc. XRF studies were undertaken on the samples to define the phases formed. Uniaxial compression and apparent porosity measurements were then performed on samples made from the cement mixtures incorporating these clinkers.

This work demonstrated that an addition of up to 12.5 % bauxite residue could be added to the clinker giving a good mineralogical performance and good resistance to compression after seven days of curing. The work demonstrated the importance of the particle size of the cement, as well as the phases, on the mechanical resistance of the specimens. For a comparable composition, the finer cements were more reactive and had better mechanical properties. A gain of approximately 10 MPa was obtained by increasing the fineness of the cement make from the clinker. Clinkers made with higher quantities of bauxite residue were found to be more friable.

In India, many of the alumina plants are actively promoting the use of bauxite residue into clinker production. Approximately 100,000 t/y of bauxite residue from the Belgaum alumina is sent to a local cement plant; moisture content is an issue so this only happens in the dry season; the intention is to install a pressure filter in order to increase the amount. The Lanjigarh alumina plant sell about 100,000 t/y to a local cement plant. Muri have sold small quantities and Renukoot are engaged in discussions to resolve logistics issues. Utkal and Lanjigarh are both involved in trials to make geopolymer concretes using their bauxite residue.

6. Potential issues

When considering the widespread industrial implementation of using bauxite residue in cement it is important to consider the potential limitations to using more. It must be recognised that 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. Invariably the plant will be located adjacent to a limestone or chalk quarry so their costs will be very low. A key aspect will be the relative costs of other iron and alumina sources in the area. 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.

6.1 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 firing the clinker, 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 Mykolayiv using air drying.

6.2 Hazardous rating of bauxite residue in some jurisdictions

There have been many discussions, particularly in the EU, concerning the hazardous nature of bauxite residue because 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.

6.3 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, if the alkalinity is too high, it can cause pitting of aluminium which is a part of the UN transport code.

6.4 Alkalinity/high sodium

The high pH is a problem from both a health and safety aspect and potentially adverse effects in cement production. During clinker production, the high sodium may adversely affect the refractory lining or affect viscosity control. Meanwhile 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.

From the clinker chemistry point-of-view, reactions during sintering will destroy almost all existing mineral structures and form new clinker minerals. After that, sodium can be bound in different compounds, of which typically 50 % is soluble, hence the issue of limiting overall sodium content to avoid risk of alkali-aggregate reaction in presence of reactive (amorphous) aggregates. In more conventional cases, sodium (and potassium) come from clays or fuel ashes, but, whatever the original structure in which sodium is bound, it will end up in new compounds. The generally maximum acceptable admissible soda content in clinker is less than 3.0 %.

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 aluminates (C_3A) 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.

However, a large fraction of the alkalis is volatilised inside the cement kiln. Alkalis tend to decrease the temperature of melt formation, but in the absence of SO_3 , decrease the viscosity of the melt. Potassium compounds are more volatile than sodium ones. Alkali in clinker occurs in three forms, as alkali sulfates, alkali aluminates and alumino-ferrites, and in calcium silicates. Most commonly found

alkali sulfates are arcanite (K_2SO_4), Sodium potassium sulfate (aphthitalite $Na_2SO_4 \cdot 3K_2SO_4$) and calcium potassium sulfate (calcium langbeinite, $2Ca_2O_4 \cdot K_2SO_4$). To maintain a consistent, correct operation of the kiln, in practice a tight balance between alkalis and sulfates is carried out. If one stays close to the one on one molar ratio of alkali to sulfate in the raw meal, then most of the alkali will be present and volatilised as alkali sulfates, and the formation of free alkali is avoided (free alkalis give flash set). This is also called the Degree of Sulfatisation of the raw meal.

The compensation of high levels of alkalis by sulfate may then lead to the problem of clogging. The volatilised alkali sulfates and chlorides condense at cooler areas in the kiln and start forming clinker rings that obstruct the flow of the materials. Three regimes may be defined as a function of clinker meal chlorine and sulfate content. The higher the content of volatiles, the more often you need to clean and repair the refractory lining. The use of alternative fuels with high levels of sulfate and chlorine has pushed the development of by-pass systems that take away part of the volatilised sulfates and chlorides. These systems are now installed on most modernised clinker kilns.

6.5 Heavy metals

The presence of chromium has been raised as an issue in the use of bauxite residue in Greece and the Ukraine; this issue 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.

6.6 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. The cement process, specifically kiln conditions, can influence how much chromium (VI) will form. In the kiln, the oxidizing atmosphere will play the largest role, with more oxygen in the burning zone leading to increased chromium (VI) formation. Alkali concentration is also of importance, since chromium (VI) in clinker is primarily in the form of chromates. In the finish mill, thermodynamically favourable conditions for oxidation to chromium (VI) exists, including high air sweep, moisture from gypsum dehydration, cooling water injection, and grinding aids, along with the high pH of the cement. Several materials have been used to reduce the level of soluble chromium (VI) formation. The most widely used material is ferrous sulfate; other materials include stannous sulfate, manganese sulfate, and stannous chloride. Some of these materials have limitations such as limited stability, limited supply, and possible influence on cement performance. In all cases, some form of dosing and mixing equipment is required.

6.7 Radioactivity

Nearly all bauxites contain low levels of naturally occurring radioactive materials (termed NORMs). During the Bayer process, the relative proportion of these radioactive species, in particular ^{238}U and ^{232}Th , increases in the bauxite residue. The increase in the proportion of radionuclides present is variable but in general, approximately doubles. However, the concentration of these radionuclides remains low and the radioactivity level is correspondingly low.

A review of data covering over 15 sites published by Nuccetelli *et al* in 2015 indicates the following average values for the radioactivity levels in bauxite residue: ^{226}Ra 337 Bq/kg, ^{232}Th 480 Bq/kg and ^{40}K 205 Bq/kg.

A number of countries and organisations have proposed guidelines for the acceptable levels of the active dose allowable from construction products used in buildings. The EU has been foremost amongst these and has collected a substantial background of relevant information for building materials and waste products. Considerable effort is being undertaken in the EU on a new harmonised directive, EU-BSS (Basic Safety Standard), which would provide additional guidelines for the use of by-products such as bauxite residue. The EU Radiation Protection Guideline 112 utilises the Markkanen room model and recommends a maximum range of 0.3 – 1 mSv per year for building materials; the particular limit being determined by the expected exposure. At a dose rate of less than 0.3 mSv per year, there are no restrictions on use of the material.

Another, and more sophisticated, mathematical model to assess the potential indoor exposure arising from radionuclides found in building is the ISS (Istituto Superiore di Santia) room model. This model uses more factors than the Markkanen model in its analysis and calculations have been undertaken for various bauxite residue contents in bricks or tiles. At bauxite residue levels up to 5 %, the upper limit that might be used in Portland Cement clinker production, the model shows a dose of 0.02 mSv per year due to bauxite residues with an 'average' level of radionuclides and 0.055 mSv per year for the bauxite residue with the highest content of radionuclides assessed in the Nuccetelli *et al* study. These levels are much lower than any of the proposed maximum allowable levels for use of construction products and very low in comparison to exposure from other commonly undertaken activities. For example, the dose from a return transatlantic flight is 0.16 mSv and that from a CT chest scan is 6.6 mSv.

6.8 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.

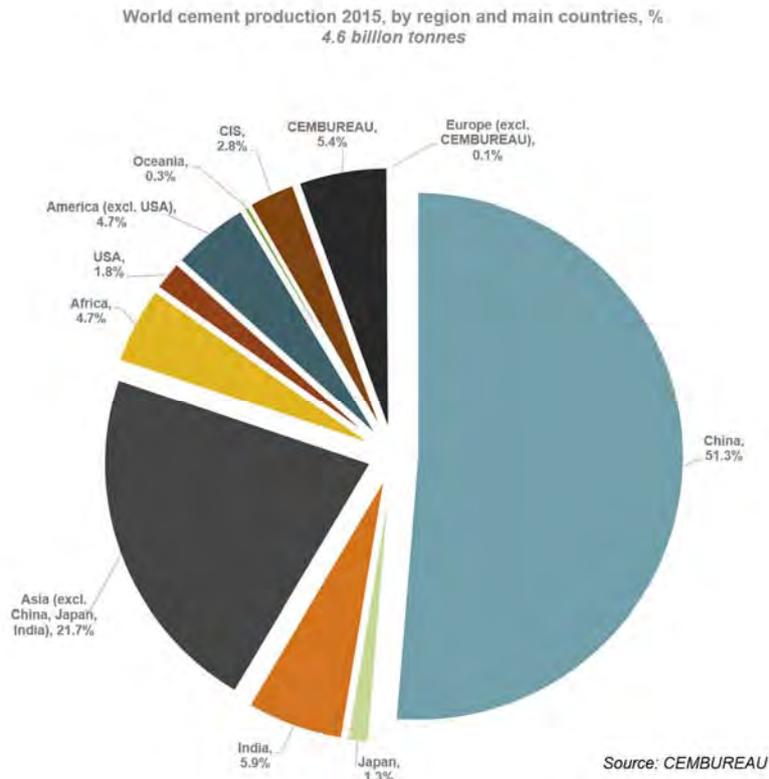
Table 4: Summary of limitations

Issue	Information	Comments
Moisture	Affects transport and energy costs	Press filtration to 25 to 28 % moisture content beneficial
Hazard ratings	pH below 12.5 should avoid Hazardous Material classification	Readily achievable
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	Chromium perceived as the major concern	
Chromium	Many sources Oxidised to chromium (VI) in the kiln can be reduced by various metal sulfates Sodium increases solubility of chromates	
Radioactivity	U and Th contents a perceived concern for domestic construction products.	

7. Growth opportunities

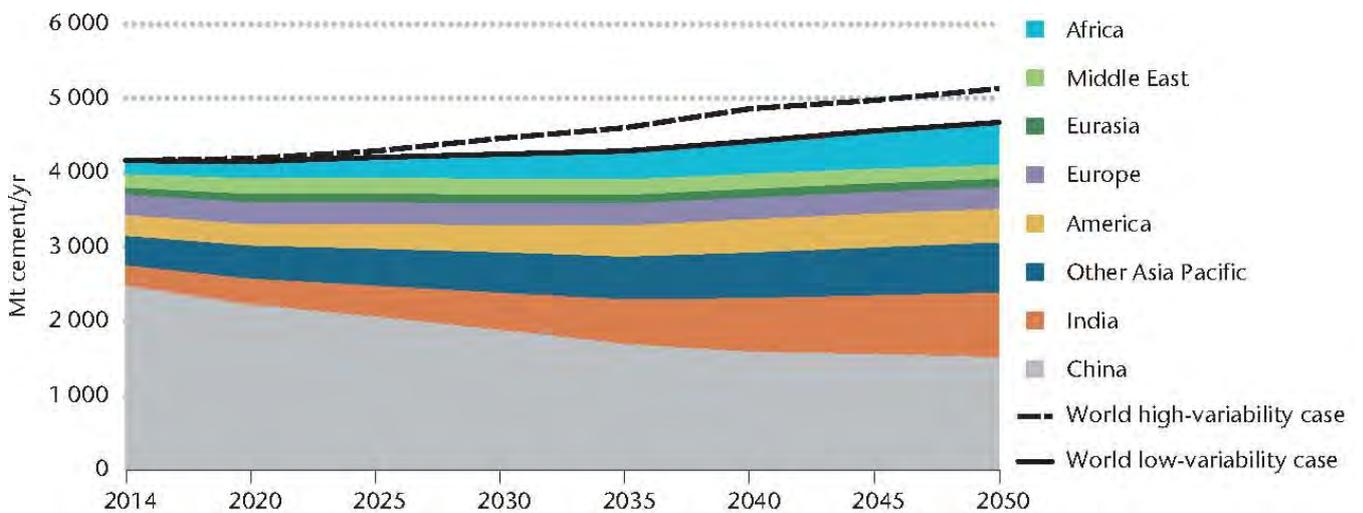
Data in Appendix 2 shows cement production in 2015 from various the US Geological Survey, CEMBUREA (the European Cement Association) and Statista. CEMBUREAU data indicates a 2015 production cement production level of 4,600 million tonnes per year of which China accounts for over half the production and 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



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 t, Oceania Production 7 million t, 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 an utilisation rate of 2.5 %, less than two hundred thousand tonnes of bauxite residue would be required.

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.

8. Summary

The prospects for using bauxite residue in Portland cement has been explored for over 80 years with many promising technical studies and several successful large scale commercial initiatives. The iron and aluminium compounds contained in the bauxite residue provide valuable additions in the production of Portland cement at a low cost.

The best estimates are that between 1,000,000 to 1,500,000 tonnes of bauxite residue are currently used annually in the production of Portland Cement clinker. The cement plants currently utilising the bauxite residue in clinker production are based in China, Ukraine, India, Russia, Georgia, Moldova, Cyprus and Greece.

From the evidence from the cement plants that are already using bauxite residue on an industrial scale, it is clear that bauxite residue can satisfactorily be used in cement clinker manufacture with

only slight changes to their operating process. With the appropriate bauxite residue, typically a usage rate of 3 to 5 % can be accommodated. From the industrial experience to date, key aspects seem to be:

- a relatively low moisture content - approximately 30 % moisture has been used in several plants and this can readily be achieved by bauxite residue producers, some alumina refineries have used a plate and frame filter press to produce a satisfactory product whilst others have achieved a satisfactory level by air drying the bauxite residue;
- a moderately low sodium content, a value of < 2.5 % Na₂O has been indicated as satisfactory but it will depend on the composition of the other raw materials;
- the appropriate aluminium oxide to iron oxide ratio (an iron oxide to alumina ratio of 0.8:1.2 in the raw mix was found to give the best results in one study although some plants will use the bauxite residue to supplement the iron level whilst others use it for the alumina content);
- and the reasonable proximity of a cement plant (a distance of up to 1200 km has been found to be acceptable in one case).

Table 6 summarises the main plants using bauxite residue and potential users.

Table 6: Cement plants using bauxite residue

Status	Bauxite residue source	Users	Quantity used (kt/y)
Actual Usage			
Now	Mykolayiv, Ukraine	Formerly 10 cement plants (now 6)	Up to 250
Now	Distomon, Greece	TITAN plant, Patras	22 between 2012 and 2015
Now	Shangdong, China	Integrated cement plant	?
Now	China – several plants	Local cement plants	?
Now	India	Cement	> 200
Potential Usage			
Potential	Distomon, Greece	Trial Lafarge 3,500 tonnes	300
Potential	India	Various	2500
Abandoned			
2011	Ewarton, Jamaica	St Catherine cement plant	100
2003/2004	Showa Denko, Japan	Trial 700 tonnes	
1986/1987	Ewarton, Jamaica	Caribbean Cement Limited, Kingston	40 to 50

There is believed to be scope for many more clinker producers to use bauxite residue leading to improvements in the environmental footprints of both the aluminium and cement industries.

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) = $\text{C}_2(\text{AF})$.

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 $1,500\text{ }^\circ\text{C}$ 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)

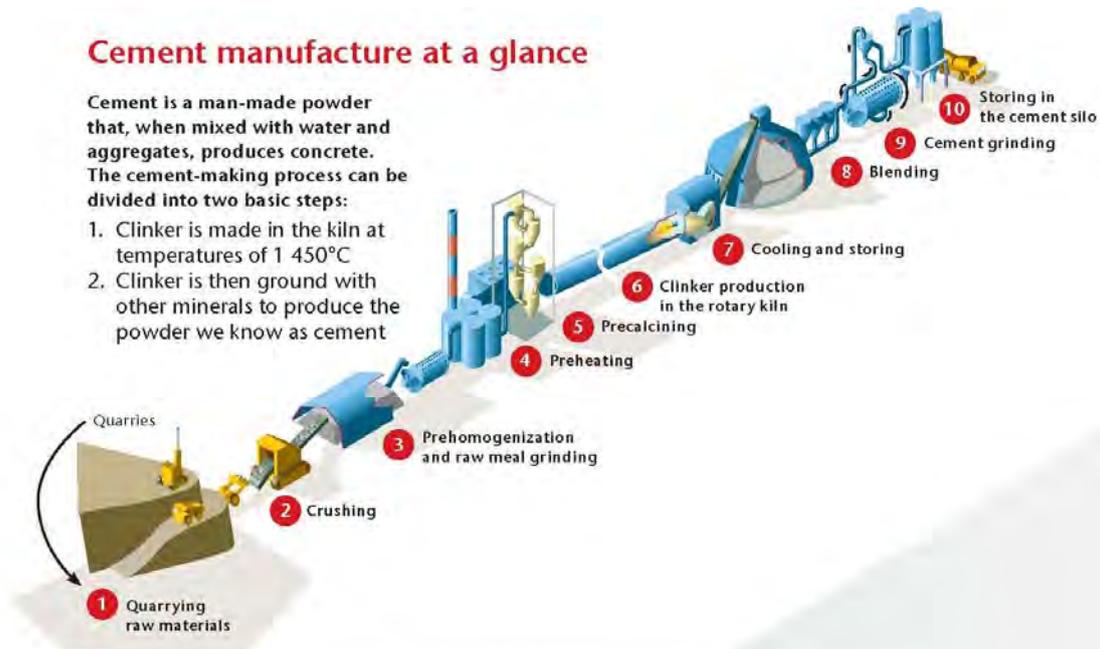
nomenclature respectively, contains up to 95 % ground granulated blast furnace slag, with the rest Portland clinker and a little gypsum. All compositions produce high ultimate strength, but as slag content is increased, early strength is reduced, while sulfate resistance increases and heat evolution 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.

Cement manufacture at a glance

Cement is a man-made powder that, when mixed with water and aggregates, produces concrete. The cement-making process can be divided into two basic steps:

1. Clinker is made in the kiln at temperatures of 1 450°C
2. Clinker is then ground with other minerals to produce the powder we know as cement



1. Quarrying raw materials

Naturally occurring calcareous deposits such as limestone, marl or chalk provide calcium carbonate (CaCO_3) and are extracted from quarries, often located close to the cement plant. Very small amounts of "corrective" materials such as iron ore, bauxite, shale, clay or sand may be needed to provide extra iron oxide (Fe_2O_3), alumina (Al_2O_3) and silica (SiO_2) to adapt the chemical composition of the raw mix to the process and product requirements.

2. Crushing

The raw material is quarried and transported to the primary/secondary crushers and broken into 10cm large pieces.

3. Prehomogenization and raw meal grinding

Prehomogenization takes place in which different raw materials are mixed to maintain the required chemical composition, and the crushed pieces are then milled together to produce "raw meal". To ensure high cement quality, the chemistry of the raw materials and raw meal is very carefully monitored and controlled.

4. Preheating

A preheater is a series of vertical cyclones through which the raw meal is passed, coming into contact with

swirling hot kiln exhaust gases moving in the opposite direction. In these cyclones, thermal energy is recovered from the hot flue gases, and the raw meal is preheated before it enters the kiln, so the necessary chemical reactions occur faster and more efficiently. Depending on the raw material moisture content, a kiln may have up to six stages of cyclones with increasing heat recovery with each extra stage.

5. Precalcining

Calcination is the decomposition of limestone to lime. Part of the reaction takes place in the "precalciner", a combustion chamber at the bottom of the preheater above the kiln, and part in the kiln. Here, the chemical decomposition of limestone typically emits 60-65% of total emissions. Fuel combustion generates the rest, 65% of which occur in the precalciner.

6. Clinker production in the rotary kiln

The precalcined meal then enters the kiln. Fuel is fired directly into the kiln to reach temperatures of up to 1,450°C. As the kiln rotates, about 3-5 times per minute, the material slides and tumbles down through progressively hotter zones towards the flame. The intense heat causes chemical and physical reactions that partially melt the meal into clinker.

7. Cooling and storing

From the kiln, the hot clinker falls onto a grate cooler where it is cooled by incoming combustion air, thereby minimising energy loss from the system. A

typical cement plant will have clinker storage between clinker production and grinding. Clinker is commonly traded.

8. Blending

Clinker is mixed with other mineral components. All cement types contain around 4-5% gypsum to control the setting time of the product. If significant amounts of slag, fly ash, limestone or other materials are used to replace clinker, the product is called "blended cement".

9. Cement grinding

The cooled clinker and gypsum mixture is ground into a grey powder, Ordinary Portland Cement (OPC), or ground with other mineral components to make blended cement. Traditionally, ball mills have been used for grinding, although more efficient technologies - roller presses and vertical mills - are used in many modern plants today.

10. Storing in the cement silo

The final product is homogenised and stored in cement silos and dispatched from there to either a packing station (for bagged cement) or to a silo truck.

Note: There are older, much less efficient technologies, for example the wet kiln into which the raw material is fed as slurry and not as a powder (dry kiln).

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 ($\text{CaO}\cdot\text{Al}_2\text{O}_3$ or CA in Cement chemist notation, CCN) and mayenite $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, 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 ($\text{Ca}_4(\text{AlO}_2)_6\text{SO}_4$ or $\text{C}_4\text{A}_3\text{S}$ 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 $1,500\text{ }^\circ\text{C}$ 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 $1,200\text{ }^\circ\text{C}$, 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 ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	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%; SiO₂=21.5%; Al₂O₃=5.2% and Fe₂O₃=2.8%

The Bogue calculation is therefore:

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

$$C_2S = 8.6024SiO_2 + 1.1Fe_2O_3 + 5.0683Al_2O_3 - 3.0710CaO$$

$$C_3A = 2.6504Al_2O_3 - 1.6920Fe_2O_3$$

$$C_4AF = 3.0432Fe_2O_3$$

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 7.

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, 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 1773 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.

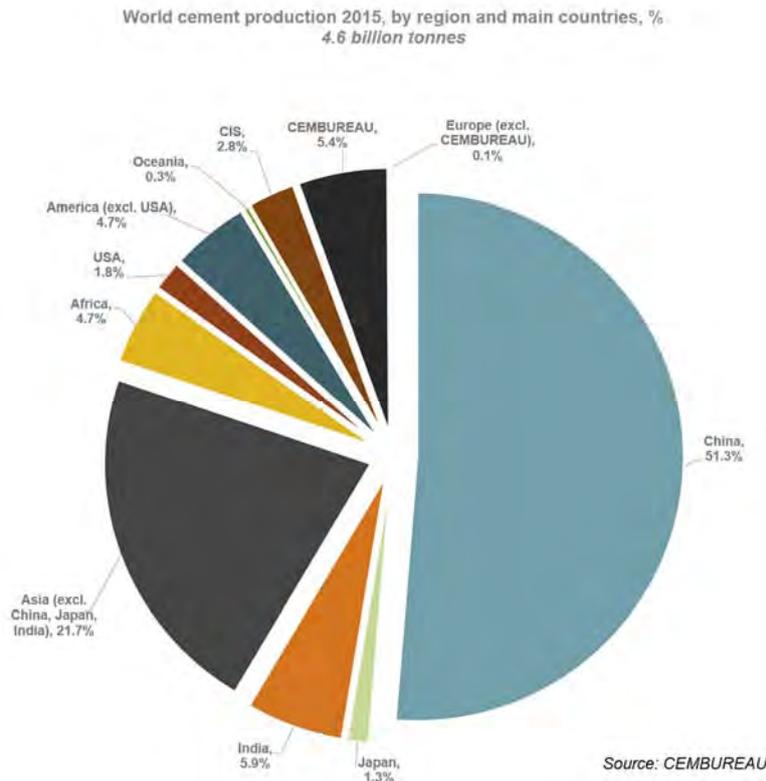


Figure 1: Worldwide cement production 2015

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.

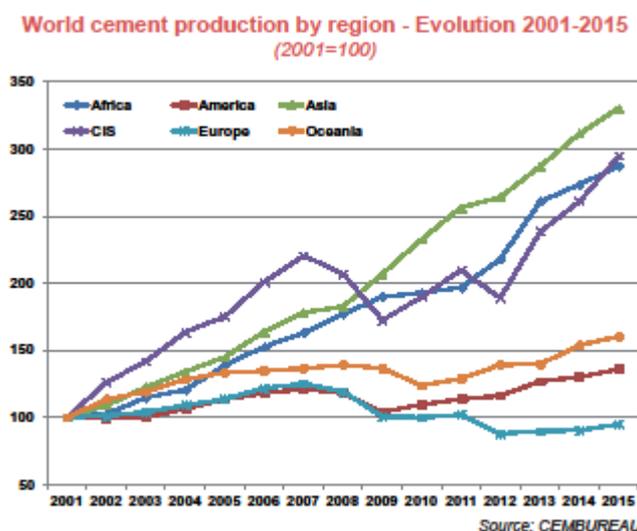


Figure 4: Cement production by region 2001 - 2015

Statista

Data from Statista:

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

Indicates global production of cement in 2014 at 4100 million tonnes and forecasts a value of 4400 million tonnes by 2020.

Table 7: 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 LafargeHolcim.

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 K	Blastfurnace slag S	Silica fume D ²⁾	Pozzolana		Fly ash		Burnt shale T	Limestone*			
natural P	calcined Q	siliceous V				calcareous W	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?hkey=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.aspx>

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.

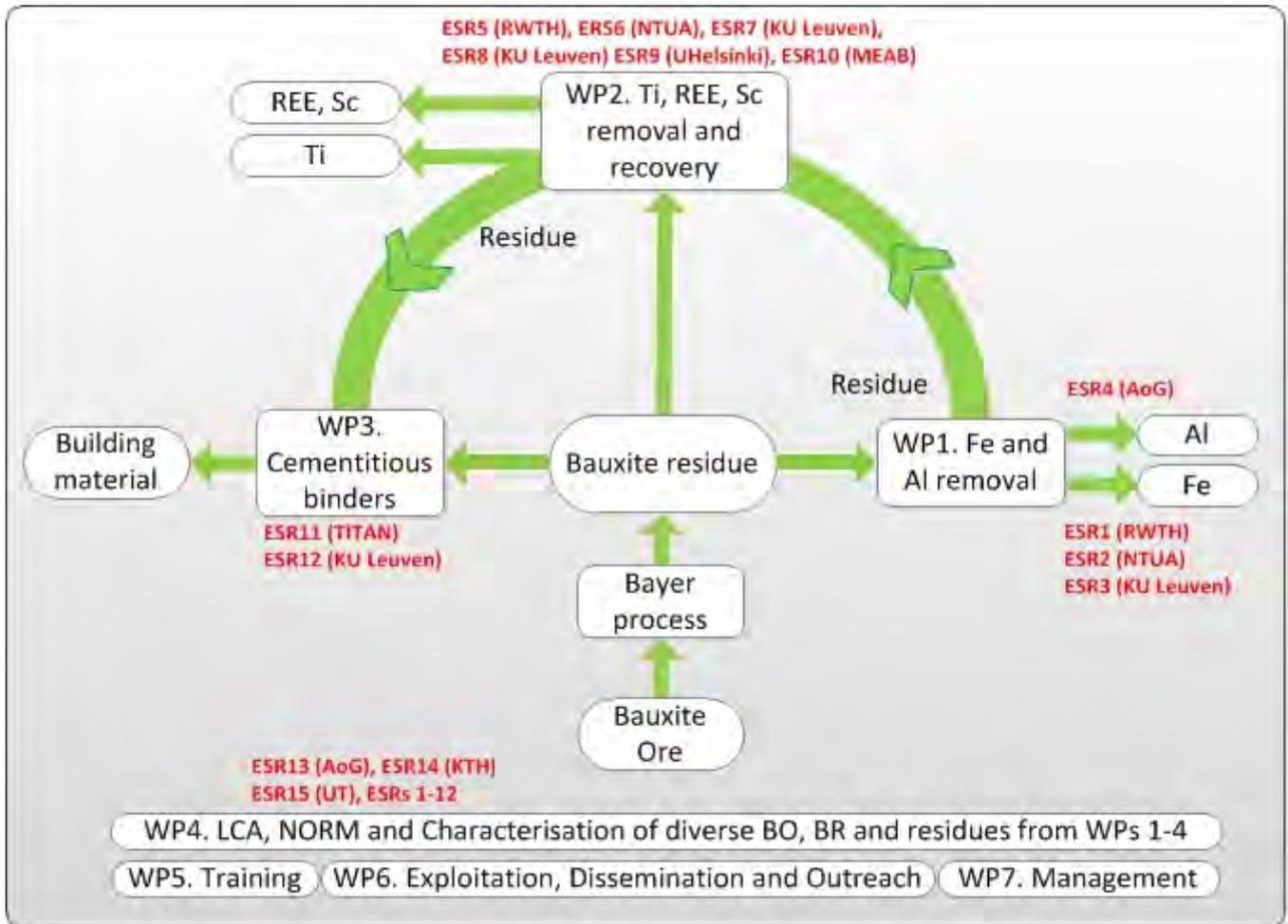
Key data

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, Sherbrooke 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 $\alpha\text{-L-C}_2\text{S}$. 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 CO₂ 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 CO₂ than OPC; see www.geopolymer.org.

Gross CO₂ emissions: all direct CO₂ emissions (excluding on-site electricity production) excluding CO₂ emissions from biomass which are considered climate neutral.

Net CO₂ emissions: gross CO₂ 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