Opportunities for use of bauxite residue in special cements
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International Aluminium Institute: www.world-aluminium.org

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

The global objectives of the Institute are:

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

¹ To deliver beneficial services to society through the use of aluminium products, while bringing a net reduction in greenhouse gas emissions across their full lifecycle.
² To deliver aluminium products that meet the needs of society and improve individuals’ quality of life while minimizing environmental impact and optimizing sustainable end of life strategies, including recycling and other material and energy recovery and reutilization measures.

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

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

The review has highlighted that the prospects of large scale utilisation of bauxite residue in cement are very promising. Firstly, because the iron and aluminium components of the bauxite residue are valuable additions in the production of both Portland Cement and ‘special’ cement clinkers; and secondly it has been shown at a laboratory scale by several research groups that bauxite residue may successfully replace clinker in blended cements at dosages between 10 and 20 wt%. If used as produced, this would have a significant impact on the cement industry CO₂ emissions as the clinker production is responsible for 85 % of the total emissions in an integrated cement plant.

Calcium sulfoaluminate cements require both a higher Fe₂O₃ and Al₂O₃ content in the raw meal which could be partially satisfied by using bauxite residue. Despite some promising studies on using bauxite residue in special cements such as calcium sulfoaluminate cements, there does not appear to be any industrial usage. These belite cements generate less carbon dioxide than Portland Cement so offer environmentally attractive options. Iron rich, special setting cements with improved strength when compared to Portland Cement have been made with levels of up to 40 % bauxite residue.
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1. Background
The International Aluminium Institute is an industry body representing all the major producers of aluminium, alumina and bauxite and has a key target of maximising the sustainable mining and production of all elements within the production chain. Bauxite residue (sometimes called red mud) is an inevitable secondary product that is generated in the extraction of alumina (aluminium oxide) from bauxite by the Bayer process. Virtually all aluminium metal is made by the electrolytic smelting of alumina and over 95% of alumina is manufactured by the Bayer process. There is no economic alternative route existing or likely to emerge within the next 50 years so the generation of bauxite residue will continue at a high level for many decades. Production of bauxite residue in 2017 is estimated to be over 160 million tonnes per year. The International Aluminium Institute is keen to encourage the cement industry to investigate, and wherever possible exploit, all the possible approaches to use bauxite residue in clinker production or the manufacture of supplementary cementious materials.

This paper serves to give some guidance to cement companies, universities and research institutes on some of the relevant background to encourage them to do further work in the use of bauxite residue in calcium sulfoaluminate and related special cements.

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
Opportunities for use of bauxite residue in special cements

Temperatures above 825 °C for about 10 hours at atmospheric pressure:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

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

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \]

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

\[ \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \]

This reaction takes a significant amount of time because the partial pressure of carbon dioxide in the air is low. The carbonation reaction requires the dry cement to be exposed to air, for this reason the slaked lime is a non-hydraulic cement and cannot be used under water.

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

- Belite (2CaO·SiO₂ or dicalcium silicate or C₂S);
- Alite (3CaO·SiO₂ or C₃S or tricalcium silicate);
- Tricalcium aluminate (3CaO·Al₂O₃ or C₃A) (historically, and still occasionally, called 'celite');
- Brownmillerite or ferrite or alumino-ferrite (4CaO·Al₂O₃·Fe₂O₃ or C₄AF).

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 Ca₂SiO₄ 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: Ca₃SiO₅, the composition and structure of which are modified through location in the foreign ions lattice, particularly Mg²⁺, Al³⁺ and Fe³⁺. Alite reacts with water relatively quickly also in ordinary cements. Of all phases, alite plays the most important role in hardness
development. This phase contribution is especially important in establishing the 28-day hardness.

The ferritic phase of an ordinary cement clinker is 5—15 %. It is a tetracalcium alumino-ferrite, (4CaO·Al₂O₃·Fe₂O₃ or C₄AF), the composition of which changes drastically with changing Al/Fe ratio and location in the structure of foreign ions. The rate at which the ferritic phase reacts with water can vary due to differences in the composition or other characteristics, but, as a rule, it is initially high and is intermediate between speeds for alite and belite at later stages. The 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 C₄AF 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 — 3CaO·Al₂O₃), significantly changed in composition and sometimes also in structure due to the presence of foreign ions, particularly Si⁴⁺, Fe³⁺, 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.

**Calcium sulfoaluminate cements**

Typically, calcium sulfoaluminate cements (CSA) are made from 75-85 % calcium sulfoaluminate clinker made from calcite, clay and anhydrite and have ye'elimite (Ca₆(AlO₂)₃SO₄ or Ca₃Al₂S in CCN) as a primary phase with belite, ferrite, calcium aluminate, perovskite, gehlenite and calcium sulfo silicate as the minor phases. This clinker is mixed with 15-25 % calcium sulfate. 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 CO₂ emission around half that associated with Portland clinker. However, SO₂ emissions are usually significantly higher.

**Special cement: Alite-calcium sulfoaluminate cement**

Alite-calcium sulfoaluminate cement comprises 90-95 % Portland cement clinker, 3-5 % ye'elimite and 2-5 % additional calcium/alkali sulfates. Alite forms at approximately 1,450 °C whilst ye'elimite decomposes at < 1,350 °C so it is necessary to either use a two stage firing process (30 min at 1,450 °C and 1 hour at 1,250 °C) or stabilise the alite and ye'elimite using mineralisers such as CaF₂, MgO, BaO or SrO.

The clinkering process involves the reaction of tricalcium aluminate and calcium sulfate to form ye'elimite.
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.

Appendix 9 defines some terms commonly used in the cement industry.

3. Overview of the use of bauxite residue in cement

Bauxite residue may be used in cement production in several ways including as a raw material in the production of Portland cement clinker, as pozzolanic material which is used in mortar or concrete mix or in certain types of ‘special’ cement.

The chemical composition of calcium sulfoaluminate - belite cement typically comprises about 8-30 % Al₂O₃, up to 10 % Fe₂O₃, 5-25 % SiO₂, 40-70 % CaO, up to 5 % MgO, up to 3 % Na₂O + K₂O, 8-22 % SO₃; meanwhile Al₂O₃, Fe₂O₃, SiO₂ and CaO are all are present in bauxite residue in varying proportions as discussed below so can provide useful additions at minimal cost.

3.1 Key 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical range (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>5 - 60</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5 - 30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.3 - 15</td>
</tr>
<tr>
<td>CaO</td>
<td>2 - 14</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3 - 50</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1 - 10</td>
</tr>
</tbody>
</table>

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

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

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical range (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodalite (3Na₂O·Al₂O₃·2SiO₂·O·2H₂O·2NaX where X could be CO₃²⁻, Cl⁻, OH⁻, SO₄²⁻, or Al(OH)₄⁻)</td>
<td>4 - 40</td>
</tr>
<tr>
<td>Haematite (Fe₂O₃)</td>
<td>10 - 30</td>
</tr>
<tr>
<td>Al - goethite ((Fe, Al)₂O₃·nH₂O)</td>
<td>10 - 30</td>
</tr>
<tr>
<td>Magnetite (Fe₃O₄)</td>
<td>0 - 8</td>
</tr>
<tr>
<td>Silica (SiO₂) crystalline and amorphous</td>
<td>3 - 20</td>
</tr>
<tr>
<td>Calcium aluminate (3CaO·Al₂O₃·6H₂O)</td>
<td>2 - 20</td>
</tr>
<tr>
<td>Boehmite (AlOOH)</td>
<td>0 - 20</td>
</tr>
<tr>
<td>Titanium Dioxide (TiO₂) anatase and rutile</td>
<td>2 - 15</td>
</tr>
<tr>
<td>Muscovite (K₂O·3Al₂O₃·6SiO₂·2H₂O)</td>
<td>0 - 15</td>
</tr>
<tr>
<td>Calcite (CaCO₃)</td>
<td>2 - 20</td>
</tr>
<tr>
<td>Kaolinite (Al₂O₃·2SiO₂·2H₂O)</td>
<td>0 - 5</td>
</tr>
<tr>
<td>Gibbsite (Al(OH)₃)</td>
<td>0 - 5</td>
</tr>
<tr>
<td>Perovskite (CaTiO₃)</td>
<td>0 - 12</td>
</tr>
<tr>
<td>Cancrinite (Na₆[Al₆Si₆O₂₄]·2CaCO₃)</td>
<td>0 - 50</td>
</tr>
<tr>
<td>Diaspore (AlOOH)</td>
<td>0 - 5</td>
</tr>
</tbody>
</table>
In addition there are various other minerals sometimes found at low levels including Brookite (an orthorhombic variant of TiO₂), ilmenite (FeTiO₃), Carnegieite (Si₆Al₄Na₄O₁₆), Dolomite (CaMg(CO₃)₂), Hydrogarnet (Ca₃Al₂(O₂H₂)₃), various Hydroxycancrinite/Cancrinite (Na₈Ca₆[Al₄Si₄O₂₄](CO₃)₂·2H₂O), ((Na,Ca)₉(Si₆Al₅)₂₆(CO₃)₄·4H₂O), Cancrinite-NO₃ (Na₇Al₄Si₆O₃₅·5H₂O·1.74), Cancrisilite-CO₃ (Na₇·86(Al₃SiO₄)₆(CO₃)(H₂O)₂·3.3), Katoite-Si (Ca₃Al₂(SiO₄)(OH)₂), Lawsonite (CaAl₂Si₂O₇(OH)·H₂O), Nepheline (Na₂KAl₃Si₃O₁₆), Nosean (Na₈Al₆Si₄O₂₄·SO₄), Portlandite (Ca(OH)₂), Schaeferite (Na₈Ca₆.3(Mg₁.85Mn₀.15)(VO₄)₂·86(PO₄)₀·12₈), 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.

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 (3Na₂O·Al₂O₃·2SiO₂·2H₂O·2NaX where X could be CO₃²⁻, Cl⁻, OH⁻, SO₄²⁻, or Al(OH)₄⁻) arises from the reaction between sodium aluminate and soluble sodium silicates.

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

The feed bauxite used will have a major impact on the particle size distribution of the residue; the coarse fraction (greater than 100 μm) which is generally high in quartz is separated at some alumina refineries from the finer silty muds (typically 80 % less than 10 μm with a substantial fraction less
than 1 μm). The coarse fraction is much easier to wash, has much better draining behaviour so has a lower residual caustic content.

4. Industrial production of calcium sulfoaluminate special cements
Calcium sulfoaluminate cements have been produced in China since the 1970s and it is estimated that annual production in China is approximately two to three million tonnes per year. They are produced from limestone, bauxite and calcium sulfate; after grinding the raw materials to homogenise them, they constituents are heated to 1,250-1,300 °C and ground to the required size.

They require lower energy to produce than Portland Cement clinker, produce less carbon dioxide emissions but generate more sulfur dioxide emissions. Despite their good hydraulic activity, good sulfate resistance, fast strength development (compressive strength of the order of 40 MPa after 24 hours, the high cost of bauxite has been an impediment to their growth. The utilisation of bauxite residue presents an opportunity for reducing the cost of production significantly.

5. Laboratory investigations of Sulfoaluminate and other special cements
Special cements such as calcium sulfoaluminate have been of interest to researchers for over 50 years has considerable efforts have been made to fine lower cost raw materials.

Alcoa funded a work programme at the University of Aveiro, Portugal looking at the use of bauxite residue in the production of sulfoaluminate clinkers. Bauxite residue from San Ciprian with a composition of 18.76 % Al₂O₃, 51.8 % Fe₂O₃, 5.54 % SiO₂, 11.18 % TiO₂, 3.27 % CaO, and 6.84 % Na₂O was used in the trials at a level of 9.3 %. The particle size ranged from 0.1 to 7 μm (median 0.78 μm) and the surface area was 20 m²/g. The clinkers were then mixed with 5% calcium sulfate to produce a cement. Mortars were then prepared and tested. In general, the results were poor with some samples showing poor workability and others gave low 7-day compressive strength values.

A project at the University of Sao Carlos in Sao Paulo, Brazil looked at the incorporation of bauxite residue from Pocos de Caldas in the production of sulfo belite clinkers; the bauxite residue used was filtered and ground and had a composition of 24 % Al₂O₃, 25 % Fe₂O₃, 21 % SiO₂, 3 % CaO, and 15 % other. XRD showed that satisfactory sulfoaluminate clinkers could be produced with 10 % additions of bauxite residue. Clinkers with levels of 13.1 % and 15.4 % bauxite residue were made which when incorporated into formulations containing 17.7 % and 21.4 % of gypsum gave mechanical resistances comparable to OPC cements after 7 and 28-day curing times. These formulations would have lower environmental impact and lower processing costs.

Other studies in India and Europe have reported more favourable results. Considerable in house but unpublished work has been undertaken in Europe by cement companies using bauxite residue in sulfoaluminate cements looking to replace the bauxite with bauxite. Despite the success in some of these projects on a small scale, and the potential benefit in terms of reduced generation of carbon
dioxide, these approaches have not yet been adopted. Despite the energy savings and reduction of carbon dioxide emissions, one reason for the lack of implementation has been the cost involved in the cement plant changing its manufacturing route.

Work on producing ‘special cements’ from bauxite residue has been undertaken by Singh et al at Banaras Hindu University and The Tata Research Development and Design Centre. Bauxite residue from Hindalco’s Renukoot plant was used in conjunction with lime, gypsum, and bauxite. A firing temperature of 1,300 °C was used and particularly high 28-day compressive strengths were obtained. An iron oxide to alumina ratio of 0.8:1.2 in the raw mix was found to give the best results. For a lime, bauxite residue and bauxite mix the strength development was due to the formation of brownmillerite (4CaO·Al₂O₃·Fe₂O₃), tricalcium aluminate (3CaO·Al₂O₃) and (12CaO·7Al₂O₃). Meanwhile for a lime, bauxite residue, gypsum and bauxite mix the strength development was due to the formation of brownmillerite (4CaO·Al₂O₃·Fe₂O₃), tricalcium aluminate (3CaO·Al₂O₃) and calcium sulfoaluminate (Ca₄(AlO₂)₆SO₄), ye’elimite in its naturally occurring form.

Studies in China reported by Lucio Grow have demonstrated success on a 1,500 t/d rotary kiln in making sulfoaluminate cement using bauxite residue from Chalco Shandong. The Shandong province has found the material made to comply with National standard GB20472-2006 and that the cement can reach the technical specification for 42.5 grade sulfoaluminate cement. The material has also been tested to National standard GB6566-2010 (limitation for radioactivity for construction materials) and the results show that the natural radiation from Ra²²⁶, Th²³² and K⁴⁰ are in compliance with the standard and there are no restrictions in any application area. Various other wastes such as fly ash, coal gangue, carbide slag, gypsum from desulphurisation and aluminium ‘ash’ have also be included in the trials.

Additions of 5% of the sulfoaluminate clinker to Portland Cement clinker gave a very substantial improvement in one day compressive and bending strengths. The 28-day compressive strength was also 29 % higher and the 28-day bending strength 24 % better. The sulfoaluminate clinker made using bauxite residue was reportedly cheaper to produce than the Portland clinker. High quality bricks were also made using the sulfoaluminate cement as binding material together with 35% addition of bauxite residue.

Bauxite residue from Renukoot with a composition of 18.2 % Al₂O₃, 33.1 % Fe₂O₃, 8.8 % SiO₂, 19.6 % TiO₂, 3.27 % CaO, and 5.8 % Na₂O was used in the trials at levels of between 25 to 40 %. Despite these promising results, no larger scale trial have yet been undertaken.

Several studies have shown that haematite rich (alpha-Fe₂O₃) bauxite residue can provide improvements in the manufacture of sulfate resistant cements. The addition of 2 – 10 % of bauxite residue reduces the temperature of the melt formation by 200 °C.

Iron can partially substitute for aluminium in ye’elimite which is the main component of calcium sulfoaluminate cements. Depending on the amount of substitution, this can change the reaction
mechanisms and reactivity. Using iron rich materials such as bauxite residue can contribute to reduced carbon dioxide emissions.

**Developments in low ye’elimite calcium aluminate clinkers**

Two recent approaches to make low ye’elimite (30 %) calcium aluminate clinkers with higher belite and ferrite contents, these will have lower strength developments.

HolcimLafarge have patented an approach involving doping C2S with boron to obtain a more reactive alpha- C2S rather than beta-C2S.

Heidelberg Cement have patented a method relating to the formation and activation of ternesite (Ca₅Si₂O₈(SO₄) clinker phase.

As clinkering is at a lower temperature (1,250 °C) and less calcium carbonate is used in the raw materials, their carbon dioxide emissions are reduced by 20 %. In addition, as less bauxite is needed in the manufacture, their cost is reduced.

**6 Summary**

Despite special cements such as calcium sulfoaluminate and belite have been used to a limited extent for several decades, their usage has been limited, partly because of the relatively high cost of bauxite. A particular attraction of these types of cements are the lower kiln temperatures that are required to make the clinker compared to Portland Cement clinker resulting in much reduced carbon dioxide emissions. Calcium sulfoaluminate cements require both a higher Fe₂O₃ and Al₂O₃ content in the raw meal which could be partially satisfied by using bauxite residue. The use of bauxite residue offers a lower cost approach and some promising studies on using bauxite residue in special cements such as calcium sulfoaluminate cements, there does not appear to be any industrial usage of bauxite residue. These belite cements generate less carbon dioxide than Portland Cement so offer environmentally attractive options. Iron rich, special setting cements with improved strength when compared to Portland cement have been made with levels of up to 40 % bauxite residue.
Appendix 1 – Background to types of cement and Bouge calculation

Nomenclature

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

\[ A = \text{Al}_2\text{O}_3, \quad F = \text{Fe}_2\text{O}_3, \quad S = \text{SiO}_2, \quad C = \text{CaO}, \quad H = \text{H}_2\text{O}. \]

So alite (tri-calcium silicate) = C\text{}_3\text{S}, belite (di-calcium silicate) = C\text{}_2\text{S}, calcium aluminate = C\text{}_3\text{A}, ferrite (calcium aluminate ferrite) = C\text{}_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 °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.
Opportunities for use of bauxite residue in special cements

Figure 3: Schematic representation of cement manufacturing process.
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 $\text{CaAl}_2\text{O}_4$ ($\text{CaO}-\text{Al}_2\text{O}_3$ or CA in Cement chemist notation, CCN) and mayenite $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (12 $\text{CaO}$-$7\text{Al}_2\text{O}_3$, or $\text{C}_2\text{A}_7$ 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 ($\text{Ca}_2(\text{AlO}_2)_3\text{SO}_4$ or $\text{C}_9\text{A}_3\text{S}$ 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 $\text{CO}_2$ emission around half that associated with Portland clinker. However, $\text{SO}_2$ 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 ($\text{Ca}_3\text{SiO}_5$), a mineral in concrete that cures within hours of pouring and is therefore responsible for much of its initial strength. However, alite also must be heated to 1,500 °C in the clinker-forming process. Some research suggests that alite can be replaced by a different mineral, such as belite ($\text{Ca}_2\text{SiO}_4$). Belite is also a mineral already used in concrete. It has a roasting temperature of 1,200 °C, which is significantly lower than that of alite. Furthermore, belite is stronger once concrete cures. However, belite takes on the order of days or months to set completely, which leaves concrete weak for an unacceptably long period of time. Current research is focusing on finding possible impurity additives, like magnesium, that might speed up the curing process. It is also worthwhile to consider that belite takes more energy to grind, which may make its full life impact similar to or even higher than alite.

Another approach has been the partial replacement of conventional clinker with such alternatives as
fly ash, bottom ash, and slag, all of which are by-products of other industries that would otherwise end up in landfills.

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

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

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

- **Alite**: C₃S, or tricalcium silicate
- **Belite**: C₂S, or dicalcium silicate
- **Aluminate phase**: C₃A, or tricalcium aluminate
- **Ferrite phase**: C₄AF, 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**

<table>
<thead>
<tr>
<th>Clinker analysis (wt%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>Fe₂O₃</td>
<td>CaO</td>
<td>MgO</td>
<td>K₂O</td>
<td>Na₂O</td>
<td>SO₃</td>
<td>LOI</td>
</tr>
<tr>
<td>21.5</td>
<td>5.2</td>
<td>2.8</td>
<td>66.6</td>
<td>1.0</td>
<td>0.6</td>
<td>0.2</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Free lime = 1.0 % CaO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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:

\[ C_3S = 4.0710CaO - 7.6024SiO₂ - 1.4297Fe₂O₃ - 6.7187Al₂O₃ \]

\[ C_2S = 8.6024SiO₂ + 1.0785Fe₂O₃ + 5.0683Al₂O₃ - 3.0710CaO \]

\[ C₃A = 2.6504Al₂O₃ - 1.6920Fe₂O₃ \]

\[ C₄AF = 3.0432Fe₂O₃ \]

Therefore:

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

\[ C2S = (8.6024 \times 21.5) + (1.0785 \times 2.8) + (5.0683 \times 5.2) - (3.0710 \times 65.6) \]

\[ C₃A = (2.6504 \times 5.2) - (1.6920 \times 2.8) \]
C₄AF = 3.0432 x 2.8

So:

C₃S = 64.7 %
C₂S = 12.9 %
C₃A = 9.0 %
C₄AF = 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 \((0.7 \times \text{SO}_3)\) 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 CO₂ content of the cement and calculating the corresponding CaO. If either slag or fly ash is present, in principle the formula could be adjusted to take it into account, but the slag or ash composition would need to be known accurately and in practice this is not an adjustment normally made.
Appendix 2 – Annual cement production and producers

A number of sources of information were obtained on global cement production: the US Geological Survey, CEMBUREA (the European Cement Association); Statistica.

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

US Geological Survey
In 2014, the world production of hydraulic cement was 4,180 million tonnes. The top three producers were China with 2,500, 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:


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

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

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

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

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

The performance in the rest of the world, which includes many emerging economies in Asia, Africa and Latin America and representing some 1,020 million tonnes cement demand in 2010, was
positive and more than offset the declines in North America and Europe. Annual consumption growth was recorded at 7.4 % in 2010, moderating to 5.1 % and 4.3 % in 2011 and 2012, respectively.

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

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

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

Figure 1: Worldwide cement production 2015

The figure below from CEMBUREAU shows the growth in production between 2001 and now. Particularly noteworthy is the growth in Asia, Africa and the CIS; production in Europe has declined.
Figure 2: Cement production by region 2001 - 2015

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

Table 3: Major cement producers, Largest cement producers – 2013

<table>
<thead>
<tr>
<th>Rank</th>
<th>Company/Group</th>
<th>Country</th>
<th>Capacity (Mt/y)</th>
<th>No. of plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lafarge</td>
<td>France</td>
<td>225</td>
<td>166</td>
</tr>
<tr>
<td>2</td>
<td>Holcim</td>
<td>Switzerland</td>
<td>217</td>
<td>149</td>
</tr>
<tr>
<td>3</td>
<td>CNBM</td>
<td>China</td>
<td>200</td>
<td>69</td>
</tr>
<tr>
<td>4</td>
<td>Anhui Conch</td>
<td>China</td>
<td>180</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>HeidelbergCement</td>
<td>Germany</td>
<td>118</td>
<td>71</td>
</tr>
<tr>
<td>6</td>
<td>Jidong</td>
<td>China</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>Cemex</td>
<td>Mexico</td>
<td>96</td>
<td>61</td>
</tr>
<tr>
<td>8</td>
<td>China Resources</td>
<td>China</td>
<td>89</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>Sinoma</td>
<td>China</td>
<td>87</td>
<td>24</td>
</tr>
<tr>
<td>10</td>
<td>Shanshui</td>
<td>China</td>
<td>84</td>
<td>13</td>
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</tbody>
</table>
Opportunities for use of bauxite residue in special cements

<table>
<thead>
<tr>
<th></th>
<th>Company</th>
<th>Country</th>
<th>Value</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Italcementi</td>
<td>Italy</td>
<td>74</td>
<td>55</td>
</tr>
<tr>
<td>12</td>
<td>Taiwan Cement</td>
<td>Taiwan</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Votorantim*</td>
<td>Brazil</td>
<td>57</td>
<td>37</td>
</tr>
<tr>
<td>14</td>
<td>CRH**</td>
<td>Ireland</td>
<td>56</td>
<td>11</td>
</tr>
<tr>
<td>15</td>
<td>UltraTech</td>
<td>India</td>
<td>53</td>
<td>12</td>
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<td>Huaxin</td>
<td>China</td>
<td>52</td>
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<td>17</td>
<td>Buzzi</td>
<td>Italy</td>
<td>45</td>
<td>39</td>
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<td>18</td>
<td>Eurocement</td>
<td>Russia</td>
<td>40</td>
<td>16</td>
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<td>19</td>
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<td>China</td>
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</tr>
<tr>
<td>20</td>
<td>Jaypee***</td>
<td>India</td>
<td>34</td>
<td>16</td>
</tr>
</tbody>
</table>

Lafarge and Holcim merged in 2015 to form LafargeHolcim.
Opportunities for use of bauxite residue in special cements

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]
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I</td>
<td>Portland cement</td>
<td>Main constituents</td>
</tr>
<tr>
<td></td>
<td>CEM I</td>
<td>Silica fume</td>
</tr>
<tr>
<td></td>
<td>95-100</td>
<td>CEM I</td>
</tr>
<tr>
<td></td>
<td>Portland-slag cement</td>
<td>CEM IIIA-S</td>
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<tr>
<td></td>
<td>80-84</td>
<td>CEM IIIA-S</td>
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<tr>
<td></td>
<td>Portland-silica fume cement</td>
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<td>90-84</td>
<td>CEM IIIA-S</td>
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<tr>
<td></td>
<td>Portland-cozolana cement</td>
<td>CEM IIB-P</td>
</tr>
<tr>
<td></td>
<td>80-84</td>
<td>CEM IIB-P</td>
</tr>
<tr>
<td></td>
<td>Portland-fly ash cement</td>
<td>CEM IIB-P</td>
</tr>
<tr>
<td></td>
<td>80-84</td>
<td>CEM IIB-P</td>
</tr>
<tr>
<td></td>
<td>Portland-burnt shale cement</td>
<td>CEM IIB-T</td>
</tr>
<tr>
<td></td>
<td>80-84</td>
<td>CEM IIB-T</td>
</tr>
<tr>
<td></td>
<td>Portland-limestone cement</td>
<td>CEM IIB-L</td>
</tr>
<tr>
<td></td>
<td>80-84</td>
<td>CEM IIB-L</td>
</tr>
<tr>
<td></td>
<td>Portland-composite cement</td>
<td>CEM IIB-M</td>
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<tr>
<td></td>
<td>80-84</td>
<td>CEM IIB-M</td>
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<tr>
<td></td>
<td>CEM III</td>
<td>Blastfurnace cement</td>
</tr>
<tr>
<td></td>
<td>CEM IIIA</td>
<td>CEM IIIA</td>
</tr>
<tr>
<td></td>
<td>35-64</td>
<td>CEM IIIA</td>
</tr>
<tr>
<td></td>
<td>CEM IIIB</td>
<td>CEM IIIB</td>
</tr>
<tr>
<td></td>
<td>20-34</td>
<td>CEM IIIB</td>
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<tr>
<td></td>
<td>CEM III/C</td>
<td>CEM III/C</td>
</tr>
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<td>5-19</td>
<td>CEM III/C</td>
</tr>
<tr>
<td></td>
<td>CEM IV</td>
<td>Pozzolanic cement</td>
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<td>CEMIVA</td>
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<td>65-89</td>
<td>CEM IV/A</td>
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<tr>
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<td>CEM IV/B</td>
<td>CEM IV/B</td>
</tr>
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<td>45-64</td>
<td>CEM IV/B</td>
</tr>
<tr>
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<td>CEM V</td>
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<td>CEM V/A</td>
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<td>CEM V/B</td>
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<tr>
<td></td>
<td>20-38</td>
<td>CEM V/B</td>
</tr>
</tbody>
</table>

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 IIIA-M and CEM IIIB-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 0.2% 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 1199:1959 Methods of sampling and analysis of concrete.
IS 1727:1967 Methods of test for pozzolanic materials.


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


**USA**

Main ASTM standards

<table>
<thead>
<tr>
<th>Designation</th>
<th>Title</th>
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</thead>
<tbody>
<tr>
<td>C227 - 10</td>
<td>Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)</td>
</tr>
<tr>
<td>C441 / C441M - 11</td>
<td>Standard Test Method for Effectiveness of Pozzolans or Ground Blast-Furnace Slag in Preventing Excessive Expansion of Concrete Due to the Alkali-Silica Reaction</td>
</tr>
<tr>
<td>C586 - 11</td>
<td>Standard Test Method for Potential Alkali Reactivity of Carbonate Rocks as Concrete Aggregates (Rock-Cylinder Method)</td>
</tr>
<tr>
<td>C1105 - 08a(2016)</td>
<td>Standard Test Method for Length Change of Concrete Due to Alkali-Carbonate Rock Reaction</td>
</tr>
<tr>
<td>C1260 - 14</td>
<td>Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)</td>
</tr>
</tbody>
</table>
### Opportunities for use of bauxite residue in special cements

**Designation** | **Title**
--- | ---
C1293 - 08b(2015) | Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction

### Chemical Tests

**Designation** | **Title**
--- | ---
C25 - 11e2 | Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
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
<table>
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<th>Designation</th>
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<tr>
<td>C114 - 15</td>
<td>Standard Test Methods for Chemical Analysis of Hydraulic Cement</td>
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Appendix 4 – Industry Associations

Australia

Cement, Concrete and Aggregates Australia (CCAA):

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 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 11,00 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 (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. -
Opportunities for use of bauxite residue in special cements

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.
Opportunities for use of bauxite residue in special cements

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

Opportunities for use of bauxite residue in special cements
Appendix 6 - Organisations involved in cement/ bauxite residue research

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

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

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

Catholic University of Leuven, Belgium. Yiannis Pontikes.

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

CSIRO, Australia. C. Klauber.

KIT College of Engineering in Kohlapur, India.

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

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

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

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

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

Civil Engineering Department, Sherbrook University, Quebec, Canada.

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

VAMI, St Petersburg, Russia.

VITO, Mol, Belgium. R. Snellings.
Appendix 7 – Geopolymers

A geopolymer is an Al- and Si-rich cementitious, amorphous binder, which is formed by polymerisation of an alkali-activated solid aluminosilicate precursor. They comprise chains or a 3D framework of linked AlO₄⁵⁻ and SiO₄⁴⁻.

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% Na₂O at 800 °C, probably in air. This alkali treatment resulted in the formation of hydraulic phases, disordered peralkaline aluminosilicate, C₃A, and aL-C₃S. 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.”
Appendix 8 - Bibliography


Opportunities for use of bauxite residue in special cements


**Sulfoaluminate cement**


**Geopolymers**


Opportunities for use of bauxite residue in special cements


**Durability**

**Sustainability strategy of blended cement**


**Carbon dioxide production**

“Cement Technology Road Map” published in 2009 by the International Energy Agency and World
Opportunities for use of bauxite residue in special cements

Business Council for Sustainable Development.

Radioactivity
Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) safety guidelines.


[http://ean-norm.eu/documents/NORM%204/Pontikes.pdf](http://ean-norm.eu/documents/NORM%204/Pontikes.pdf)
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](http://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.