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Bauxite residue in the raw meal or as a pozzolanic material in cement: a “strengths, weaknesses, opportunities, threats” analysis

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International Seminar on Bauxite Residue (red mud)
November 2011, Goa, India

Contents

Bauxite residue, BR, red mud

	Typically, wt%
SiO_2	7.4 ± 1.5
Al_2O_3	18.1 ± 1.0
CaO	15.8 ± 1.7
Fe_2O_3	41.4 ± 1.7

BR consists of **hematite** Fe_2O_3, **diaspore** $Al_2O_3.H_2O$, **gibbsite** $Al_2O_3.3H_2O$, **calcite** $CaCO_3$, quartz SiO_2, perovskite $CaTiO_3$, cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \cdot 2H_2O$] …

Data for Aluminium of Greece

An alternative characterisation…

	%	Normalised, %	$/t of oxide	$/t of BR
Al_2O_3	16.63	19.05	320[1]	61
Fe_2O_3	42.58	48.77	180[1]	88
TiO_2	5.00	5.73	2300[2]	132
Sc_2O_3	0.02	0.02	1400[3]	32

313 $/t of BR

1: http://www.consensuseconomics.com/ 2: http://www.icis.com/v2/chemicals/9076545/titanium-dioxide/pricing.html
3: http://minerals.usgs.gov/minerals/pubs/commodity/scandium/820397.pdf

If red mud has a value, then is it waste?

Of course not!

2006 Red Mud Cabernet Sauvignon
A definite winner that will certainly impress - displaying lovely dark fruits; like fig and plum with haunting smokiness of roasted cedar. This wine has great cabernet structure with lively berry flavours and a lovely lasting finish.

Beauty Face Masks Red Mud
Red Mud is a new generation facial mask, specially formulated to provide the nutrients needed for youthful healthy looking skin.

Red Mud Barbecue Sauce
Red Mud is a rich, thick, and tangy BBQ sauce with just the right amount of kick. Red Mud enhances the flavor of grilled meats without overwhelming their natural flavor.

What about BR?

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Very small use in the production of heavy clay ceramics and cement production, reported for China, India, Greece.

What is the exact figure? Is there aspiration for higher usage?

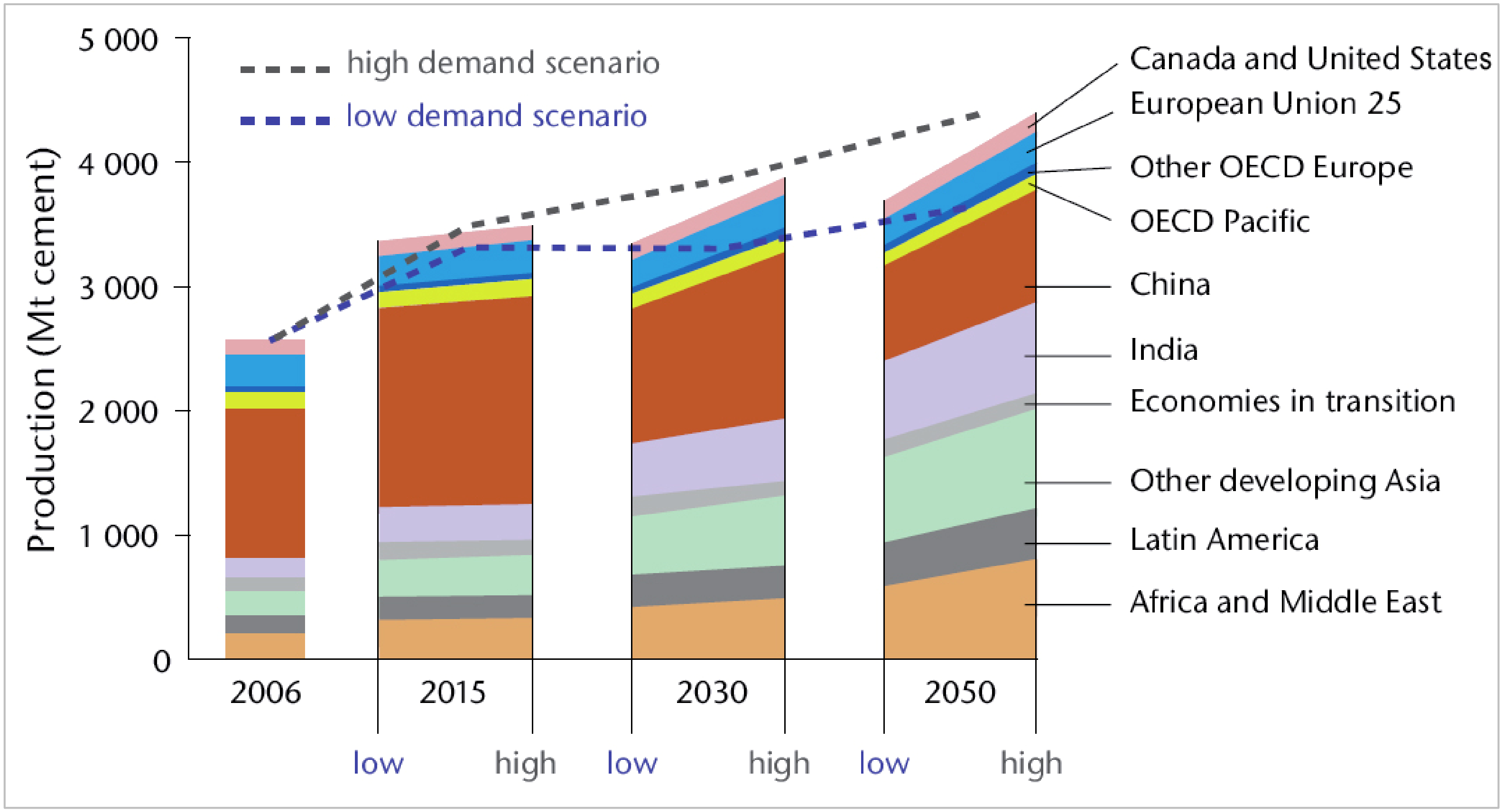
Alumina Technology Roadmap 2001 and 2006, speaks for **cradle-to-grave responsibility** of the alumina industry and a goal is set for **20% utilisation of residue by 2025**.

How is this transition going to happen?

Production of cement can contribute

Why cement?

Portland cement is the most widely used building material in the world, estimated at 2.8 billion tonnes. Use of concrete is only second to water.



And it will continue to grow…

http://www.iea.org/papers/2009/Cement_Roadmap_targets_viewing.pdf

Checklist before we start…

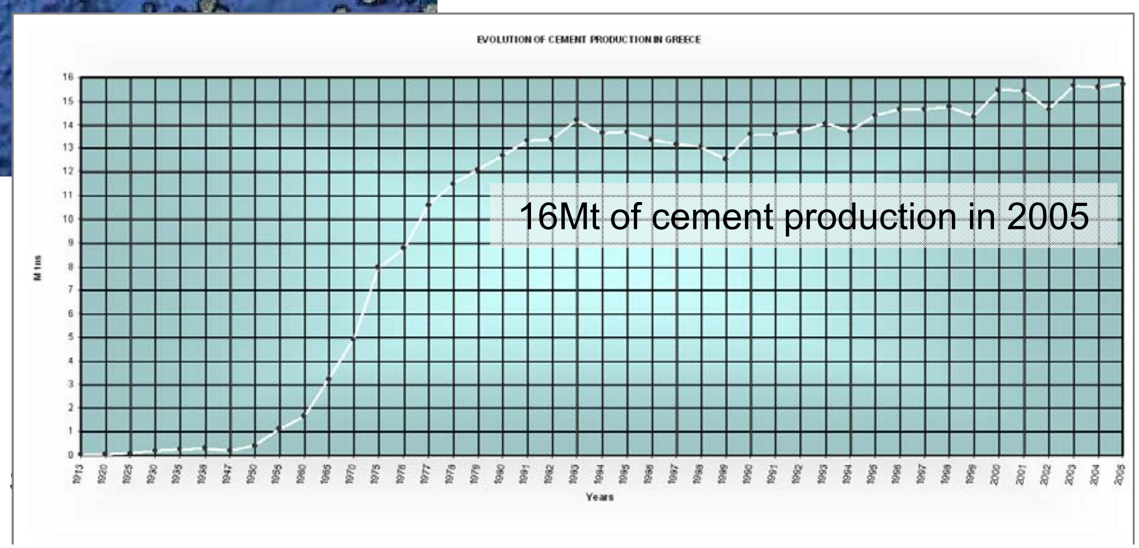
A number of requirements should be met:

- ✓ Availability of dewatered BR
- ✓ Vicinity to cement plant
- ✓ High ratio of cement to alumina production

Country (data for 2009, source USGS, in kt)	Alumina	Cement	alumina to cement, %
Australia	19948	8500	234.68
Brazil	8000	51748	15.46
China	23800	1629000	1.46
India	3700	205000	1.80
Jamaica	1774	700	253.43
Russia	2794	44300	6.31

In practice: example

2 wt% use in the raw meals would result to the utilisation of half the BR's annual production



Research domains for BR and cement

Research on BR for cement is driven by cement needs

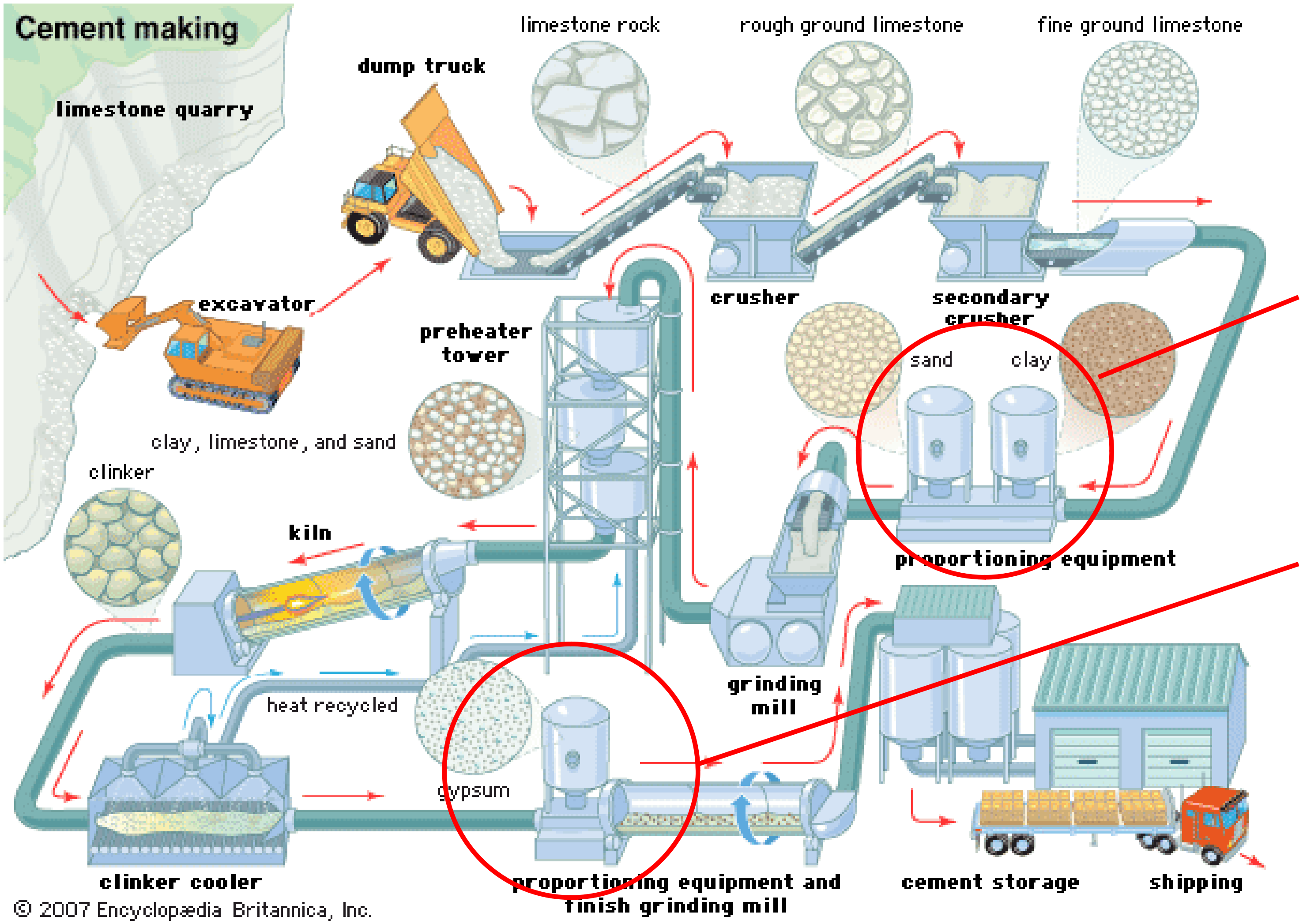
As cement industry tries to minimise CO_2 per mass of cement and increase sustainability, a number of strategies are proposed:

a) Use **alternative raw materials**
b) Produce **alternative clinker** that requires less limestone
c) Make **blended cements** with comparable performance (less clinker)

Background in "cement-world"

Alternative raw materials	Alternative clinker to OPC	Blended cements	
coal fly ash from power stations, steel slag, foundry sand, sewage sludge, lime sludge, catalysts from oil refineries and more (See also alternative fuels)	belite calcium-sulfoaluminate (BCSA), calcium ferroaluminate sulfate (CFAS), belite calcium-sulfoaluminate - ferrite (Lafarge BCSAF cements)	OPC with fly ash, ggbs and a number of pozzolanic materials, CSA-rich clinkers blended with ggbs, pfa, calcium sulfate	[Not covered here but see also geopolymers and new cement systems as alternatives]

In practice: where is BR introduced?



BR in the raw meal

BR as pozzolanic material

Alternative raw materials

In **1980**, Shimano and Koga propose the use of BR in place of slag as a source of Fe_2O_3 in the cement industry.

No distinct effect of BR addition on the clinkering process, grindability of materials, or properties of the final clinker was observed. Industrial trials were also conducted.

The optimal amount of BR was 5-20 kg/ton clinker. The authors also report on the development of a press-type filter to decrease the slurry moisture to 30 wt.%.

See also work by Tsakiridis et al., 2004, (values for setting times, water content for standard consistency and expansion, compressive strength similar to reference OPC sample) and Vangelatos et al., 2009 (additional 1 year strength and leaching).

Alternative raw materials: industrial trials

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•Transportation was done by trucks or by boat, water content between 20 and 28 wt.%.

•Storing of BR took place in metallic silos.

•For controlling the feed, a dosing system was incorporated. The material was guided by conveyor belts and mixed with the other raw materials in the mill.

•The substitution ranged from 0.5 to a maximum of 2.7 wt% in BR.

•In all industrial trials, the use of BR resulted in reduced levels of Mn, Pb, Zn and Cu in the clinker.

•Total and water soluble Cr increase in the case of the bauxite and iron ore substitution, however decrease in the case of metallurgical slag's substitution.

•An increase in the levels of Ni and V is anticipated (not measured).

•EC regulation states that the water soluble Cr [Cr(VI)] content in cement should be < 2 ppm and the industry is using $FeSO_4.7H_2O$. For 2 wt% of BR in the raw meal, substituting bauxite and iron ore, the water soluble Cr was increased from 17ppm to 24ppm. The cost of extra $FeSO_4.7H_2O$ addition was estimated to be 0.15 €/t of cement.

•The microstructure and mineralogical composition of the clinkers with BR, as well as, the mechanical properties of the cements were comparable with standard production. In addition, there were no indications for any changes in the emission levels. In both cases, definitive conclusions would require long-term measurements as well.

OPC production with BR: pilot plan trials

Contract for 100.000t/y by AGET Heracles SA. (now Lafarge)

"During the pilot project, Lafarge was able to reclaim 3,500 metric tons of red mud. The automation of the dewatering process, now under way, should permit the reclamation of up to 300,000 metric tons of mud by 2004. This solution not only preserves natural resources, but also lowers the cost of cement manufacture."

Accessed 15/11/2011: http://www.lafarge.com/wps/portal/2_4_4_1-EnDet?WCM_GLOBAL_CONTEXT=/wps/wcm/connect/Lafarge.com/AllCS/Env/NR/CP1610621381/CSEN

Alternative clinkers

Oxides, in wt.%	Singh et al., 1997	Vangelatos et al., 2009	Duvallet et al., 2009	Senff et al., 2011	Gartner and Guanshu, 2010
CaO	31.1-47.0	44.8-60.7	47.2-50.8	48.2-57.3	50-61
SiO_2	2.6-5.9	14-7-26.2	9.3-13.4	9.5-21.3	15-25
Al_2O_3	10.7-32.8	7.2-16.7	10.6-24.8	12.5-29.2	9-22
Fe_2O_3	10.4-21.5	5.9-12.3	9.9-20.7	4.2-4.6	3-11
MgO	n.r.	n.r.	1.6-1.8	n.r.	≤5
TiO_2	5.2-12.4	n.r.	n.r.	0.9-1.0	n.r.
Na_2O	0-3.3	n.r.	0.4-0.9	0.6	≤5
K_2O	n.r.	n.r.	0.2-0.4	0.01	≤5
B_2O_3	n.r.	n.r.	n.r.	n.r.	≤3
P_2O_5	n.r.	n.r.	n.r.	n.r.	≤7
ZnO+ MnO+ TiO_2	n.r.	n.r.	n.r.	n.r.	≤5
CaF_2+ $CaCl_2$	n.r.	n.r.	n.r.	n.r.	≤3
SO_3	5.4-8.7	0-11.6	4.2-6.5	5.0-7.4	3-10

Blended cements (as pozzolana)

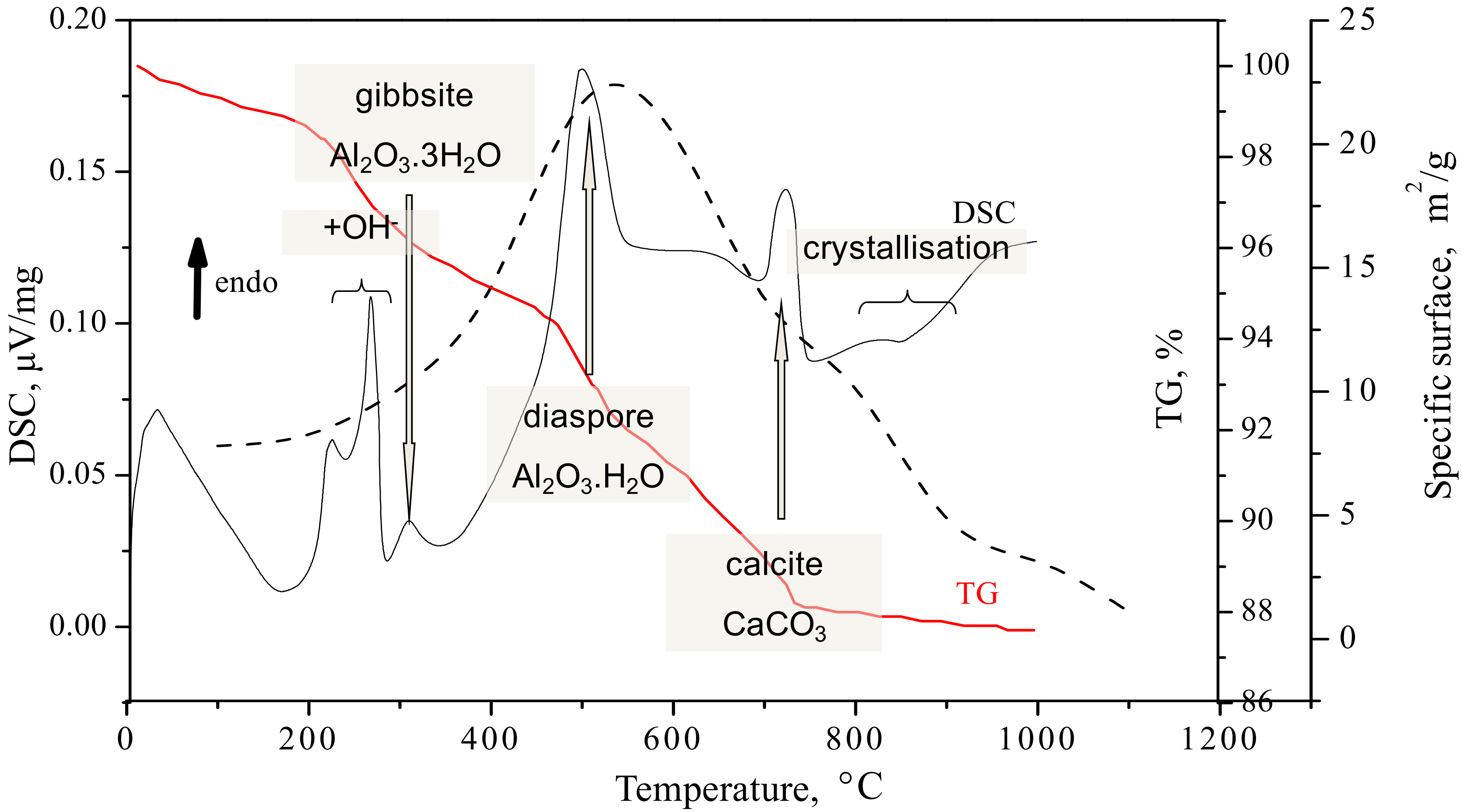
In 1992, and 1997 Pera *et al.* calcined BR from 600 °C to 800 °C, and prepared standard mortars with 10 wt.% to 30 wt.% BR (instead of OPC) which were tested for compressive strength at 90 days.

All calcined BR were found to be pozzolanic. For mixtures of OPC and more than 20 wt.% calcined BR, mono-carboaluminate ($C_4A\hat{C}H_{11}$) is suggested to form from the reaction between **portlandite, calcite and the amorphous alumina** in BR.

In most cases BR is not behaving as a filler: when the OPC control mixture obtains **65.5 ± 1.2 MPa in 28 days**, the mixture with 20 wt.% BR obtains a value between **56.6 MPa to 58.6 MPa**. Due to the presence of calcite in the specific BR, the authors also suggest prehydration.

Blended cements (as pozzolana)

The role of calcination (data relevant for AG's BR)



Blended cements (as pozzolanic and hydraulic material)

Mostly studied in China; calcination seems effective.

Examples:

Zhang et al., 2011: calcination of BR at 600 °C for 3h; mixture based on 30 wt.% BR, 21 wt.% blast furnace slag, 10 wt.% fly ash, 30 wt.% clinker, 8 wt.% gypsum and 1 wt.% compound agent; compressive strength of mortars in the range of 45.3–49.5 MPa.

Liu et al., 2011: calcination of BR at 600 °C for 3h; mixture based on 50 wt.% BR, 45 wt.% clinker and 5 wt.% gypsum; compressive strength of mortars 34.2 MPa for 28 days.

Zhang, N., et al., 2011, J. Hazard. Mater. 185, 329-335.

Liu et al., 2011, Cement and Concrete Research 41, 847–853

To remember: how much BR?

Oxides, in wt.%	OPC
CaO	65 ± 3
SiO_2	21 ± 2
Al_2O_3	5 ± 1.5
Fe_2O_3	3 ± 1
MgO	<5
TiO_2	-
SO_3	2
LOI	-

As pozzolanic: <30 wt.% addition

As pozzolanic and hydraulic material: <50 wt.% addition

SWOT for cement producers

Strengths	Weaknesses
• It is a demonstrated solution in industrial production with a proven track record. • Reduction in energy required for milling of the raw materials, as BR is fine. • Potential for reduction of firing temperature in view of improved burnability. • Low cost of use. • End-product with comparable properties. • No mono-dependence on the availability of raw materials and therefore higher resilience.	• High levels of Na set an upper limit in the maximum volume of BR that can be used, especially in the case of low-alkali cements (sum of Na_2O + $0.66K_2O$ below 0.6wt.%). • Levels of Cr in BR can result in increased addition of reducing agents (i.e. $FeSO_4.7H_2O$, $SnSO_4$) in the post-production treatment and raise the cost. • Levels of Ti can also be a regulating factor for the Ti-rich BRs. • Requirement of a silo to store BR and avoid air borne or water transferred particles as well as any leaching.

SWOT for cement producers

Opportunities	Threats
• Cement industry under pressure to cut down CO_2 emissions. Improved burnability and reduction of milling time can contribute in meeting these goals. • Image strengthening in terms of sustainability. • Possibilities for joint ventures or joint research with refineries on new high Fe-cements and related materials.	• Quality of BR can fluctuate depending on bauxite and Bayer process. • Public perception in production site or from customer's side may become an obstacle.

SWOT for refineries

Strengths	Weaknesses
• It is a demonstrated solution in industrial production with a proven track record. • Possibility for utilisation of high volumes • Possibility for revenues or at least to leverage disposal costs. • Mature corporate mentality (in cement sector) that is interested in alternative energy and materials.	• A dewatering unit is needed to reduce water content typically < 30wt%. • Not uniform waste policy. Some countries charge high prices per ton of waste for disposal and therefore waste producers are willing to cover transportation cost and deliver BR alternative wastes at cement's industry door with minimal cost. • High levels of Fe set an upper threshold in the volume that can be absorbed. Similarly for Na, Ti and Cr. • Dependence on an external industry for BR utilisation. • Availability of other domestic competitive materials that can be used as Fe source. • Even if high volumes can be consumed, it is not a single solution for refineries/countries with low cement production figures.

SWOT for refineries

Opportunities	Threats
• Low investment and risk solution • Appears as a mature path for BR disposal • Possibilities for joint ventures or joint research with cement industries on new high Fe-cements and related materials.	• Cement industry can be dominant and control price and volume of BR as it constitutes a minor constituent when many alternatives can be found. • The benefits for the cement industry are not overwhelming so level of interest from their side is typically low. Other incentives have to be found as well.

What can accelerate this transition? I

Examples on legislation

The Chinese government in 1999 bans the production and application of clay bricks in order to prevent damage to farmland. The clay brick would be prohibited in all urban districts at the end of 2010. As a consequence, the construction and building materials industry becomes a major consumer of most industrial wastes (W. Liu et al, Int. J. Miner. Process. 93 (2009) 220–231). See also the “Circular Economy Promotion Law of the People’s Republic of China, in force on Jan. 1, 2009.

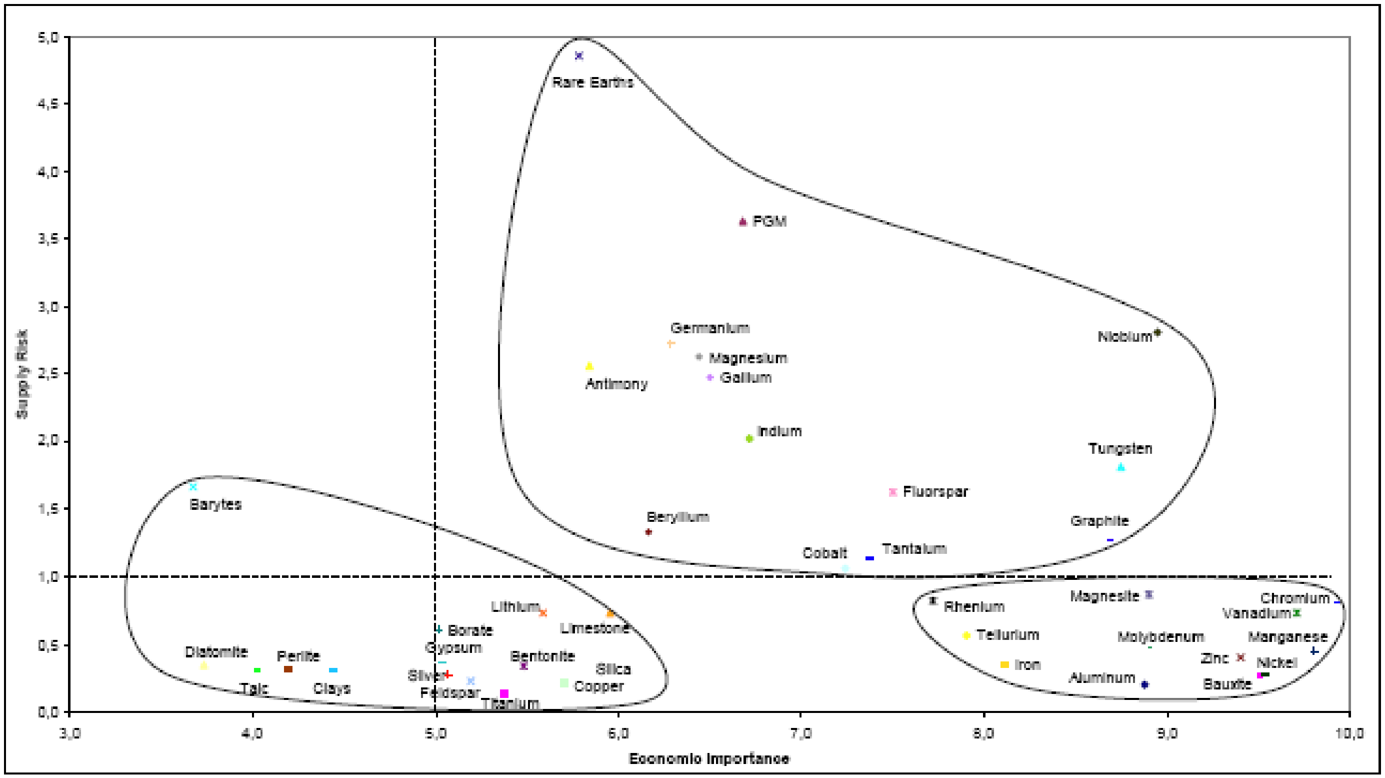
In the UK, (i) the cost of disposing incinerator bottom ash (IBA) to landfill is increasing due to the Landfill Tax and the requirements of the EU Landfill Directive; (ii) the costs of primary (natural) aggregates have increased due to the imposition of an Aggregates Levy that is charged on each tonne of extracted aggregate. As a consequence, research on IBA is more intense towards e.g. lightweight production (C.R. Cheeseman et al. , Resources, Conservation and Recycling 43 (2005) 147–162)

What can accelerate this transition? II

Examples on supply-availability VS demand

See reports on Critical Minerals (EU), the international report on Critical Energy Materials and the US DOE Strategy on Critical Materials.

Supply risk



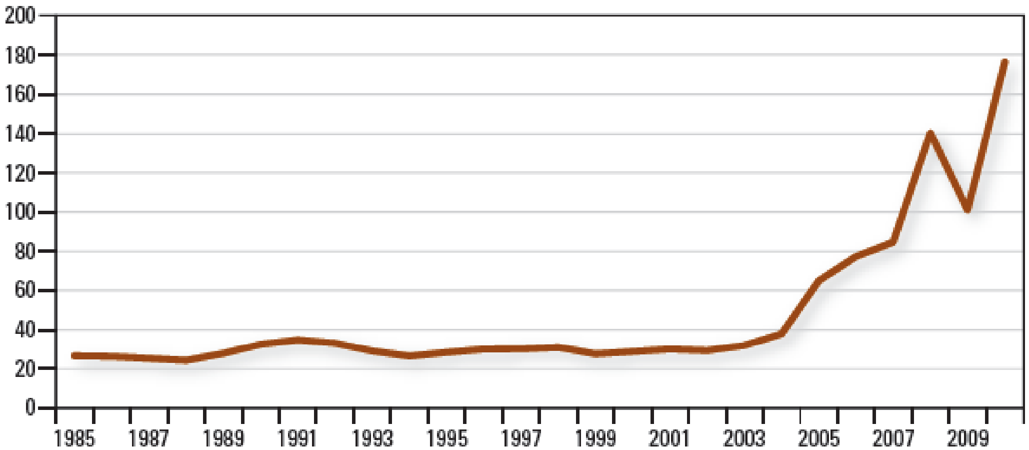
Economic importance

What can accelerate this transition? III

Examples on economic drives

FIGURE 1: Iron-ore price from 1985 to 2010 (Q2)

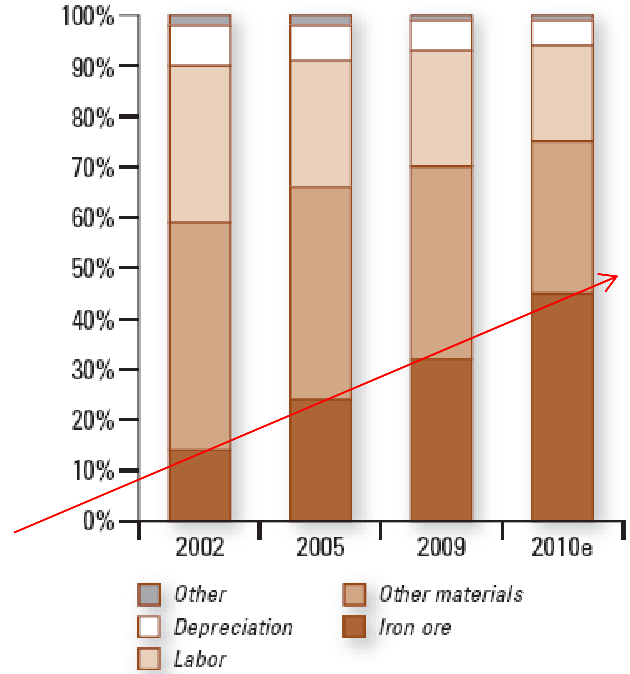
Iron-ore price *(US$ by metric ton)*[1]



[1]Iron ore is 67.55% iron content, fine, contract price to Europe, freight-on-board Ponta da Madeira, $US 0.01 per dry metric ton unit.

Source: International Monetary Fund

FIGURE 4: Steel production cost breakdown in Western Europe (2002-2010e)



Sources: World Steel Dynamics, World Steel Association; A.T. Kearney analysis

There will be probably a day where pig iron from red mud will be also economically attractive

Source: Steel's Challenge, Living with higher and more volatile iron-ore prices, A.T. Kearney

What can accelerate this transition? IV

Examples on targeted research

ULCOS stands for Ultra–Low Carbon dioxide(CO_2) Steelmaking. It is a consortium of 48 European companies and organisations from 15 European countries that have launched a cooperative research & development initiative to enable drastic reduction in Carbon dioxide(CO_2) emissions from steel production. The consortium consists of all major EU steel companies, of energy and engineering partners, research institutes and universities and is supported by the European commission.

The budget is 75 million Euro over a 6 year period. The partners in the ULCOS consortium foot the bill for 60 % of the total cost. The European commission financially contributes the remaining 40%.

More: www.ulcos.org/

A way forward

Step 1. Refineries agree to participate in a **pre-competitive** international research project.

Each contributes according to BR volume produced.

Target: 4 PhD + 1 project manager (<500k euro/year)

Aim is to develop **global solution tailor made to local conditions**.

Problem driven, science-deep approach.

A way forward

Step 2. Four research topics are chosen and four groups of academic partners. Example, BR towards a) cement, b) iron and use of slag, c) (un-)sintered building materials, d) nature development on BR ponds. A PhD grant for project X is assigned to University Y, Z and Institute Q, known to be leaders in the field.

A way forward

Step 3. Each project has an **academic advisory board** and an **industrial advisory board**.

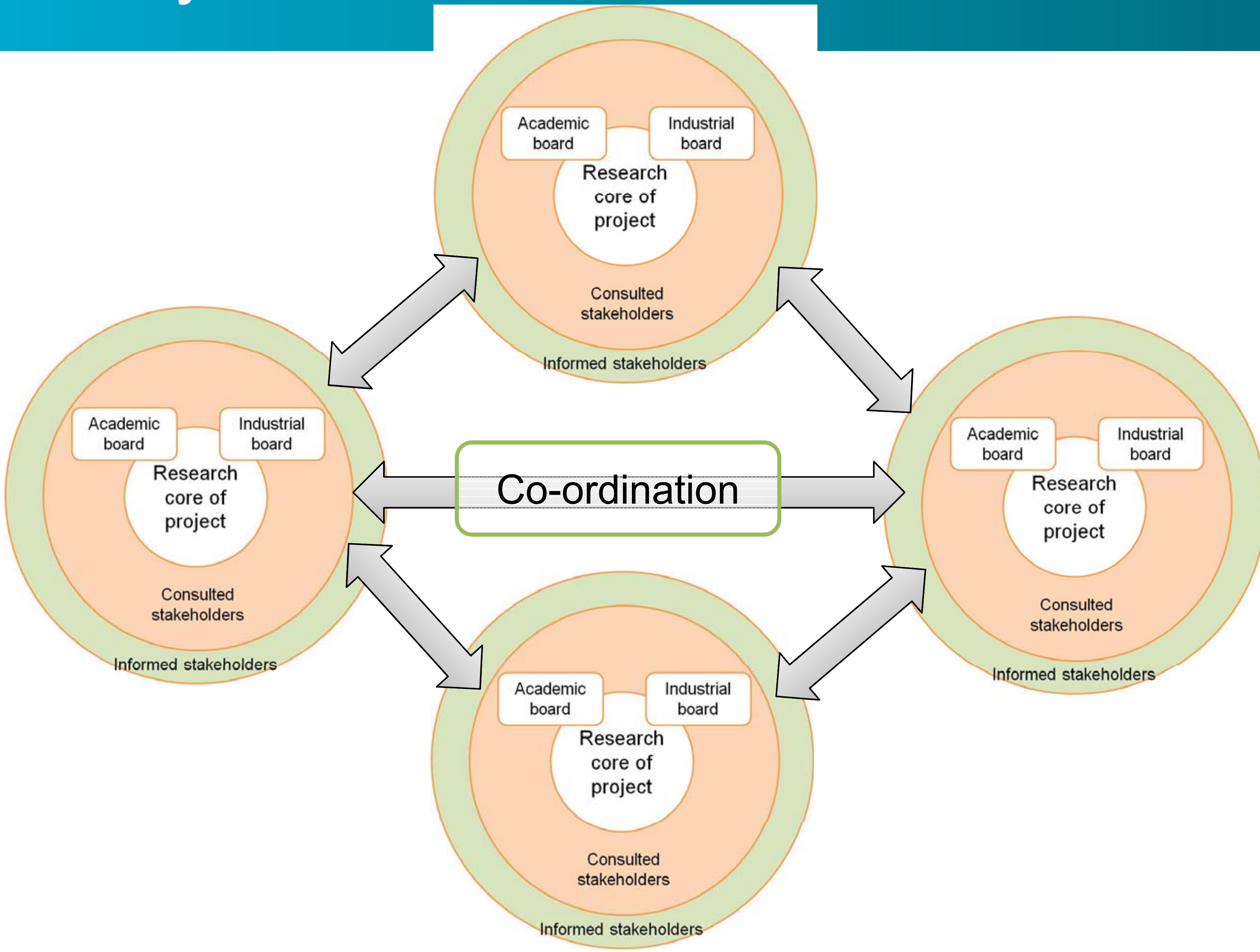
All PhDs develop their own relevant cluster of **stakeholders to be consulted and informed**. Example, PhD on cement, invites in meetings major cement producers.

Each project is **accessible and transparent to all members.**

IP shared among members.

Progress meetings combined with ICSOBA or other event.

A way forward



A way forward

If you think by now this is science-fiction, please visit:

Center for Resource Recovery and Recycling

www.wpi.edu/academics/Research/CR3/about.html

Instead of conclusions

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- The cement industry acknowledges the potential of BR; it is listed as a candidate material in cement books and industrial production has demonstrated the feasibility.
- As with every mature industry there is scepticism and in many cases the economics are not favourable.
- Refineries on the other hand can strengthen this partnership by taking actions and delivering a raw material more suitable for cement production.
- Other factors (legislation, economic incentives, research) may accelerate the transition to BR utilisation.

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