SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

Case studies in Greece for the valorisation of Bayer's process bauxite residue: aggregates, ceramics, glass-ceramics, cement and catalysis

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Contents of presentation

Bayer's process bauxite residue aka "red mud"

→ **aggregates**
→ **ceramics**
→ **glass-ceramics**
→ **cement**
→ **catalysis**

Waste → The "green" process → **Product**

Is really red mud a 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.

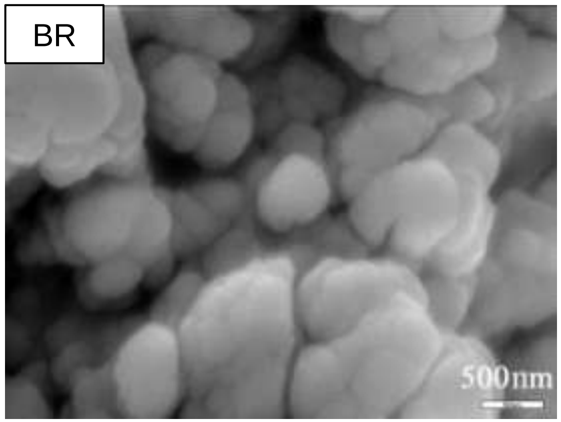
Bayer's process red mud

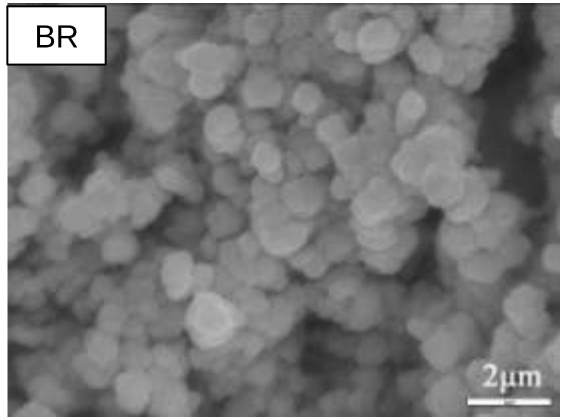
	BR, wt%	Typically, wt%
SiO_2	7.60	7.37 ± 1.47
Al_2O_3	16.63	18.12 ± 0.93
CaO	11.36	15.80 ± 1.73
Fe_2O_3	42.58	41.35 ± 1.70
MgO	0.56	0.62 ± 0.22
K_2O	0.07	0.57 ± 0.30
Na_2O	3.49	3.81 ± 1.75
TiO_2	5.00	3.81 ± 1.75
LOI	12.2	9.05 ± 0.20

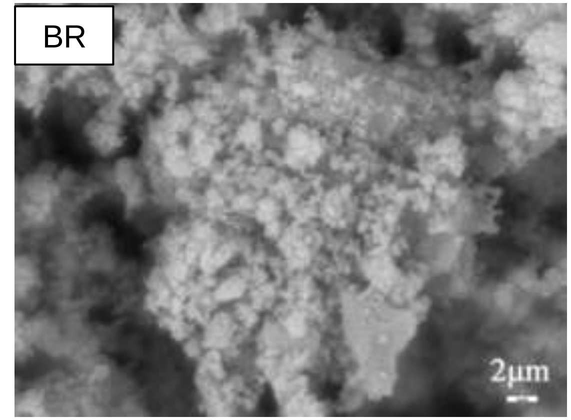
	BR, ppm
Cu	214 ± 20
Cr	2390 ± 20
Ni	1423 ± 40
Co	244 ± 20
Mn	463 ± 15
V	1246 ± 20

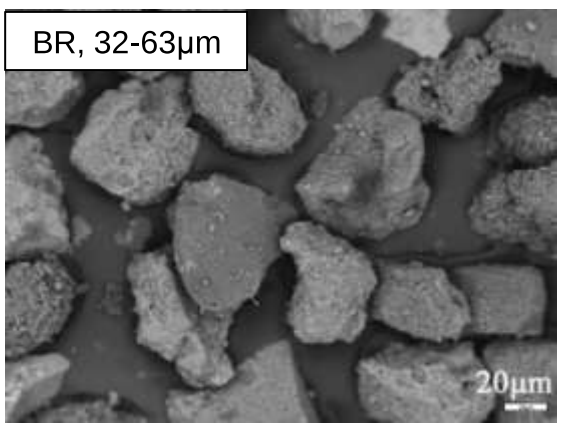
BR consists of **hematite** Fe_2O_3, **diaspore** $Al_2O_3.H_2O$, **gibbsite** Al_2O_3.3H2O, **calcite** $CaCO_3$, quartz SiO_2, perovskite $CaTiO_3$,
calcium aluminum iron silicate hydroxide [$Ca_3AlFe(SiO_4)(OH)_8$],
cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \cdot 2H_2O$] and possibly goethite FeO(OH) and sodium aluminium silicate hydrate $1.0Na_2O \cdot Al_2O_3 \cdot 1.68SiO_2 \cdot 1.73H_2O$

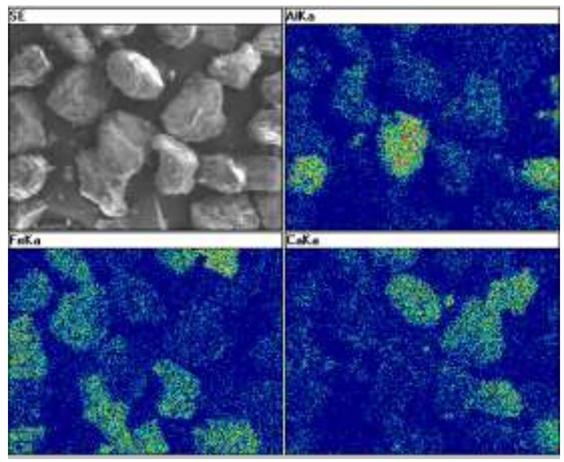
Bayer’s process red mud

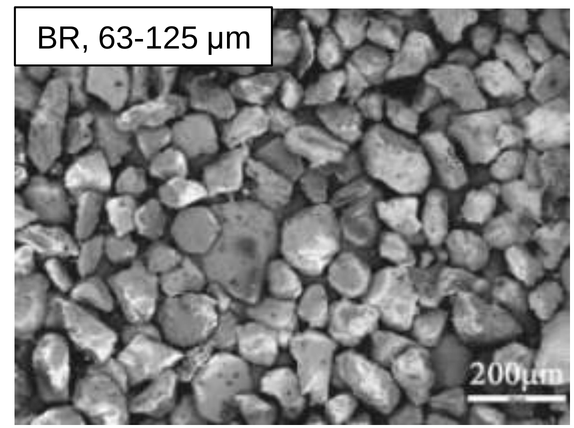










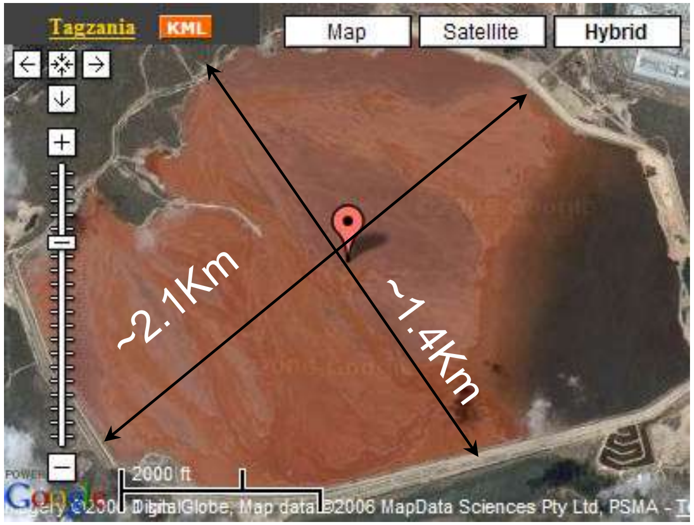


Specific weight 3.4g/cm^3, specific surface ~11m^2/g, X_{90}: 75μm

Bayer's process red mud: a different 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



This is not a disposal site!

This is an open pit mine!

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

So Bayer's process red mud is not a slag…

Correct…But it was "popular" in 2010…

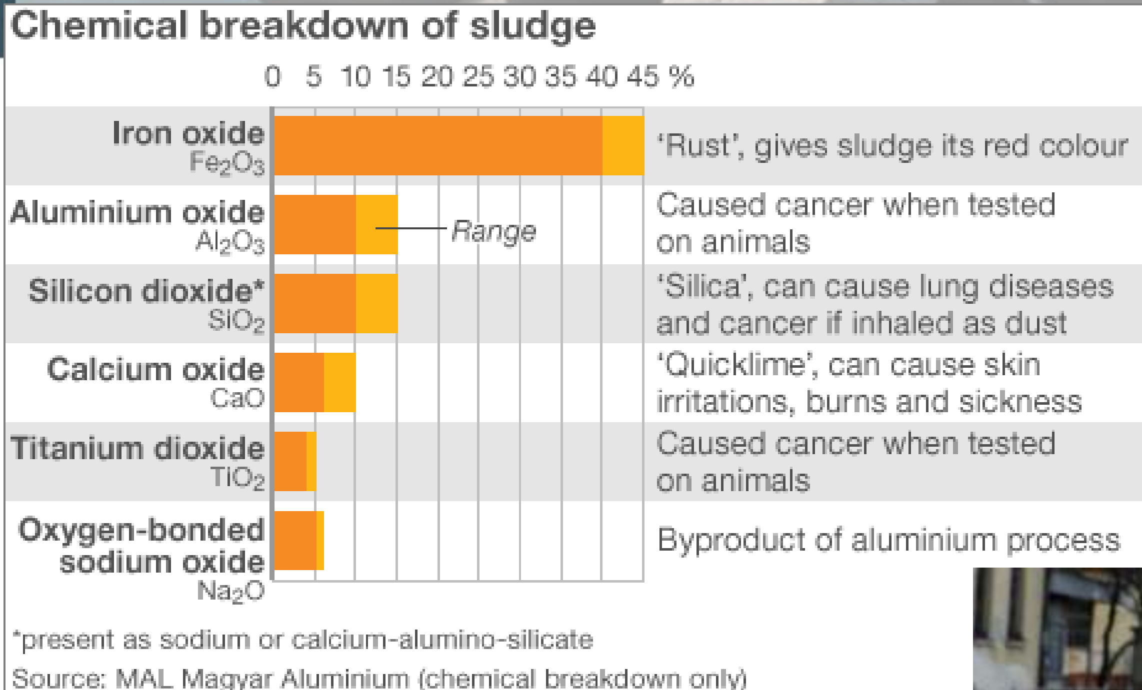
Ajka refinery, Hungary (before)

Ajka refinery, Hungary (after)

"The observed rate of motion of the dam appears very high exceeding -12 mm/yr velocity that more than -9 cm displacement over the past 7.5 years of ENVISAT observation. The signals are well above the 0.3 mm/yr average error level."

G. Grenerczy, U. Wegmüller,, The embankment failure of the mud reservoir of the alumina plant near Ajka, Hungary: implications from ENVISAT ASAR Persistent Scatterer Interferometry analysis.

The power of perception…



Source of table: BBC news

"Red mud is a toxic and radioactive waste"

From red mud to ferroalumina, FA

156 filter plates; double polypropylene filters; active surface 760m^2; productivity 350.000t/y FA; cost 2 M€; total investment for the entire quantity of RM 7 M€; within 2011 3+1 filter-presses will have been installed.

From problem to action

Production of a final “alternative” product with comparable properties with the existing one, by using existing production cycle. Focus on alternative raw materials, energy sources or on the enhancement of the process	Production of a “new” final product, by designing an industrial process that takes into account the nature of the wastes Focus on designing an “intelligent”, tailor-made process

→ Creativity, Challenges, Opportunities

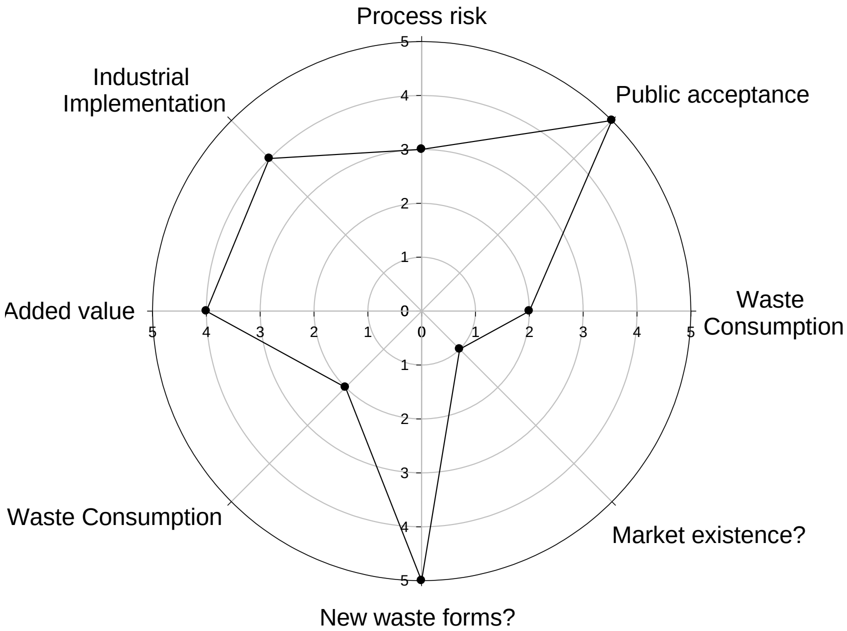
From problem to action

No panacea; one solution to cover all cases unlikely to exist.

Typically, many utilisation applications have to take place so as to absorb all the quantity of the waste.

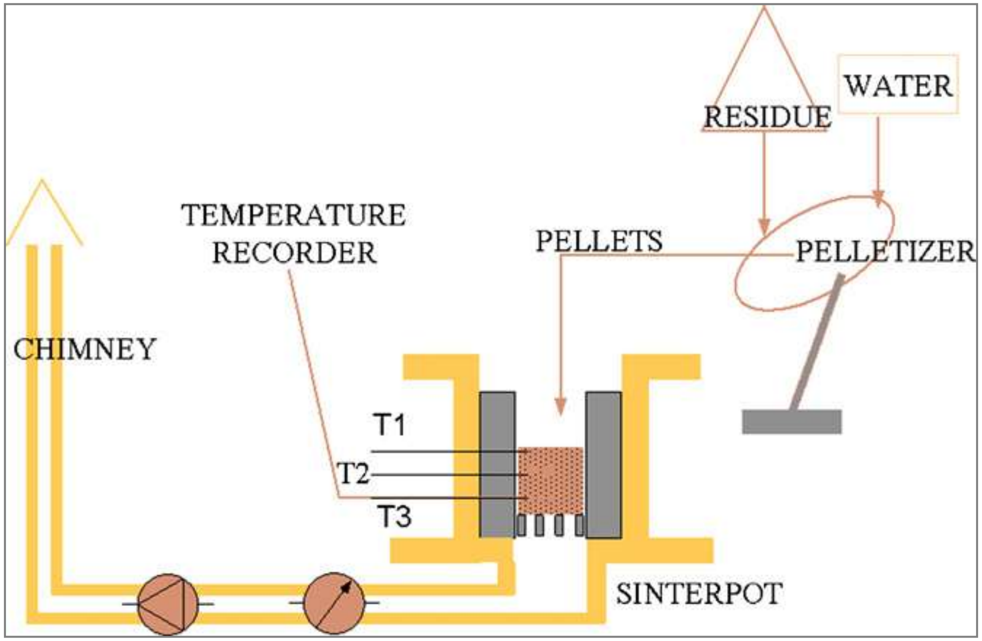
Case specific factors define best available solution, i.e. nearby industrial infrastructure, legislation, public perception…

Quantify the potential of a proposed solution:



Lightweight aggregates

Mixture	Bottom ash, wt%	Fly ash, wt%	FA, wt%	CaO (wt%)
M1	60	32	5	3
M2	60	27	10	3
M3	60	22	15	3
M4	60	17	20	3
M5	60	12	25	3
M6	60	7	30	3



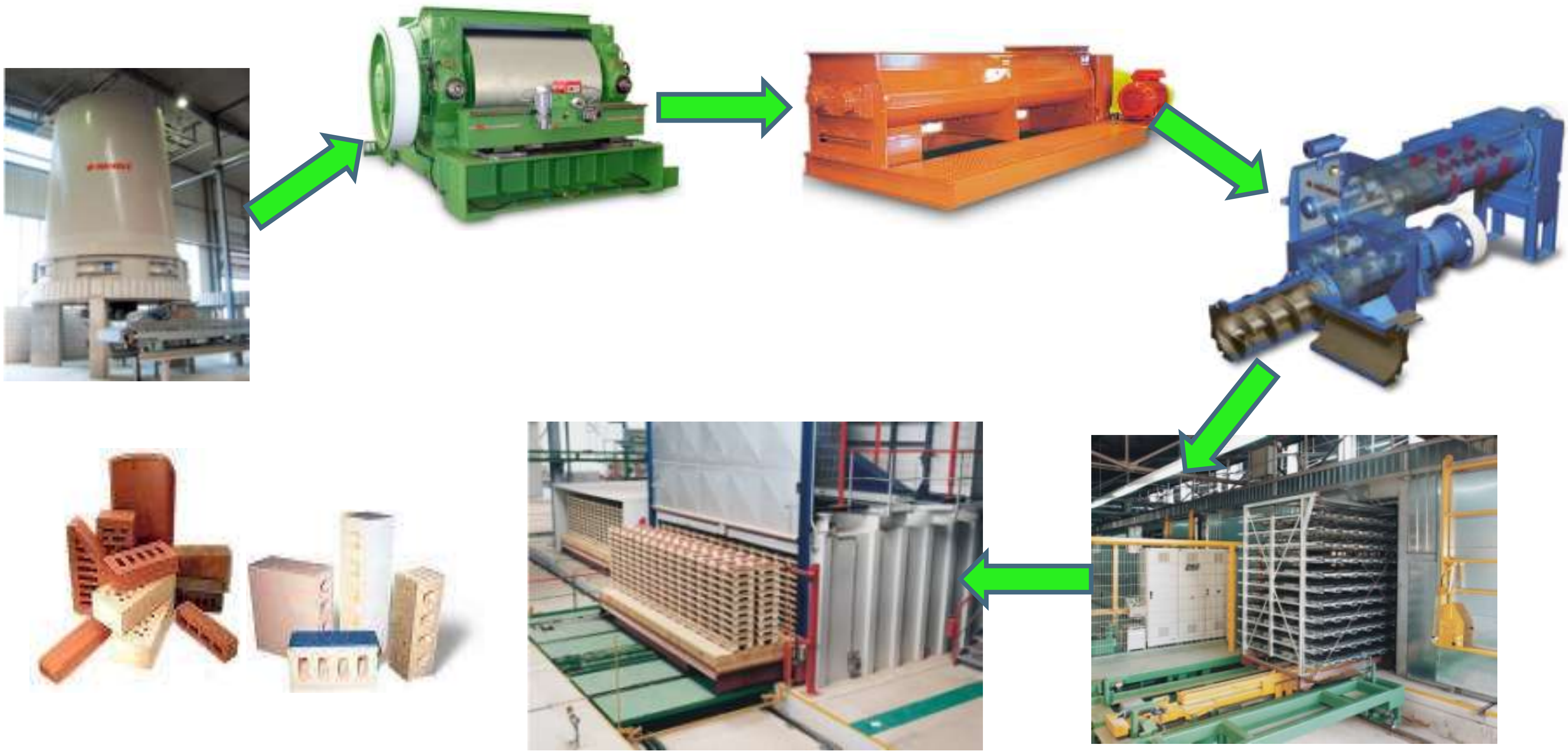
Anagnostopoulos IM, Stivanakis VE, Angelopoulos GN, Papamantellos DC. Valorization of lignite combustion residues and ferroalumina in the production of aggregates. J Hazard Mater. Vol.174, No.1-3, (2010), pp 506-11.

Lightweight aggregates

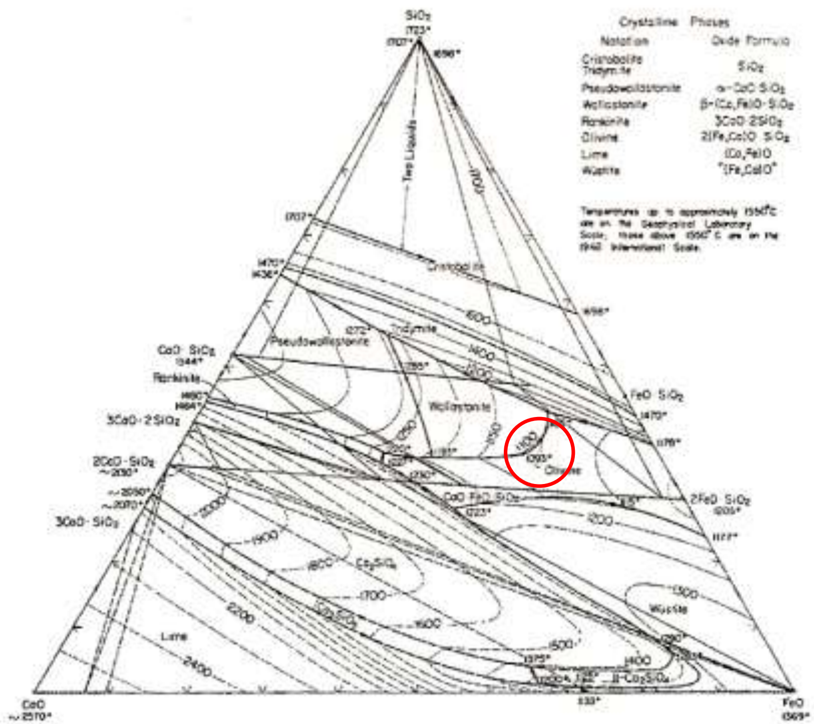
FA, %	Open porosity, %	Bulk density, g/cm^3
5	60.8	1.02
10	52.9	1.12
15	43.9	1.23
20	37.6	1.38
25	35.1	1.42
30	21.6	1.80

- "Lightweight" aggregates for FA up to 20 wt.%
- Higher compressive strength for concrete+aggregates, for FA up to 15 wt.%

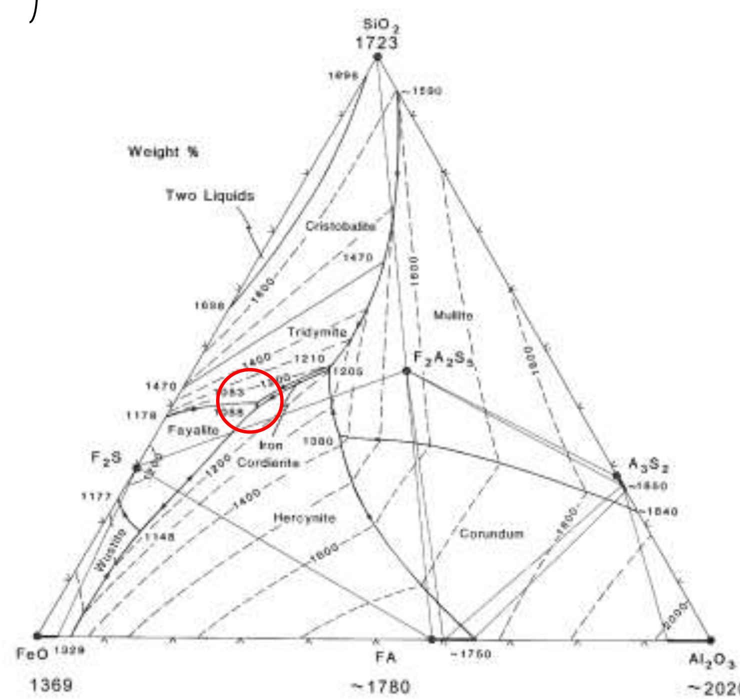
Heavy clay ceramics' production



Focus on firing



Lowest eutectic at 1093°C
for 48%FeO, 17%CaO, 35%SiO_2



Lowest eutectic at 1088°C
για 48%FeO, 13%Al_2O_3, 39%SiO_2

The engineering drive is to exploit the fluxing action of Fe^{+2}

Focus on firing:
50wt% in propane-firing kiln

50wt% R
50wt% BR

Oxidation
1000°C,
1h soaking

Reduction
800-1000°C,
1h soaking

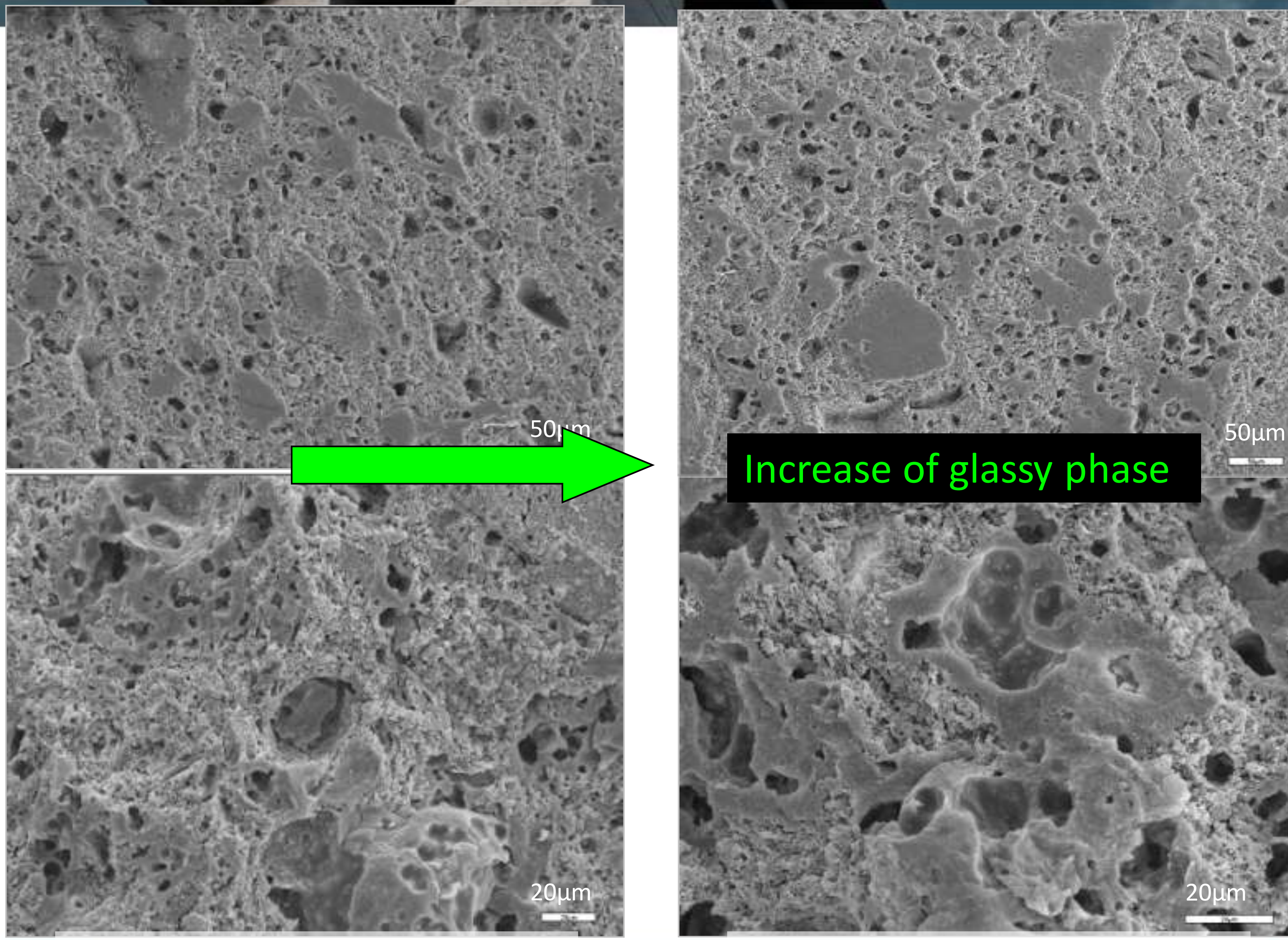
Pontikes Y, Angelopoulos GN. Effect of firing atmosphere and soaking time on heavy clay ceramics with addition of Bayer's process bauxite residue. Adv Appl Ceram. Vol.108,No.1, (2009), pp 50-6.

Focus on firing:
50wt% in propane-firing kiln

Resistance furnace		Propane-firing furnace
Water absorption: 19.4 – 20.3%	→	Water absorption: 18.2 – 18.7%
Bending strength: ~18MPa		Bending strength: ~28MPa

Water absorption reduced > 6%
Bending strength increased > 56%

Focus on firing:
50wt% in propane-firing kiln



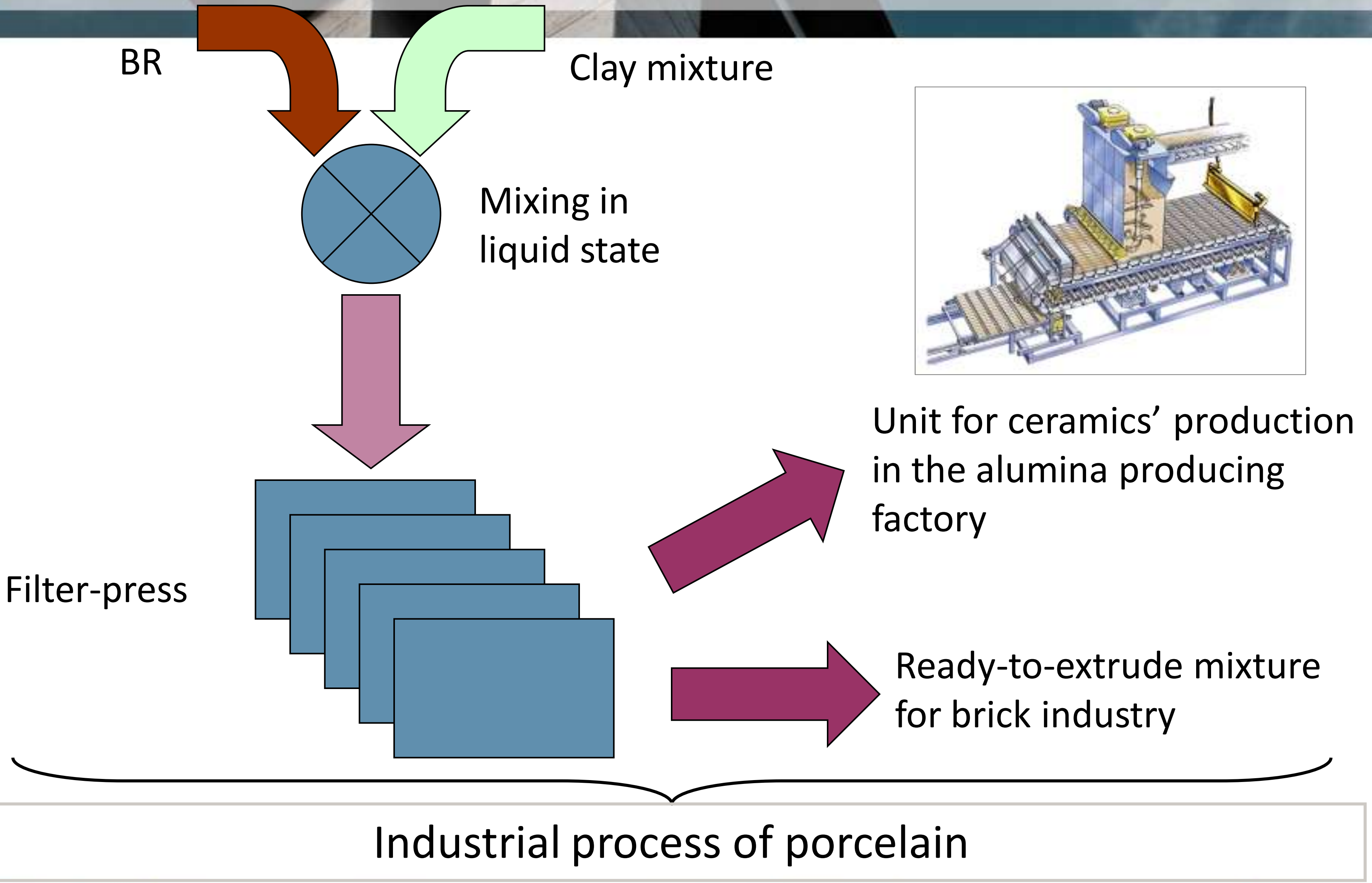
Oxidising atmosphere

Reducing atmosphere

Industrial trials

Tests in pilot plan scale have been performed in 4 industries for brick and roofing tile production. Brick quality is good, for roofing tiles marginal. No alterations in clay body/processing were made. Additions up to 23 wt% FA.

Development of process



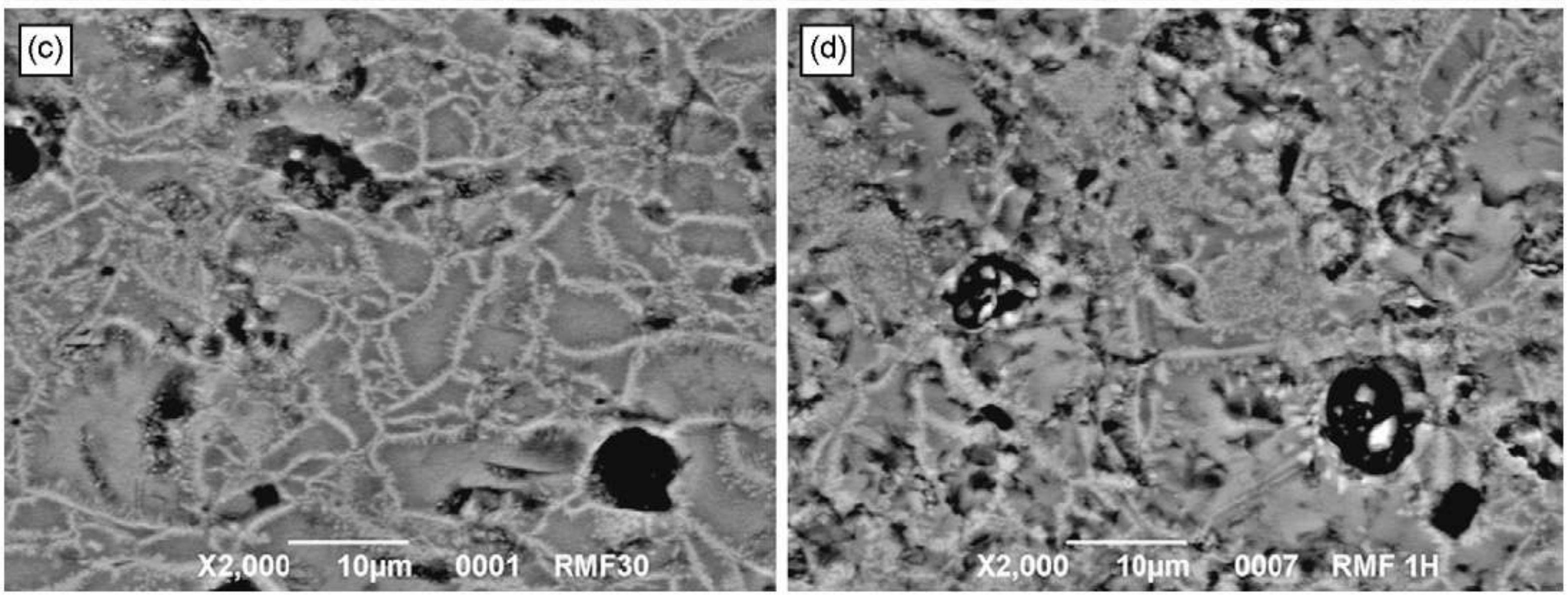
A likely final product

Glass ceramics

FA/fly ash/ polishing wastes/ $CaCO_3$ = 10/29/40/21 → Melting at 1400°C for 2 h and quenching → Milling and uniaxial pressing → Conventional and rapid sintering at 900°C, 0 to 3 h

"sinter-crystallisation":
viscous flow sintering of glass frits with concurrent crystallisation

Rapid sintering, 0.5h soaking



Rapid sintering, 1h soaking

Bernardo E, Esposito L, Rambaldi E, Tucci A, Pontikes Y, Angelopoulos GN. *Sintered esseneite-wollastonite-plagioclase glass-ceramics from vitrified waste*. J Eur Ceram Soc. Vol.29, No.14, (2009), pp 2921-7.

Glass ceramics

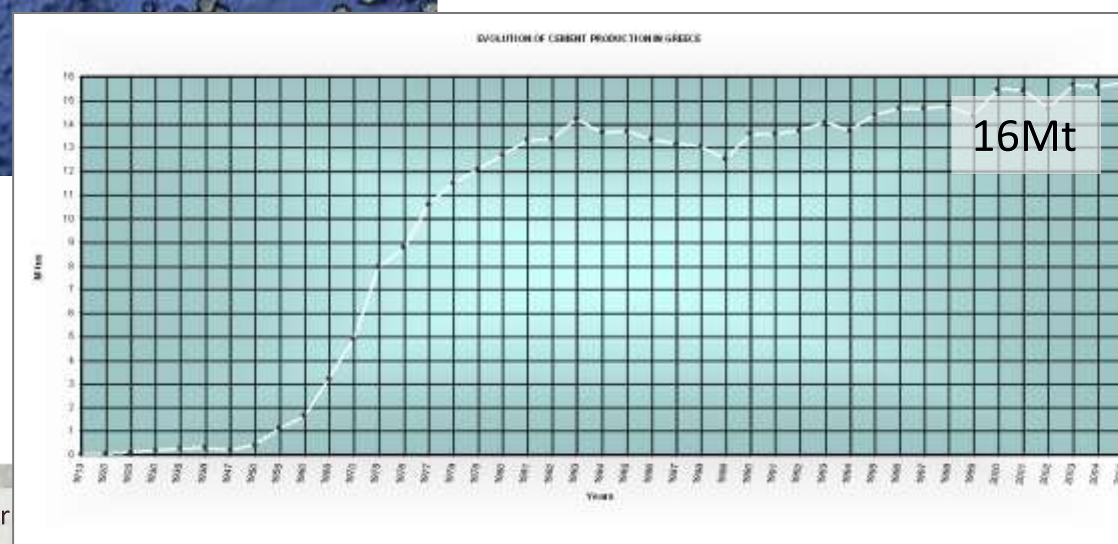
Sintering temp. (°C)	Soaking time (h)	Heating mode	Bulk density (g/cm^3)	Closed porosity (vol%)	Elastic modulus (GPa)	Bending strength (MPa)	HV (GPa)
900	0.5	C	2.82 ± 0.01	4.2	99.4 ± 1.2	89.6 ± 22.6	
900	1	C	2.84 ± 0.02	4.9	99.9 ± 0.7	100.9 ± 14.4	
900	2	C	2.84 ± 0.01	4.4	125.8 ± 4.6	132.6 ± 16.5	7.3 ± 0.3
900	0.5	R	2.80 ± 0.02	5.6	97.2 ± 7.0	96.5 ± 15.7	
900	1	R	2.82 ± 0.01	3.8	103.2 ± 6.9	102.9 ± 20.5	7.0 ± 0.3

- Dense and well crystallised glass–ceramics may be obtained with a “rapid sintering” treatment
- The well established simple and economic processing of traditional ceramic tiles can be used
- The substantial crystallisation led to remarkable mechanical properties: bending strength and Vickers micro-hardness exceeding 100 MPa and 7 GPa, respectively.

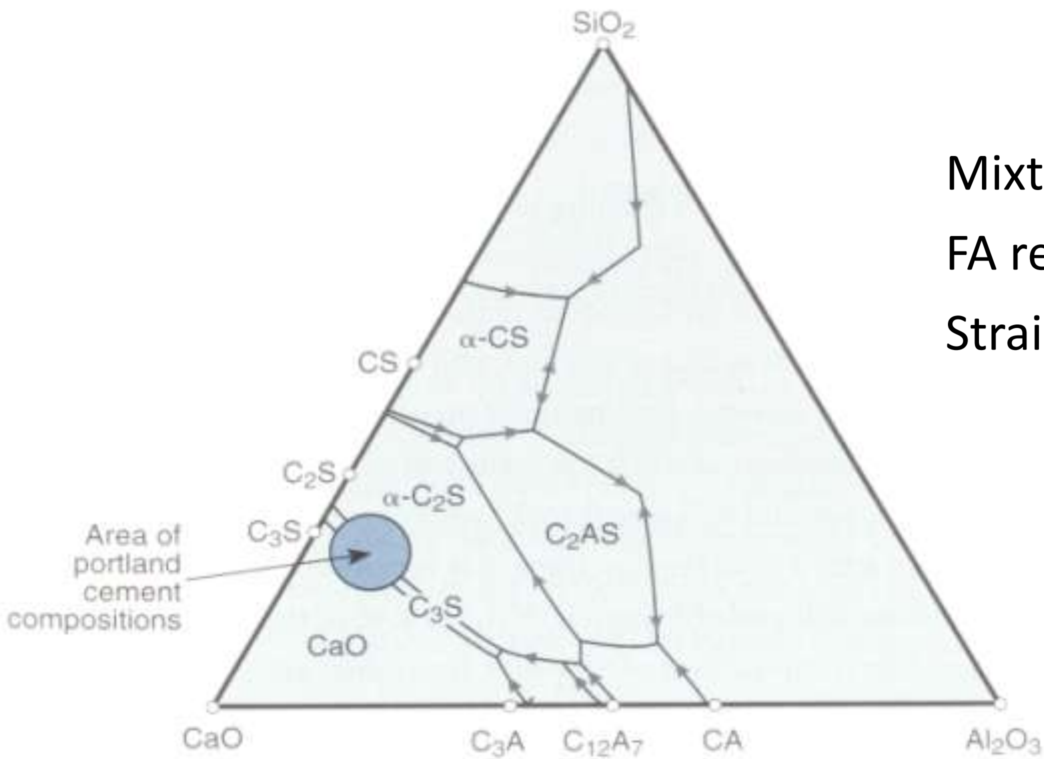
Bernardo E, Esposito L, Rambaldi E, Tucci A, Pontikes Y, Angelopoulos GN. *Sintered esseneite-wollastonite-plagioclase glass-ceramics from vitrified waste*. J Eur Ceram Soc. Vol.29, No.14, (2009), pp 2921-7.

OPC production with FA

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



OPC production with FA: lab scale



Mixture design based on Boque equations

FA replaced other Fe-rich wastes

Straight-forward use

- the alumina ratio (or modulus) $AR=Al_2O_3/Fe_2O_3$
- the silica ratio (or modulus) $SR=SiO_2/(Al_2O_3+ Fe_2O_3)$
- lime saturation factor $LSF=CaO/(2.8SiO_2+1.1\ Al_2O_3+0.65\ Fe_2O_3)$

Vangelatos, I., Angelopoulos, G. N. and Boufounos, D., Utilization of ferroalumina as raw material in the production of Ordinary Portland Cement. J. Hazard. Mater., 2009, 168, (1), 473-478.

OPC production with FA: lab scale

	Ref	1wt% FA	3wt% FA	5wt% FA
Specific Surface (cm^2/g)	3730	3810	4010	3870
Initial Setting Time (min)	100	100	80	90
Final Setting Time (min)	160	140	160	150
Water Demand (%)	21.6	22.4	22.6	22.2

	Compressive strength (MPa)					
	CEM I		Reference	1%wt FA	3%wt FA	5%wt FA
	42.5N	52.5 N				
2 days	≥ 10.0	≥ 20.0	19.2	26.5	27.4	30.8
7 days	NR*	NR*	39.2	48.2	42.9	44.3
28 days	≥ 42.5	≥ 52.5	55.6	62.9	57.5	58.4
90 days			57.5	69.6	65.2	63.0
180 days	NR*	NR*	60.2	71.2	67.8	68.3
360 days			64.3	73.1	69.8	70.2

*NR: No Requirement

Vangelatos, I., Angelopoulos, G. N. and Boufounos, D., Utilization of ferroalumina as raw material in the production of Ordinary Portland Cement. J. Hazard. Mater., 2009, 168, (1), 473-478.

OPC production with FA: lab scale

a) addition of FA as a raw material in the meal for OPC production is feasible up to the 5 wt%, with typical range 2-3 wt%,

b) FA addition does not affect the thermal behaviour of the meals and typically free lime less than 1 wt% can be obtained for T =1450 °C,

c) the microstructure of clinkers with FA is comparable to the reference sample,

d) differences in surface area, water requirement and setting time are negligible,

e) compressive strength after 2 days curing is >20 MPa, whereas after 28 days, it varies from 55 to 63 MPa (CEMI 52.5N category).

OPC production with FA: industrial trials

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

•Storing of FA 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 2.7wt% in FA.

•In all industrial trials, the use of FA 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 2wt% of FA 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 is estimated to be 0.15 €/t of cement.

•The microstructure and mineralogical composition of the clinkers with FA, 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 FA: 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 15/4/2011: http://www.lafarge.com/wps/portal/2_4_4_1-EnDet?WCM_GLOBAL_CONTEXT=/wps/wcm/connect/Lafarge.com/AllCS/Env/NR/CP1610621381/CSEN

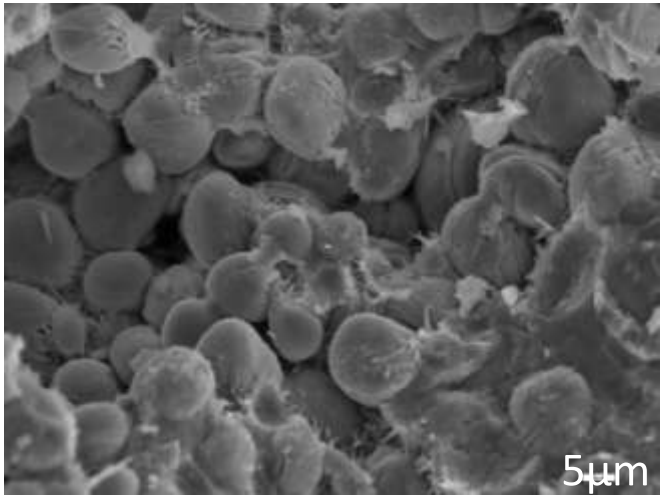
Belite-rich clinker

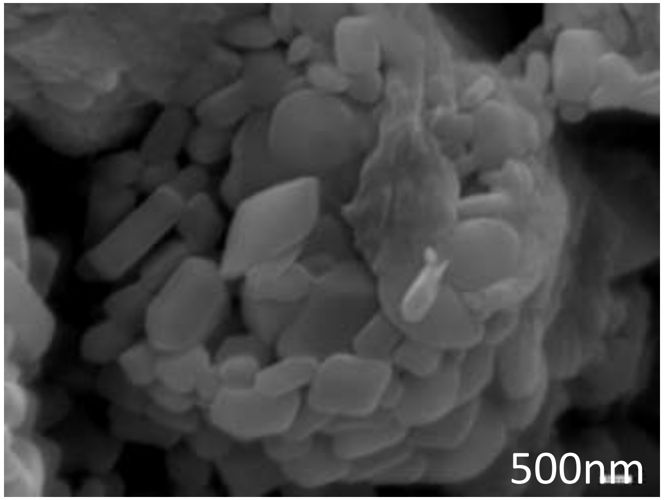
- Belite-rich clinkers are low CO_2 clinkers compared to OPC one
- Three compositions studied
- First blend was designed for high–belite content, >70 wt%, in conjunction with C_4AF content >12wt% which is the limit for OPC. This would result in higher utilisation of FA compared to addition for OPC
- The other two blends aimed at the formation of C_4AF with concurrent development of sulphur–bearing hydraulic compounds ($C_4A_3\hat{S}$, i.e. Klein compound or Ye'elimite), in order to enhance early strength

	BC	BSFC1	BSFC2
Calcite	82.80	70.00	38.00
Calcite (high purity)	-	-	14.20
FA	4.20	2.00	8.00
Shale	13.00	-	-
Bauxite	-	12.00	19.00
$CaSO_4$	-	16.00	20.80

Belite-rich clinker

FA for sulfo-aluminate-ferrite belitic type cements





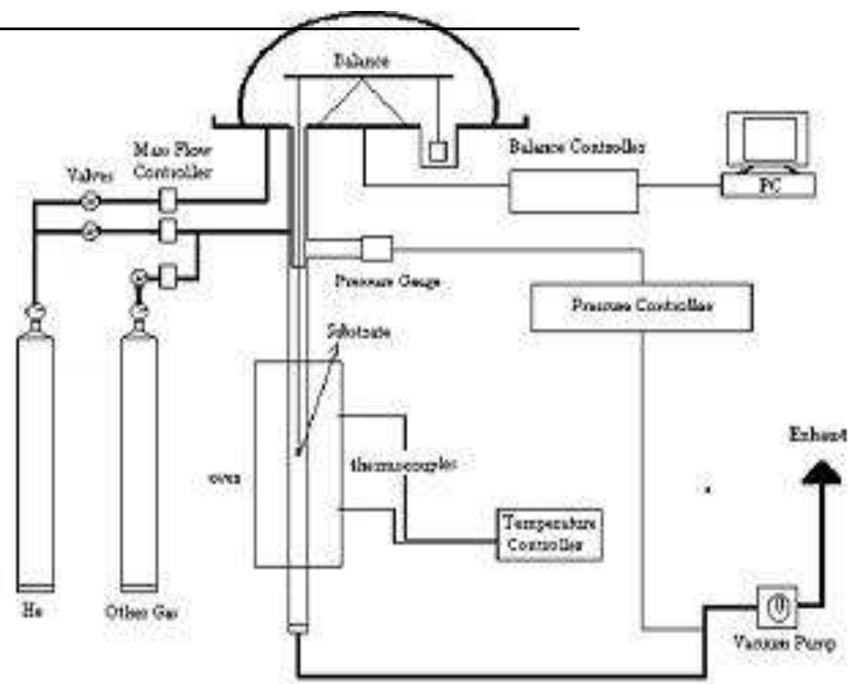
Compressive strength (MPa)	BC	BSFC1	BSFC2
1 d	-	17.6	14.9
2 d	5.0	25.8	23.5
7 d	17.5	36.8	30.1
28 d	53.7	43.7	34.2

Vangelatos, I., Pontikes, Y. and Angelopoulos, G. N., Ferroalumina as A Raw Material for the Production of “Green” Belite Type Cements. In SERES’ 09. I. International Ceramic, Glass, Porcelain Enamel, Glaze and Pigment Congress, 2009, Eskisehir, Turkey.

Catalysis for carbon nanotubes

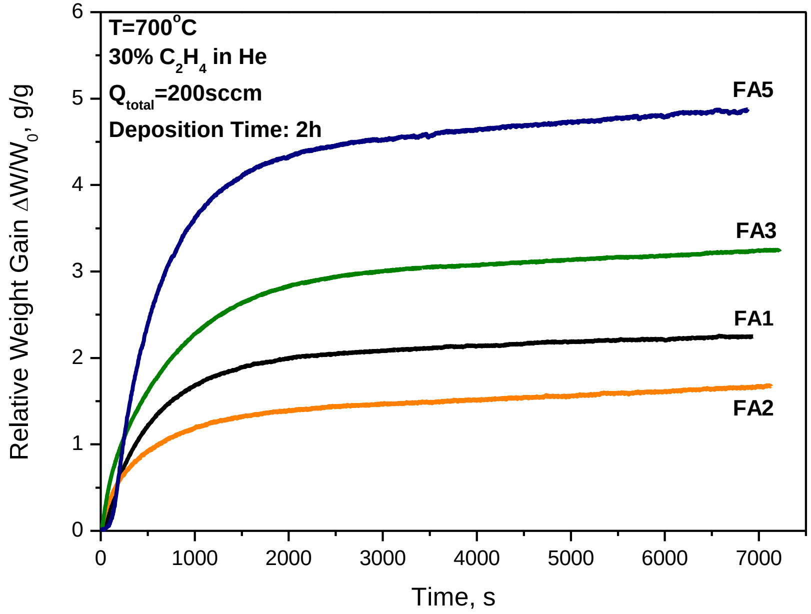
Ferroalumina quality	Description	Code name
Quality-I	Ferroalumina, “as is”	FA1
Quality-II	Ferroalumina, milled	FA2
Quality-III	Ferroalumina, particles of d< 90μm	FA3
Quality-IV	Ferroalumina, chemically treated	FA4
Quality-V	Ferroalumina, chemically & thermally treated	FA5

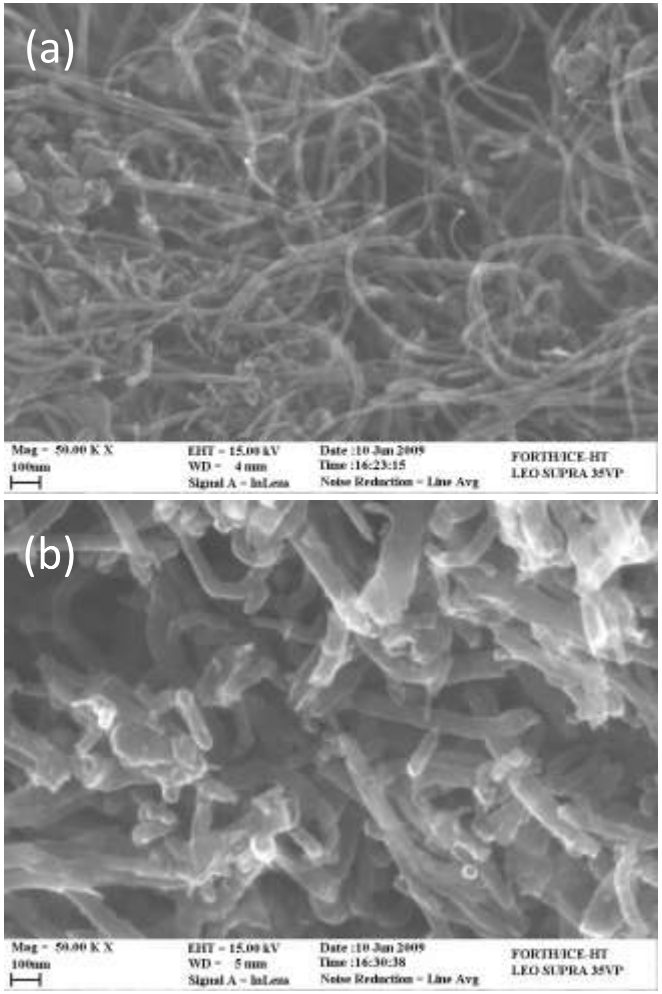
Influence of temperature and FA treatment on CNT quality and growth



Catalysis for carbon nanotubes

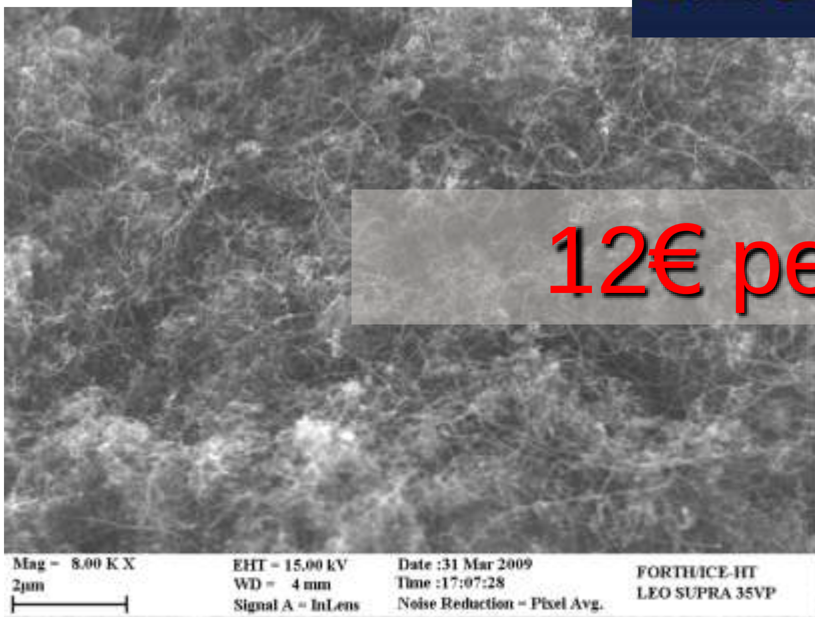
FA qualities	BET Specific surface area (m^2/g)	Initial growth rates (mg/s)	% Yield over catalyst
FA1	10	4.33	225
FA2	15	3.34	167
FA3	8	7.40	323
FA5	40	9.30	488

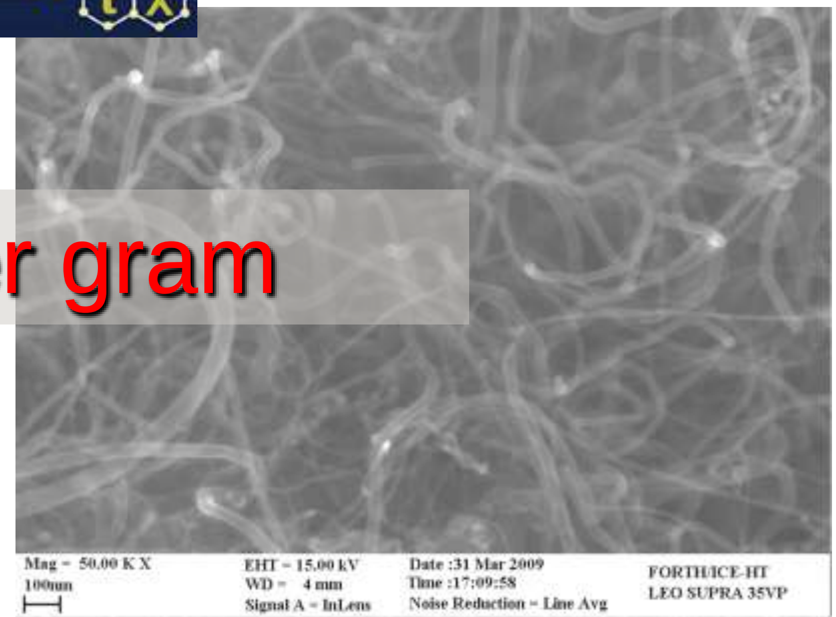




CNT deposited by ethylene decomposition over FA5 at 700°C (a) and 800°C (b)

Catalysis for carbon nanotubes





12€ per gram

High purity multi-wall carbon nanotubes (MWCNTs), of diam. 20nm to 55nm were produced via Chemical Vapour Deposition at an optimum temperature of 700°C, in 30% C_2H_4/He mixture, on chemical and thermally treated FA.

Other uses of FA

Other uses of FA have been studied elsewhere in Greece and a brief, non-exhaustive, overview is given as follows:

a) as re-vegetation cover
b) as filling material in mine open pits
c) as low permeability layer
d) in geotechnical application, such as road embankment
e) aimed for use in iron ore industry after reductive roasting and magnetic separation
f) for recovery of trace and minor elements
g) for production of alkali-activated construction materials

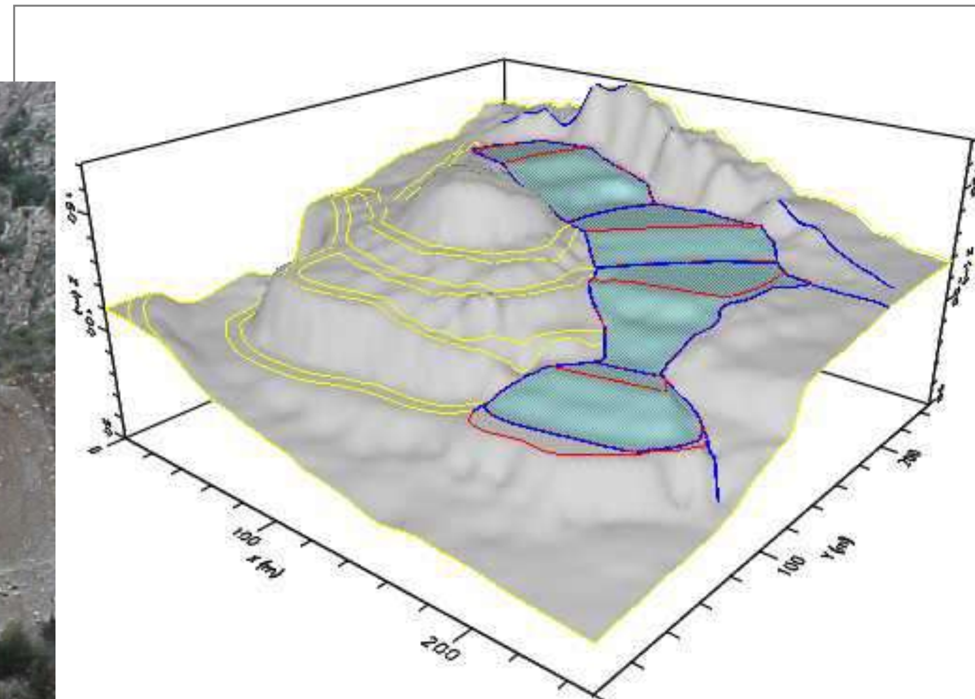
As re-vegetation cover

FA was mixed with waste gypsum, sewage sludge, $Ca(H_2PO_4)_2$, NH_4NO_3 and $FeSO_4{\cdot}7H_2O$, commercial fertilizer of type 21-0-0 (ammonium sulfate).

Xenidis A, Harokopou AD, Mylona E, Brofas G. Modifying alumina red mud to support a revegetation cover. JOM. Vol.57, No.2, (2005), pp 42-6

As filling material in open-pit mines

Layers of FA, 25-30 cm, controlled compaction, covering with other minerals, re-vegetation on top



Xenidis A, Boufounos D. Dry disposal of bauxite residues in abandoned mine open pits. Geotechnical Special Publication; 2008; New Orleans, LA; 2008. p. 40-7.

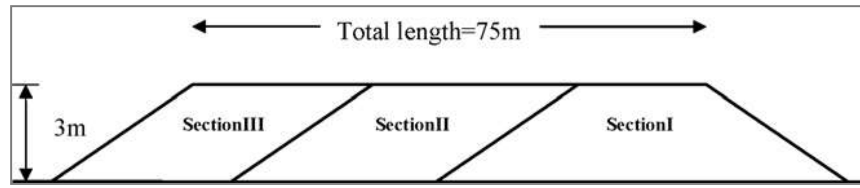
As low permeability layers in landfills

Target was to achieve hydraulic conductivity coefficient $K=1x10^{-7}$ cm/sec.
Result was $4x10^{-7}$ cm/sec.

Program LIFE03 ENV/GR/000213, Aluminium of Greece

As road embankment

Embankment 75m long, 3m high with a crown width of 8m. Three different sections of 25m long each; Section I (reference); natural soil of A-4 group, Section II; a mixture of a soil A-1 (60%) and bauxite residue (40%) and a Section II; mixture of bauxite residue with fly ash (4%). After 5 years: “excellent performance”.



Kehagia F. A successful pilot project demonstrating the re-use potential of bauxite residue in embankment construction. Resour Conserv Recy. Vol.54, No.7, (2010), pp 417-21.

Other uses…

In iron ore industry after reductive roasting and magnetic separation: Best Paper award in TMS 2010 Annual Meeting & Exhibition Light Metals, Seattle, WA, USA.

(by Xenidis A, Zografidis C, Kotsis I, Boufounos D. Reductive roasting and magnetic separation of Greek bauxite residue for its utilization in iron ore industry)

Recovery of trace and minor elements: Revived interest as China put quotas on REE export

(by Ochsenkühn-Petropoulou MT, Hatzilyberis KS, Mendrinos LN, Salmas CE. *Pilot-plant investigation of the leaching process for the recovery of scandium from red mud. Industrial and Engineering Chemistry Research. Vol.41, No.23, (2002), pp* 5794-801)

Production of alkali-activated construction materials: use also residual alkalinity

(by Dimas DD, Giannopoulou IP, Panias D. Utilization of alumina red mud for synthesis of inorganic polymeric materials. Mineral Processing and Extractive Metallurgy Review. Vol.30, No.3, (2009), pp 211-39)

Conclusions

A variety of uses for Bayer's process bauxite residue has been presented.

There are applications **industrially mature** (heavy clay ceramics and OPC), **industrially possible** (aggregates and belite-rich clinker) and **industrially promising** (glass-ceramics and catalysis for CNT).

Other applications, such as re-vegetation cover, filler for open-pit mines, embankment etc increase the resilience of the alumina company by offering flexibility and options.

The path from red mud to ferroalumina and finally, to an end-product has been rewarding but requires more than engineering.

So what is the solution?

Path 1 (actual paragraph from major consulting firm):

“Could global warming melt arctic ice making resources accessible?”

Path 2:

Sustainable materials’ management, industrial symbiosis parks, “secondary resources’ engineers”, radical change in mentality so that we do and ask for the obvious

Stay tuned!

INTERNATIONAL SEMINAR ON BAUXITE RESIDUE (RED MUD)

OCTOBER 17-19, GOA, INDIA

http://www.redmud.org

Thank you!