KATHOLIEKE UNIVERSITEIT
LEUVEN

Radioactive elements in Bayer’s process bauxite residue and their impact in valorization options

Y. Pontikes[1] , G. N. Angelopoulos[2] , B. Blanpain[1]

[1] K.U. Leuven, Belgium

[2] University of Patras, Greece

Transportation of NORM, NORM Measurements and Strategies, Building Materials

Overview of the presentation

Semantics

On the need of housing, thus building materials

KULeuven’s proposal

Case study on Bauxite Residue, red mud

Results and estimations

Need for further work and suggestion

Work presented herein based on: Pontikes, Y., Vangelatos, I., Boufounos, D., Fafoutis, D., Angelopoulos, G. (2006). Environmental aspects on the use of Bayer’s process Bauxite Residue in the production of ceramics. In Vincenzini, P. (Ed.), *Advances in Science and Technology: Vol. 45*. International Ceramics Congress and 4th Forum on New Materials. Acireale, Sicily, Italy, 4-9, June 2006 (pp. 2176-2181).

Semantics (for the coffee break!)

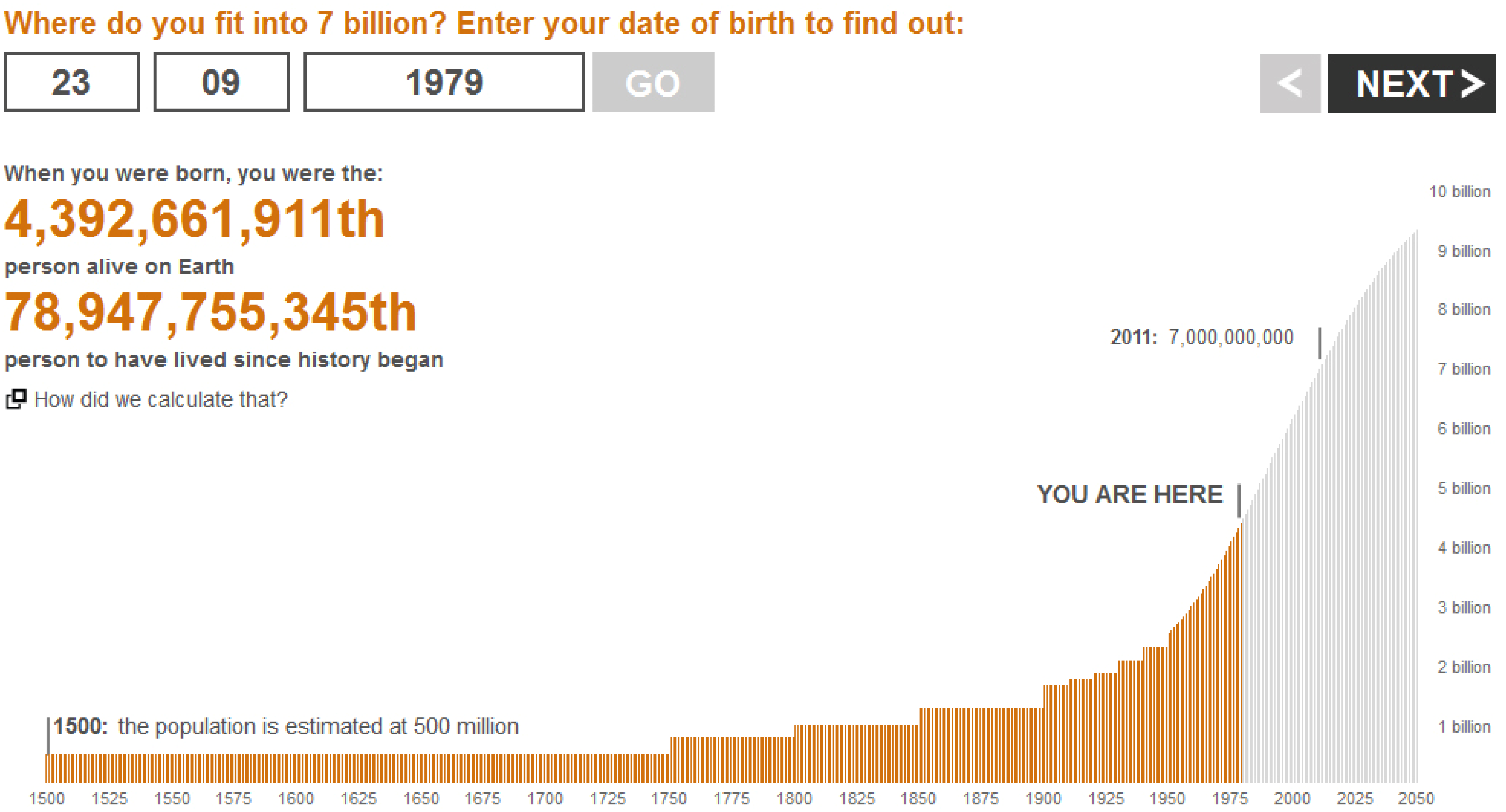
In this presentation, by convention, the following will be used and associated meaning would be implied:

NORM: Naturally Occurring Radioactive Material; all matter.

NERM: Nature-Enhanced Radioactive Material; higher radionuclide concentration compared to similar material because of physical or chemical process taking place in nature; bauxite is NERM

TERM: Technology-Enhanced Radioactive Material; higher radionuclide concentration compared to parent material due to anthropogenic activity; bauxite residue is TERM

See the big picture: megatrend



Where do you fit into 7 billion? Enter your date of birth to find out:

23 | 09 | 1979

When you were born, you were the:

4,392,661,911th

person alive on Earth

78,947,755,345th

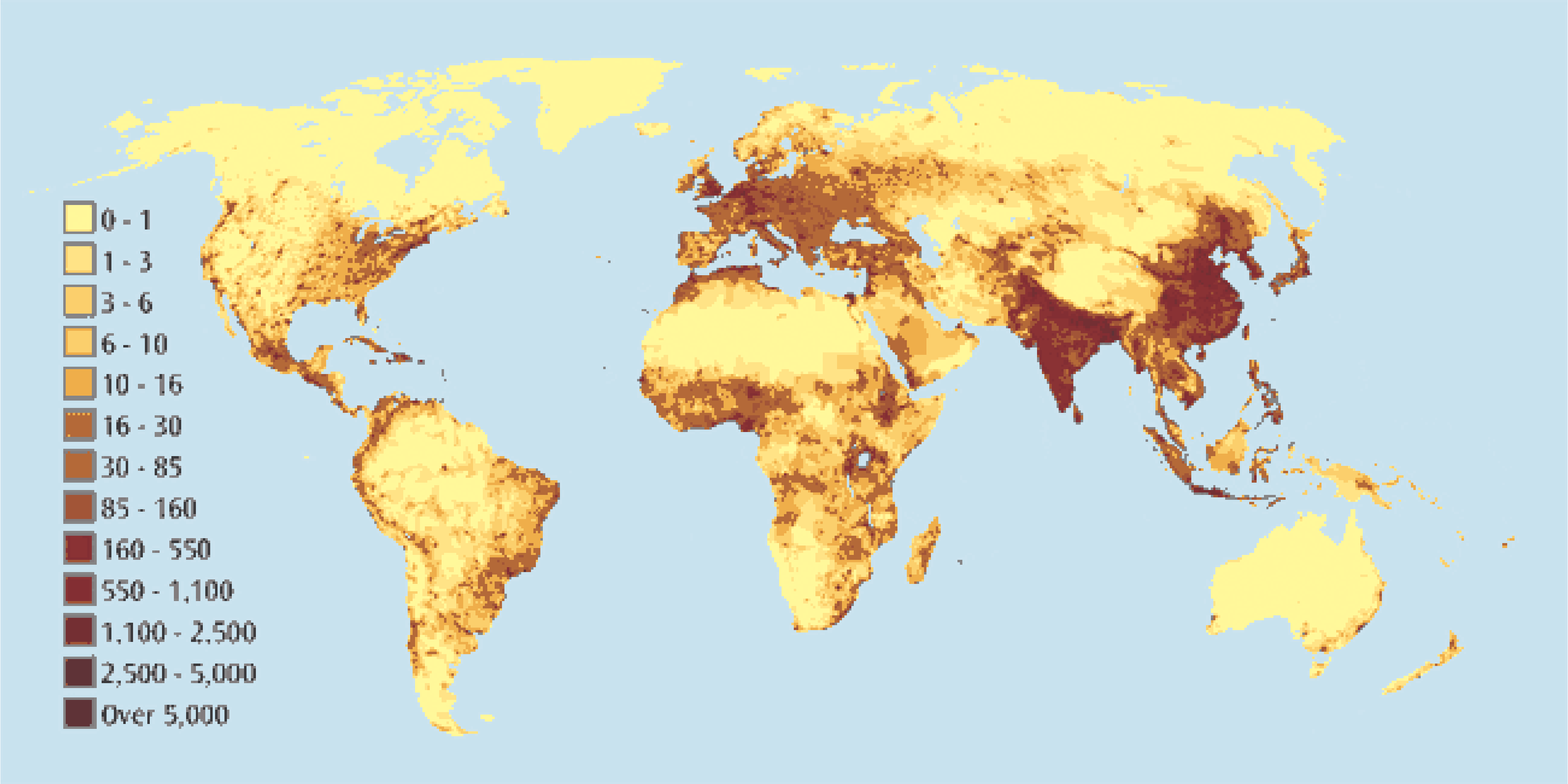
person to have lived since history began

How did we calculate that?

http://www.bbc.co.uk/news/world-15391515

Artist: MsgtBob, source: www.worth1000.com

Where are these 7 billion people?



http://www.theglobaleducationproject.org/earth/human-conditions.php

...and where are they staying?

http://www.overseaspropertymall.com

http://rio-de-janeiro.amazingcities.co.uk/favelas-in-rio-de-janeiro-brazil/

Great need for cheap, accessible and safe construction materials; likely 1 billion more slum dwellers within 30 years

(The Challenge of Slums - UN-HABITAT's Global Report on Human Settlements, www.unchs.org)

...and in Europe?

Europe is facing its own challenges.

- Lack of resources (see EU report on Critical Minerals),
- Weak industrial activity regarding mining and commodities
- High standards of living

⇓

Higher demand for innovation and high-tech/niche products, if strategic autonomy is to be maintained.

⇓

We develop zero waste processes for wastes (extraction of valuables and use of the residue)

“Secondary Resources’ Engineering”

...and what is the role of the State?

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)

KULeuven’s standpoint: SIM²

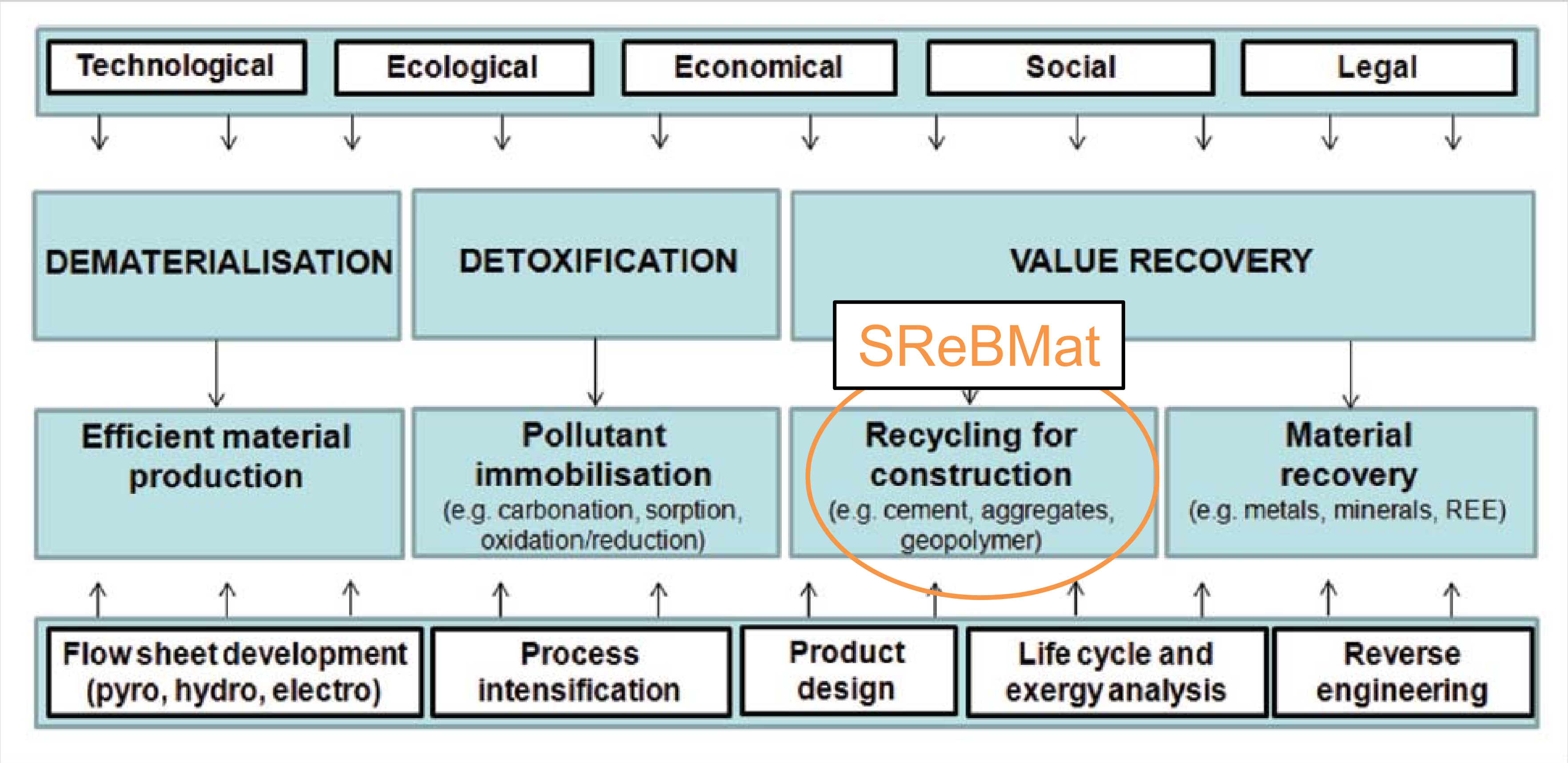
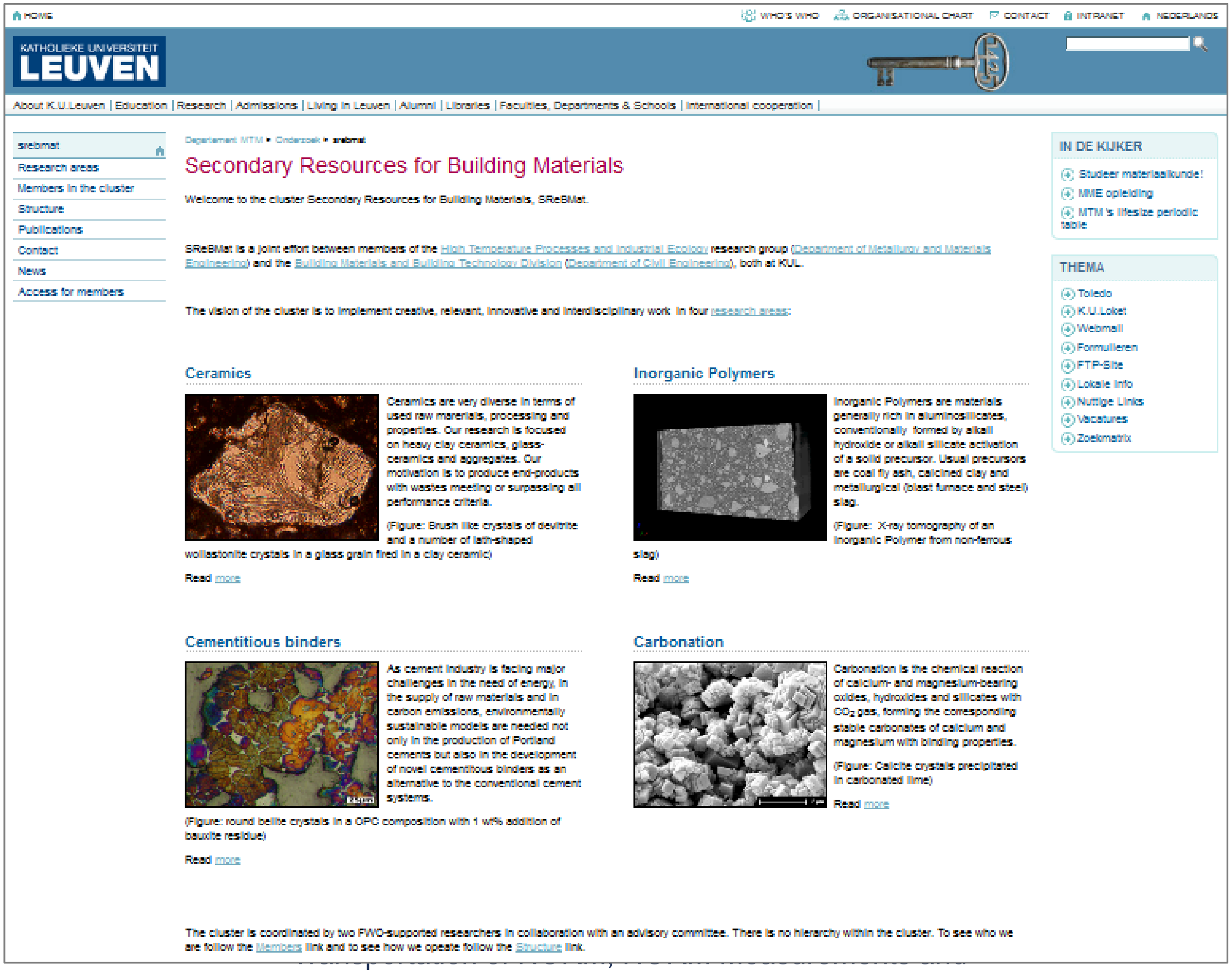


Figure 1. Research areas of SIM² consortium at K.U.Leuven.

Jones et al., JOM, 2012.

KULeuven’s standpoint

Secondary Resources for Building Materials: https://www.mtm.kuleuven.be/Onderzoek/srebmat



Secondary Resources for Building Materials

Welcome to the cluster Secondary Resources for Building Materials, SReBMat.

SReBMat is a joint effort between members of the High Temperature Processes and Industrial Ecology research group (Department of Metallurgy and Materials Engineering) and the Building Materials and Building Technology Division (Department of Civil Engineering), both at KUL.

The vision of the cluster is to implement creative, relevant, innovative and interdisciplinary work in four research areas:

Ceramics

Ceramics are very diverse in terms of used raw marerials, processing and properties. Our research is focused on heavy clay ceramics, glass-ceramics and aggregates. Our motivation is to produce end-products with wastes meeting or surpassing all performance criteria.

(Figure: Brush like crystals of devitrite and a number of lath-shaped wollastonite crystals in a glass grain fired in a clay ceramic)

Read more

Inorganic Polymers

Inorganic Polymers are materials generally rich in aluminosilicates, conventionally formed by alkali hydroxide or alkali silicate activation of a solid precursor. Usual precursors are coal fly ash, calcined clay and metallurgical (blast furnace and steel) slag.

(Figure: X-ray tomography of an inorganic Polymer from non-ferrous slag)

Read more

Cementitious binders

As cement industry is facing major challenges in the need of energy, in the supply of raw materials and in carbon emissions, environmentally sustainable models are needed not only in the production of Portland cements but also in the development of novel cementitous binders as an alternative to the conventional cement systems.

(Figure: round belite crystals in a OPC composition with 1 wt% addition of bauxite residue)

Read more

Carbonation

Carbonation is the chemical reaction of calcium- and magnesium-bearing oxides, hydroxides and silicates with CO_2 gas, forming the corresponding stable carbonates of calcium and magnesium with binding properties.

(Figure: Calcite crystals precipitated in carbonated lime)

Read more

The cluster is coordinated by two FWO-supported researchers in collaboration with an advisory committee. There is no hierarchy within the cluster. To see who we are follow the Members link and to see how we opeate follow the Structure link.

Secondary resources of interest

Slags from ferrous and non-ferrous metallurgy:
EAF, BOF, AOD and LM slags; secondary copper and lead slags

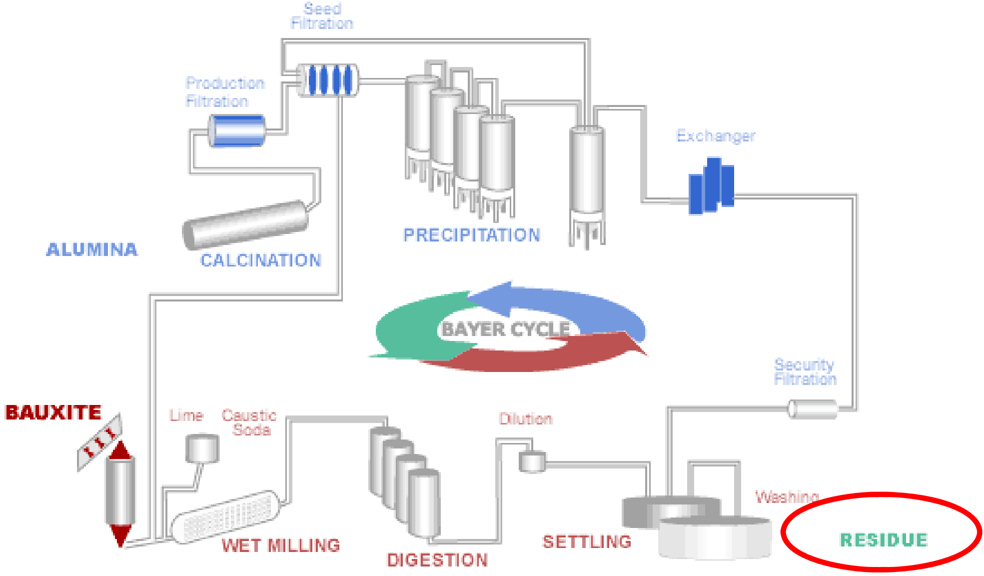
Mining residues:
Bauxite residue

Thermally treated wastes (also after landfill mining):
Municipal wastes after incineration or vitrification

Thermal residues from energy production:
Coal fly ash and bottom ash

Possible NORM? Could there be also external contamination?

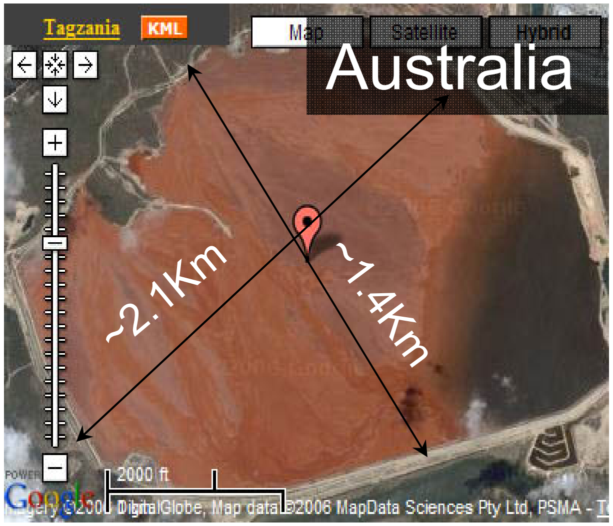
Case study: Bauxite Residue



Bauxite Residue, BR, is a slurry (~400g/l), with pH 12-13 and high ionic strength.

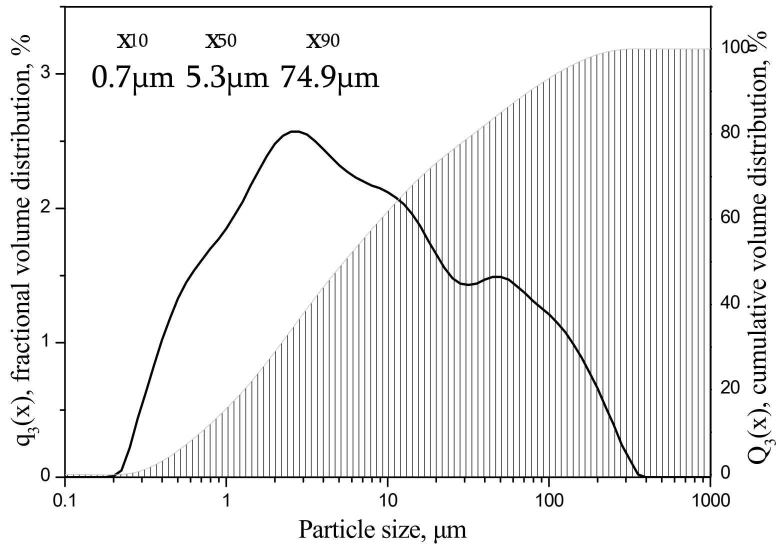
Worldwide production **~ 120Mt/y,** in stock: **2.7 billion tones**

www.redmud.org/Disposal.html



Case study: Bauxite Residue

	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**



Specific weight 3.4g/cm^3

Specific surface ~11m^2/g

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 $1.0Na_2O \cdot Al_2O_3 \cdot 1.68SiO_2 \cdot 1.73H_2O$

Bauxite Residue recently

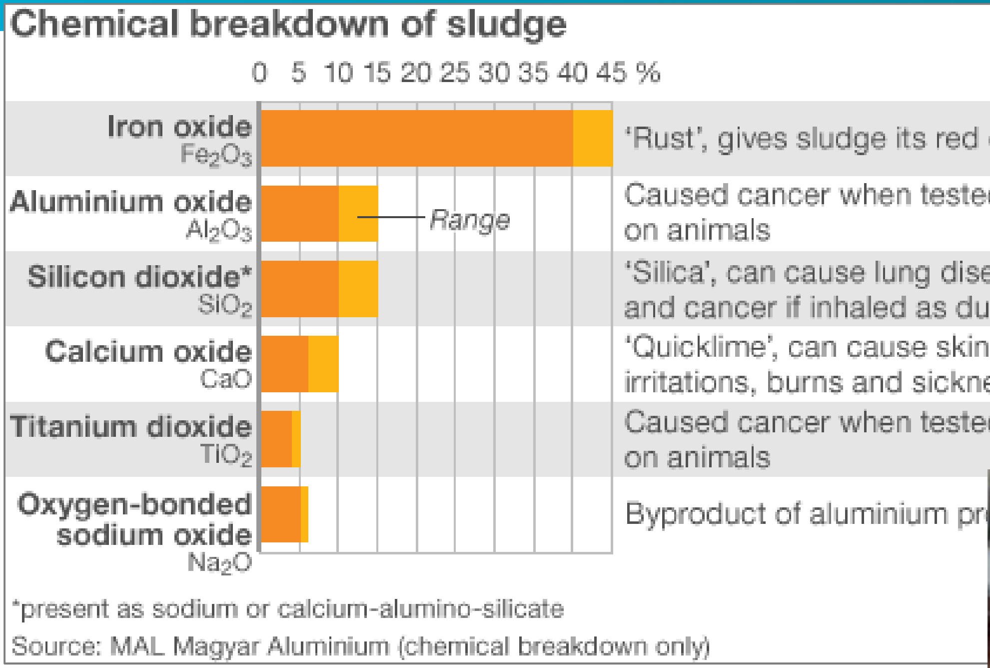
Ajka refinery, Hungary (before)

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.

“Educating” the public: perception



Chemical breakdown of sludge

Iron oxide Fe_2O_3	‘Rust’, gives sludge its red colour
Aluminium oxide Al_2O_3	Caused cancer when tested on animals
Silicon dioxide* SiO_2	‘Silica’, can cause lung diseases and cancer if inhaled as dust
Calcium oxide CaO	‘Quicklime’, can cause skin irritations, burns and sickness
Titanium dioxide TiO_2	Caused cancer when tested on animals
Oxygen-bonded sodium oxide Na_2O	Byproduct of aluminium pr

*present as sodium or calcium-alumino-silicate

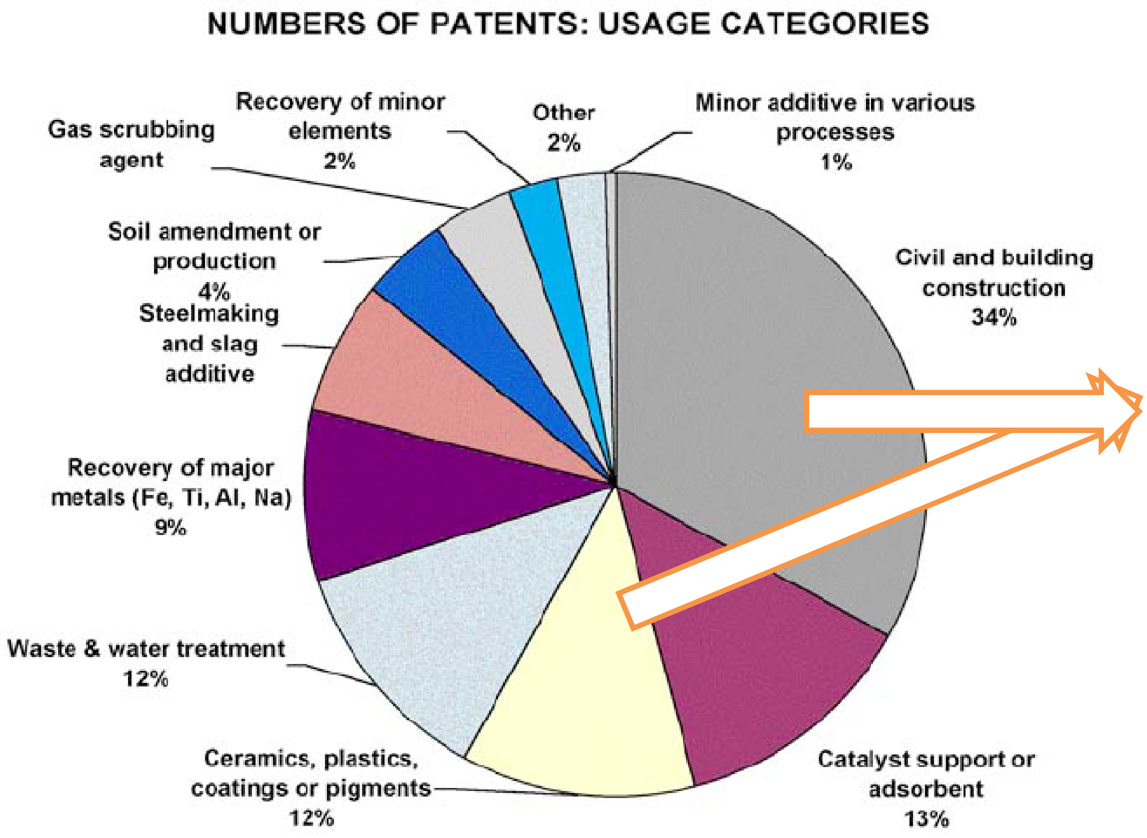
Source: MAL Magyar Aluminium (chemical breakdown only)

Source of table: BBC news

“Red mud is a toxic and radioactive waste”

Q: What is the regulatory framework for BR?

Possible applications for BR

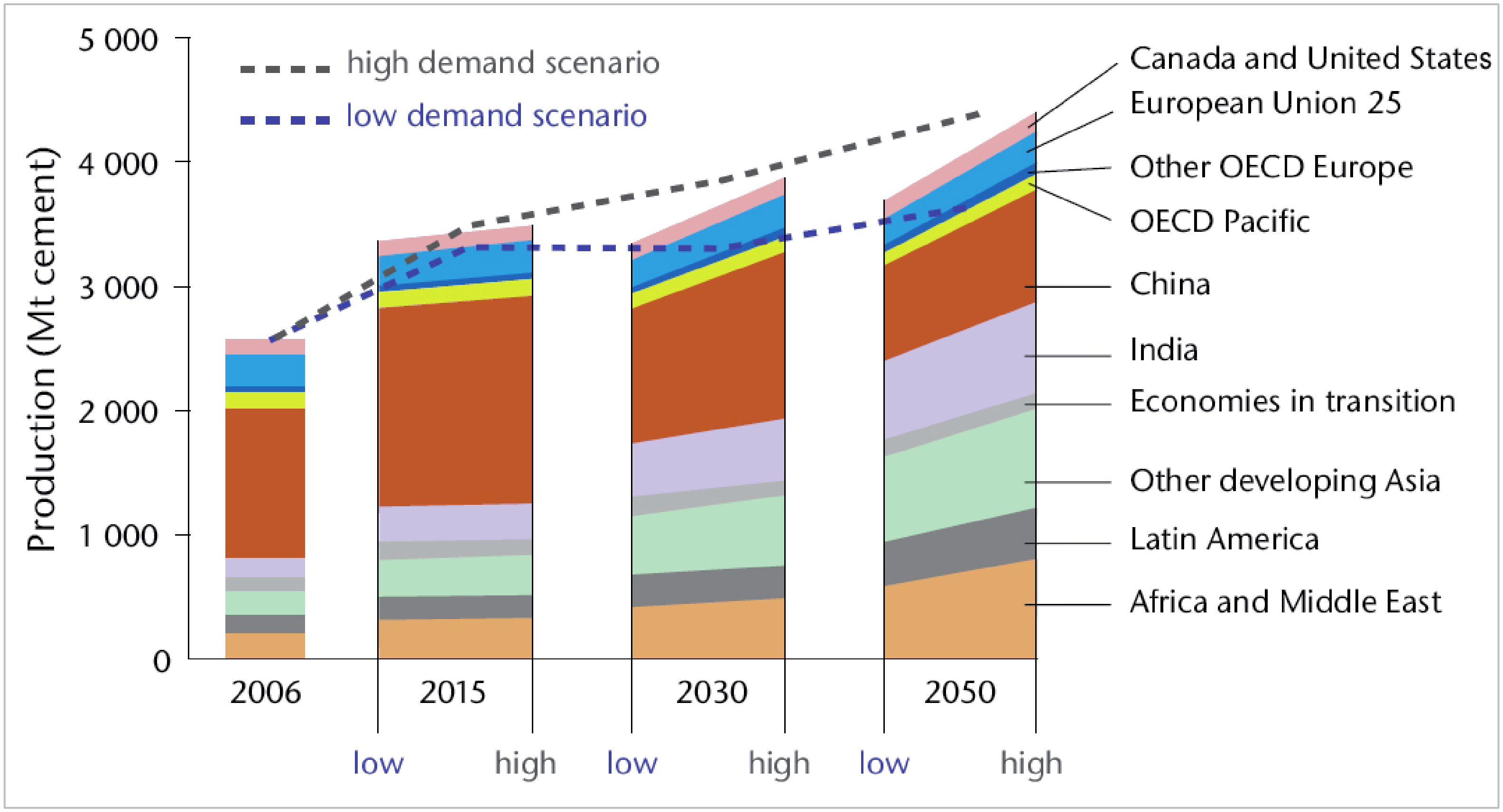


Heavy clay ceramics
Glass-ceramics
Cement
Concrete
Aggregates

C. Klauber, et al, Review of Bauxite Residue Re-use Options, in: CSIRO Minerals, Waterford, WA., 2009, pp. 1-77.

Example: cement production

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

Example: ceramic production

Industrial experiments

Future?

And what about natural radioactivity?

Red mud products show fairly high levels of radioactivity, but **they do not pose a problem in their application as paving**…[Beretka J., Mathew P.J.,1985].

... Using readily available red mud for the constructing walls in a typical Jamaican low-income house **is likely to result in effective γ dose-equivalent increments above background on the order of 0.72 mSv y^{-1} or less** to individual dwellers. [Pinnock W. R., 1991].

Limit is 1 mSv y^{-1}. Measured value for a room built with bricks having a composition 50%BR, 43% sand and 7% cement (in wt%?). Levels of natural radioactivity for BR used comparable to Greek BR. Room dimensions close to prototype room, occupation 24h d^{-1}

And what about natural radioactivity?

The use of waste bauxite residue was trialled in a test building in the early 1980s. However, the Health Department rejected the building after **tests registered radioactivity readings which bordered on the maximum acceptable radiation exposure levels for 19 hours a day**. The residue contained radioactive thorium and uranium. [The West Australian, 1 February 2002].

... Natural radiation presents a problem for using the residue to produce building material and for building upon disposal areas. **The radiation concern represents an unacceptable commercial risk to making building products from the residue.** [Bauxite Residue Technology Roadmap, 2000].

Literature summary and the goal

- The literature reports an increase in natural radioactivity for traditional ceramics with BR addition.
- Increased levels do not necessarily lead to environmentally problematic behaviour.
- It is likely that a maximum percentage addition for BR addition in the raw materials blend will be specified.
- It is also likely that different scenarios would have to be considered where the characteristics of the end-product (total porosity, pore size distribution, glazing, etc), and the use of material (i.e. superficial, bulk, external, internal) will be taken into account.

Introduction of BR in building materials has to reassure

environmental friendly (i.e. leaching and radioactivity) behaviour

Measurement of NORM

Experimental

Gamma ray spectroscopy using a 70% efficiency high purity germanium detector. Measured by the Greek Atomic Energy Commission according to the standard method [IAEA, 1989].

Analysis

Based on applying scenarios for activity indexes and on the methodology presented by Markannen and endorsed by EC.

Comparing different BR

Country	**Reference**	**^{238}U Bq/kg**	**^{226}Ra Bq/kg**	**^{228}Ra Bq/kg**	**^{228}Th Bq/kg**	**^{232}Th Bq/kg**	**^{40}K Bq/kg**
Greece	This work	149 ± 32	379 ± 43	419 ± 31	472 ± 23	472* ± 23	21 ± 11
Australia	[Beretka, J. et al., 1985]	n.r.	326	n.r.	n.r.	1129	30
Australia	[Cooper B. M., et al, 1995]	400 ± 20	310 ± 20	1150 ± 50	1350 ± 40	n.r.	350 ± 20
Australia	[O' Connor, B. H., 2004]	(150-600)	n.r.	n.r.	n.r.	(1000-1900)	(70-230)
Jamaica	[Pinnock W. R., 1991]	n.r.	370	n.r.	n.r.	328	265
Jamaica	[Pinnock W. R., 1991]	n.r.	1047	n.r.	n.r.	350	335
China	[Wang, K., 1992]	n.r.	477	n.r.	n.r.	705	153

The activity index

To quantify the effect from natural occurring radioactivity, “activity indexes” are employed. They are calculated on the basis of the measured activity concentrations of radium ($_{226}$Ra), thorium ($_{232}$Th) and potassium ($_{40}$K) (and $_{137}$Cs exceptionally).

Activity Index: case A

➡ Case A: Bricks

$$I_1 = \frac{C_{Ra}}{300 Bq\ kg^{-1}} + \frac{C_{Th}}{200 Bq\ kg^{-1}} + \frac{C_K}{3000 Bq\ kg^{-1}} = 1$$

Maximum addition in mixture of raw materials ≤ 14wt.%.
(Dose criterion 1 mS a^{-1})

Activity Index: case B

➡ Case B: Floor and roofing tiles

$$I_1 = \frac{C_{Ra}}{300 Bq\ kg^{-1}} + \frac{C_{Th}}{200 Bq\ kg^{-1}} + \frac{C_K}{3000 Bq\ kg^{-1}} = 6$$

No restrictions from a radiological point of view apply
(Dose criterion 1 mS a^{-1})

Activity Index: case C

Case C: Ceramics for exterior applications
(“materials used for streets and playgrounds”)

$$I_1 = \frac{C_{Th}}{500 Bq\ kg^{-1}} + \frac{C_{Ra}}{700 Bq\ kg^{-1}} + \frac{C_K}{8000 Bq\ kg^{-1}} + \frac{C_{Cs}}{2000 Bq\ kg^{-1}} = 1$$

Maximum addition in mixture of raw materials ≤ 61 wt.%.
(Dose criterion 0.1 mS a^{-1})

Conditions for the Activity Index

The activity index I_1 has been based on the following assumptions:

a) Room of dimensions 4m x 5m x 2.8m,

b) All surfaces (walls, floor and ceiling) are made of the same material

c) Material used has density 2350 kg m^{-3} and surface structure is 20cm thick

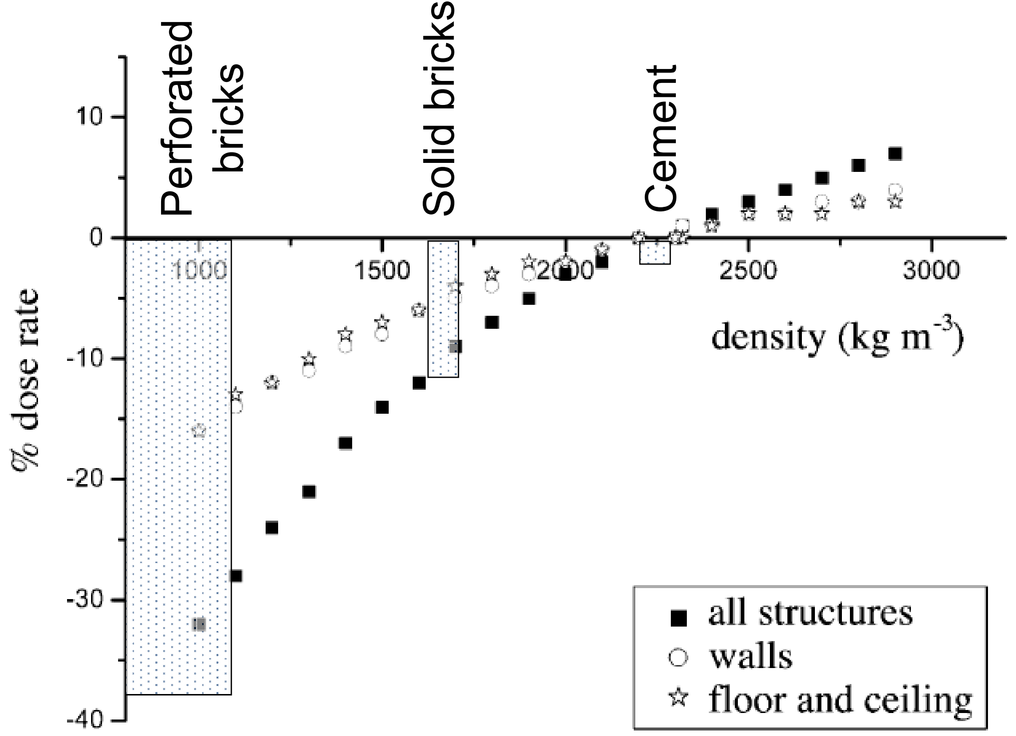
d) No windows and doors present

e) Occupation in the house 7000 h a^{-1} (19 h per day approximately).

f) The conversion factor 0.7 Sv Gy^{-1}, [UNSCEAR, 1993] is used for converting the absorbed dose in air to the effective dose and the gamma dose rate from Earth's crust is 50 nGy h^{-1}.

g) No adjoining rooms are taken into consideration

Sensitivity analysis of the model



S. Risica et al. / The Science of the Total Environment 272 (2001) 119–126

Brick densities:
850kg/m^3 ~ 1050kg/m^3 (Greece)
They are perforated (hollow).

Model highly sensible in density.

Model would predict ≈ −30% dose rate, than the case where d = 2350 kg/m^{-3}.

Not comparison (known) with experimentally measured gamma rays emission.

Over-estimation seems logical.

Markannen's methodology

Case Study:

What if floor and ceiling were made of cement and walls were made of bricks?

We apply Markannen's (cited in EC directive) methodology.

Consider material X for brick: $_{226}$Ra: 278 Bq kg^{-1}, $_{232}$Th: 347 Bq kg^{-1} and $_{40}$K: 223 Bq kg^{-1}.

For concrete: "bibliography" values.

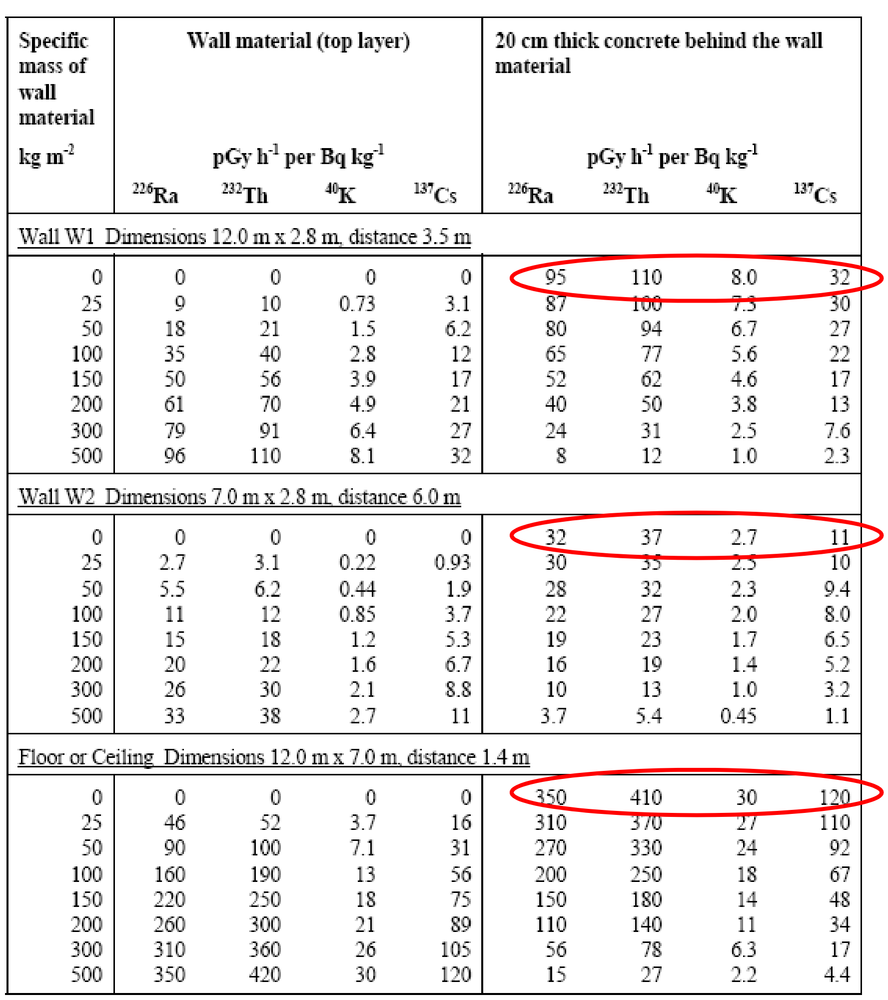


Table IX. Specific dose rate in air from the different structures in the room of Figure 1.

Specific mass of wall material kg m^{-2}	Wall material (top layer) pGy h^{-1} per Bq kg^{-1}				20 cm thick concrete behind the wall material pGy h^{-1} per Bq kg^{-1}			
	^{226}Ra	^{232}Th	^{40}K	^{137}Cs	^{226}Ra	^{232}Th	^{40}K	^{137}Cs
Wall W1 Dimensions 12.0 m x 2.8 m, distance 3.5 m								
0	0	0	0	0	95	110	8.0	32
25	9	10	0.73	3.1	87	100	7.3	30
50	18	21	1.5	6.2	80	94	6.7	27
100	35	40	2.8	12	65	77	5.6	22
150	50	56	3.9	17	52	62	4.6	17
200	61	70	4.9	21	40	50	3.8	13
300	79	91	6.4	27	24	31	2.5	7.6
500	96	110	8.1	32	8	12	1.0	2.3
Wall W2 Dimensions 7.0 m x 2.8 m, distance 6.0 m								
0	0	0	0	0	32	37	2.7	11
25	2.7	3.1	0.22	0.93	30	35	2.5	10
50	5.5	6.2	0.44	1.9	28	32	2.3	9.4
100	11	12	0.85	3.7	22	27	2.0	8.0
150	15	18	1.2	5.3	19	23	1.7	6.5
200	20	22	1.6	6.7	16	19	1.4	5.2
300	26	30	2.1	8.8	10	13	1.0	3.2
500	33	38	2.7	11	3.7	5.4	0.45	1.1
Floor or Ceiling Dimensions 12.0 m x 7.0 m, distance 1.4 m								
0	0	0	0	0	350	410	30	120
25	46	52	3.7	16	310	370	27	110
50	90	100	7.1	31	270	330	24	92
100	160	190	13	56	200	250	18	67
150	220	250	18	75	150	180	14	48
200	260	300	21	89	110	140	11	34
300	310	360	26	105	56	78	6.3	17
500	350	420	30	120	15	27	2.2	4.4

Markannen’s methodology

Source	Calculation	Dose rate
2 x W1	2 · (95 · **278** + 110 · **347** + 8 · **223**)	0.133 μGy h^{-1}
2 x W2	2 · (32 · **278** + 37 · **347** + 2.7 · **223**)	0.045 μGy h^{-1}
Floor and ceiling	2 · (350 · **40** + 410 · **30** + 30 · **400**)	0.077 μGy h^{-1}
Dose rate in the room (cosmic radiation excluded)		0.254 μGy h^{-1}

To find the **excess gamma dose** rate we subtract the gamma dose rate from Earth’s crust:

0.254 μGy h^{-1}– 0.050 μGy h^{-1} = 0.204 μGy h^{-1},

Therefore:

0.7 Sv Gy^{-1} * 7000 h a^{-1} * 0.204 μGy h^{-1} = **1mSv**

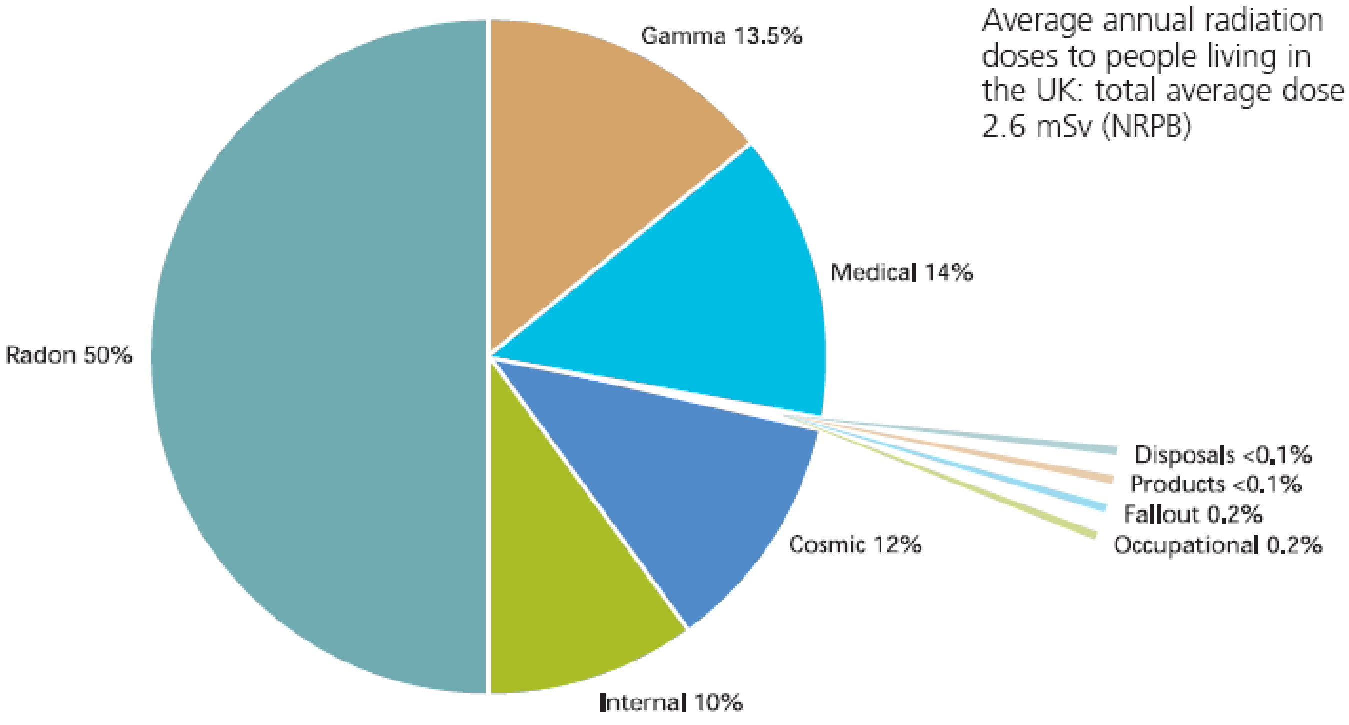
Markannen’s methodology

The material X described before is a
71wt.% BR and 29wt.% Greek clay brick.
Therefore if we make floor and ceiling out of cement,
bricks may have up to 71wt.% BR.

To verify the Markannen method followed, we considered 14wt.% BR in all surface structures, like in the activity index, and we found annual dose rate 0.96 mSv ≈ 1.0 mSv (self-consistent).

Regarding Radon and Thoron

Gamma rays would account for 14% of the annual radiation dose. Radon is 50%. [Nuclear Industry Association, UK]



Average annual radiation doses to people living in the UK: total average dose 2.6 mSv (NRPB)

Regarding Radon and Thoron

Both gases. Emission related to open porosity, surface porosity etc. In general (EC, 1999):

When gamma doses are limited to levels below 1 mSv a^{-1}, the $_{226}$Ra concentrations in the materials are limited, in practice, to levels which are unlikely to cause indoor radon concentrations exceeding the design level of the Commission Recommendation (200 Bq m^{-3}).

But:

Separate limitations for radon or thoron exhaling from building materials should be considered where previous evaluations show that **building materials may be a significant source of indoor radon or thoron** and restrictions put on this source is found to be an efficient and a cost effective way to limit exposures to indoor radon or thoron.

Comparison of end-products

		$_{226}$Ra Bq kg^{-1}	$_{232}$Th Bq kg^{-1}	$_{40}$K Bq kg^{-1}	$_{238}$U Bq kg^{-1}	**Reference**
14wt.% BR brick	Greece	82	104	615	127	This work, calculated
Clay brick	Greece	(18–66)	(5–79)	(100–1050)	(20–100)	S. Stoulos, et al., 2003.
Red brick	EU*	50	50	670	n.r.	EC, 1999.
Sand-lime brick	EU*	10	10	330	n.r.	EC, 1999.
Cement	EU*	40	30	400	n.r.	EC, 1999.
White porcelain tile	Italy	n.r.	(40-89)	(528-1000)	(118-247)	Bruzzi L, *et al.*, 1993.
Granite tiles	Italy	n.r.	(50-340)	(650-1630)	(81-148)	Bruzzi L, *et al.*, 1997.

EU*: Typical concentrations are population-weighted national means of different Member States.
In brackets: variation

Conclusions

- By applying the activity index, BR addition in the raw blend may vary from 14wt.% to 100wt.%, depending on the type of ceramic and the extent of use in the dwelling.
- A critical view on the assumptions the activity index has been based on is required and it should be used as a screening tool.
- In any event, actual decisions on the use of a material with BR should be based on realistic conditions.
- Higher addition percentages of BR in raw mixture for bricks, seem possible if floor and ceiling are made of cement.

Way forward

➢Even in literature, activity index is described as “regulation” not as a screening tool. No comply = danger

➢Public perception is a major non-technical barrier. Even if a brick is safe, it will not be sold if “contains more radioactivity” than alternative. Is this something for the Society to increase its awareness and be more proactive? We are inter-linked

➢It is accepted that the model overestimates in case of bricks. Who is developing the “more elaborated” model required? Why don’t we adopt a model from literature (possibly already validated) to account for difference in density, variations in building materials etc? Precision and validation is key

➢“Building material” implies any of the following (indicative): solid and perforated bricks, facade, floor, wall and roofing tiles, concrete etc. Each product comes with different scenario regarding use in dwelling, exposure etc. There is need for specific activity index per material

➢What about other materials, i.e. mineral wool or glass?

➢Who is guaranteeing the final product in terms of safety? Liabilities?

➢In general, a more clear framework (terminology, assessment, regulation) would be beneficial for waste-users

Acknowledgements/Contact

YP is thankful to the Research Foundation – Flanders (FWO) for the post-doctoral fellowship.

More information:

http://www.redmud.org/home.html

https://www.mtm.kuleuven.be/Onderzoek/srebmat/

Thank you