Radionuclide behaviour in potential applications of phosphogypsum

Fernando P. Carvalho, João M. Oliveira, Margarida Malta
Laboratório de Protecção e Segurança Radiológica,
Instituto Superior Técnico, Universidade de Lisboa,
Estrada Nacional 10, km 139, 2695-066 Bobadela LRS, Portugal
E-mail : carvalho@itn.pt

OUTLINE

- Recycling phosphogypsum
- Radionuclides in phosphogypsum and cement components
- Cement production
- Tests on radionuclide behaviour
- Conclusions

PHOSPHOGYPSUM AVAILABILITY

- Abundant in many countries (*ca* $3x10^9$ tonnes) as a by-producyt of phosphoric acid production
- Phosphogypsum piles:
  - largely unused
  - potential for re-use
  - environmental liability
  - caused several environmental disasters
- For low price or for free, industry would like to get read of it. The «holly graal» for phosphate industry is to became: «stack free»!

USES OF PHOSPHOGYPSUM: DRAWBACKS

- Several uses have been attempted: plaster, briques, soil amendment, road pavement, cement additive, etc.

- Re-use is difficult when phosphogypsum contains high concentrations of radionuclides and other metals

(...it is easy when phosphogypsum is low in radioactivity)

QUERIES

1) **BSS recommendations (keep radiation exposure low, justification, etc.) and SPREADING phosphogypsum in the environment/applications seems conflicting**

2) **with re-use, the uranium recover from non-conventional sources (reprocessing PG) will become impossible**

3) **no clear option was made about recovery of uranium from phosphoric acid yet, <u>but</u> improved quality of fertilizers and PG may require removal of uranium (and Cd, As, Hg) .**

INCORPORATION IN CEMENTS

- Might be the best matrix for long term immobilization of radionuclides

- Application of cement may be controlled and restricted to use in bridges, viaducts, etc., thus avoiding use in buildings and close contact /direct exposure of people.

Phosphogypsum ponds (Portugal)

Incorporation in cement

We decided to test this option.

Questions asked:

1) **Manufacture of cement includes step for clinker production in furnaces at ~1200º C: what is the fate of radionuclides ?**

2) **Concrete preparation involves mixing with high water volumes and hardening of cement requires continued watering for days. Can radionuclides from PG dissolve and be released with water?**

3) **Concrete structures built with cement containing PG will last for decades. Can these structures become a source of**
   - **gamma radiation (external radiation),**
   - **radon,**
   - **radionuclide leaching into the environment?**

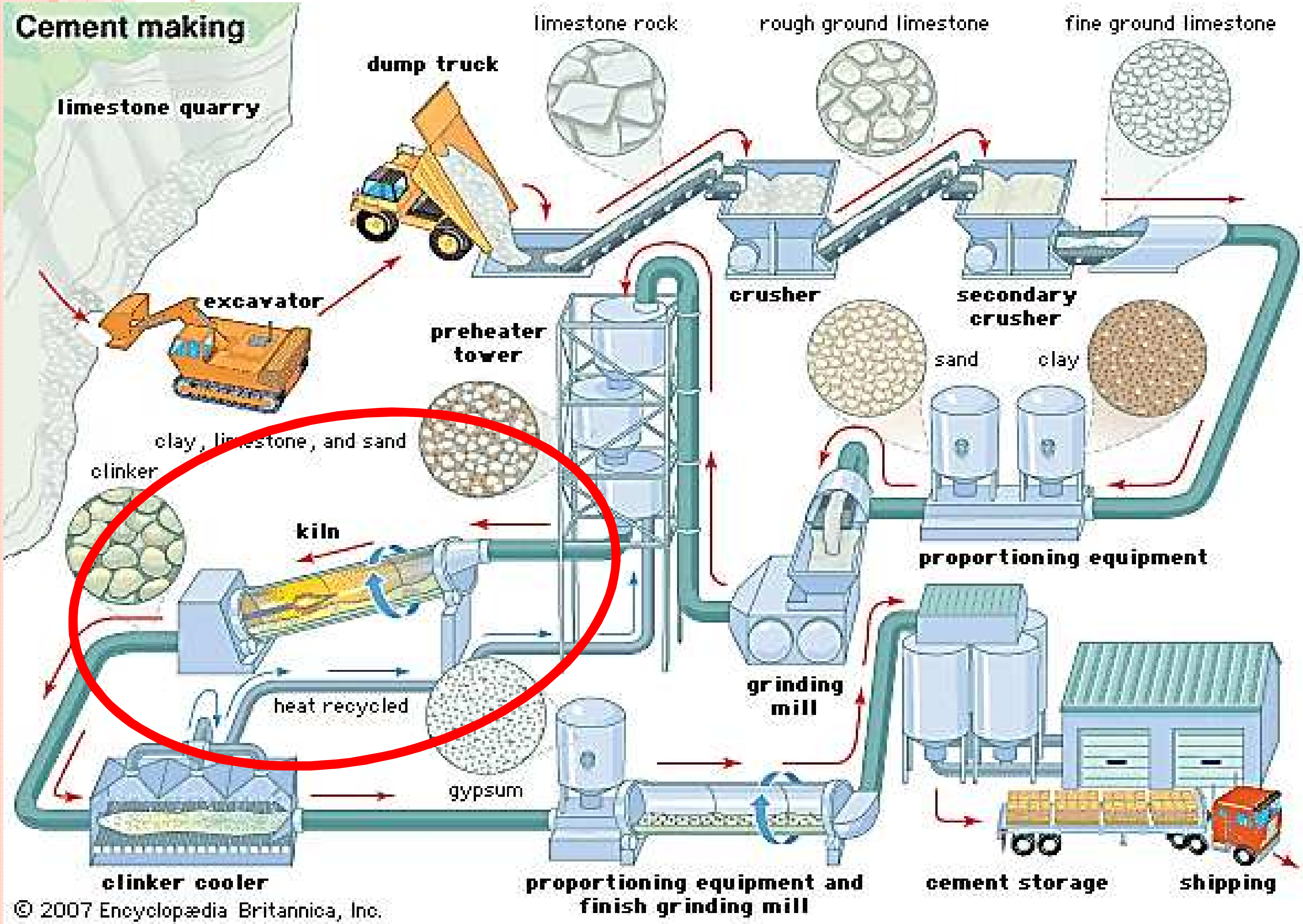
Starting point: materials and radionuclides in cement

Radionuclide concentrations (Bq/kg) in phosphogypsum and in common components of cement

Material	^{238}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
Phosphogypsum	200	730	345	830	830
Common components of cement:					
Limestone	24	28	24	17	32
Process sand	19	29	33	16	15
Fly ash	107	102	855	110	99
Natural gypsum	21	17	30	15	21
Clinker	38	55	30	42	6

Natural gypsum in cement: up to 5% weight (max 10%)

HYDRAULIC CEMENT MANUFACTURE



Question 1)
High temperatures in clinker production

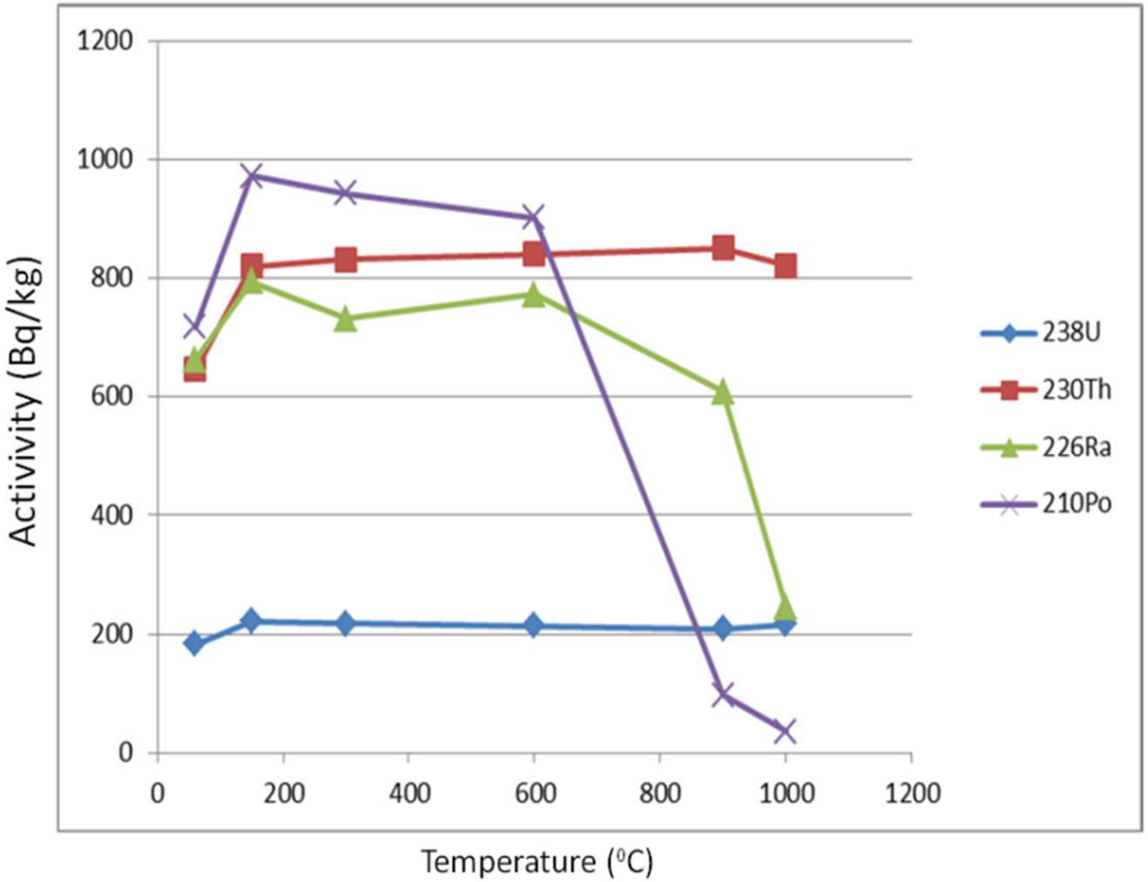


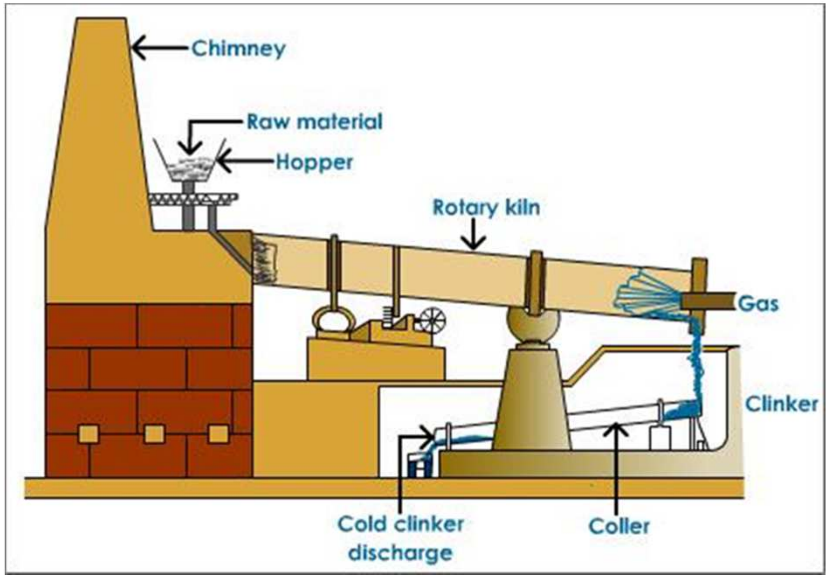
Figure 1. Evolution of radionuclide concentration with temperature of phosphogypsum heating

Effect of strong heating:

- **95% of 210Po is volatilized**
- **97% of 210Pb is volatilized**
- **60-65% of 226Ra is volatilized**
- **U and Th remain in solids (refractory)**

Fate of volatilized radionuclides

Dry process:
components are mixed and transfered to the kiln for calcination with a fuel



- **Radionuclides may remain in the furnace and condensate on surfaces (recycled with hot gases)**

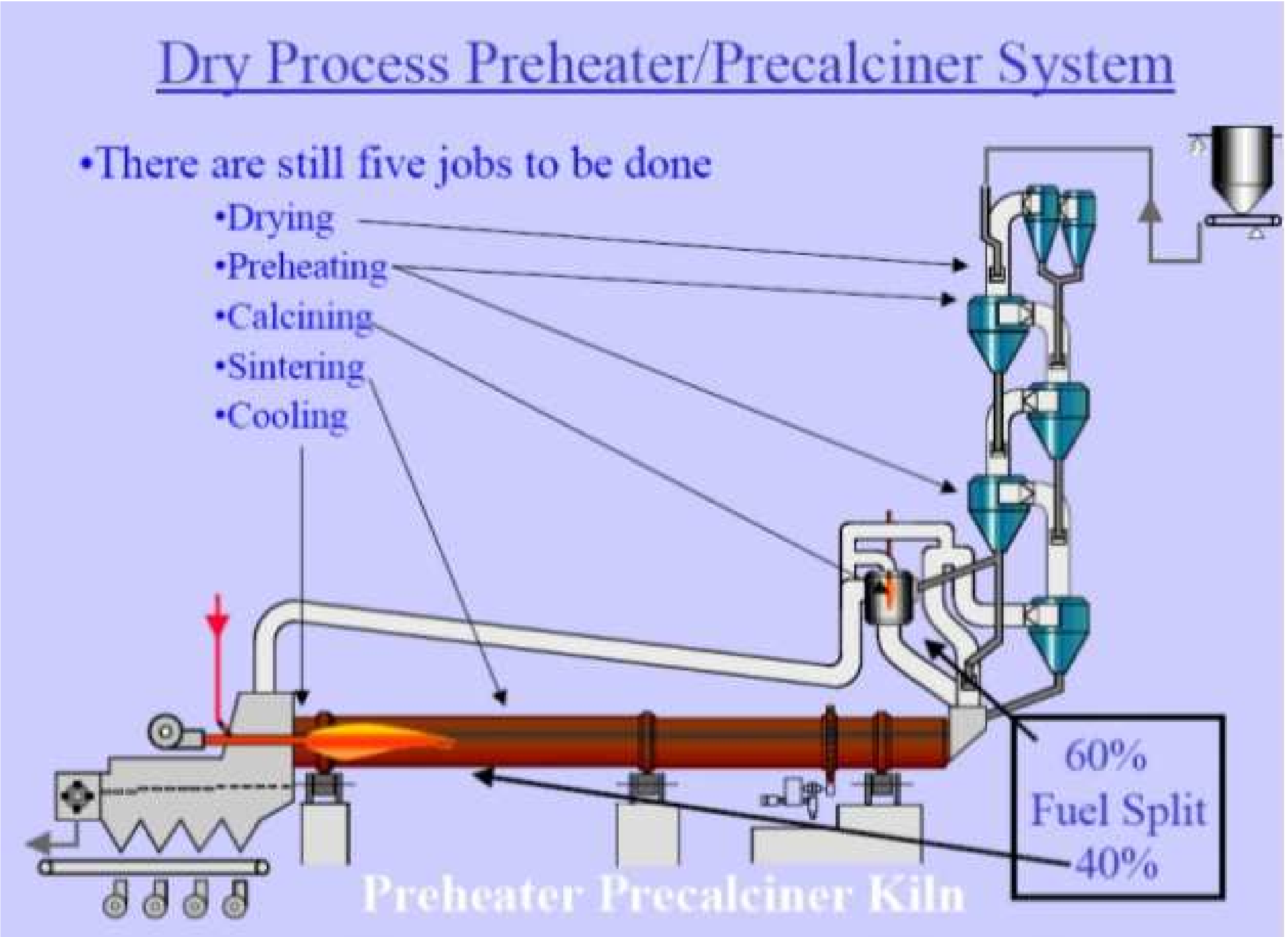
- **Escape to the atmosphere (open chimney)**

➢ **Requires throrough radiological risk assessment**

Temperature in the kiln: 600º to 1300ºC

MANUFACTURE

Recycling the heat for energy savings and ^{210}Po trap



Question 2)
Contact with water and solubilization

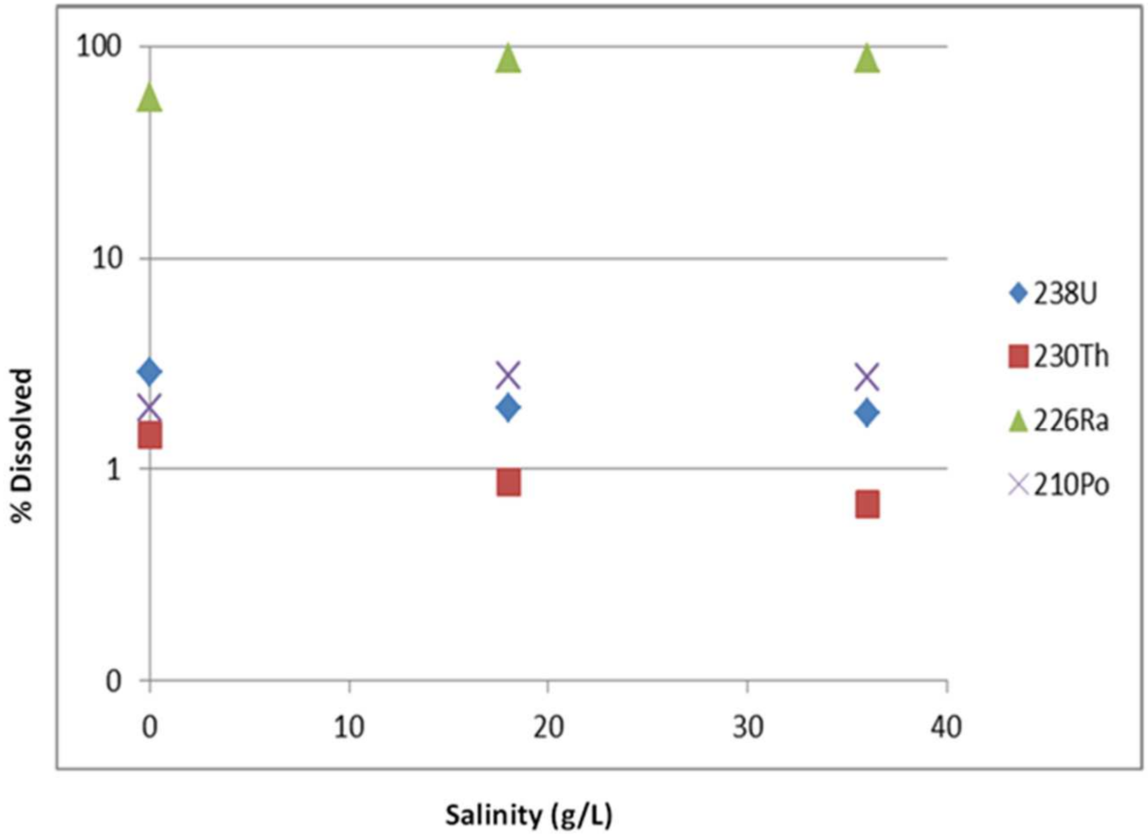


Figure 2. Dissolution of radionuclides from phosphogypsum with increased salinity of water.

Effect of water:

Almost all 226Ra is dissolved

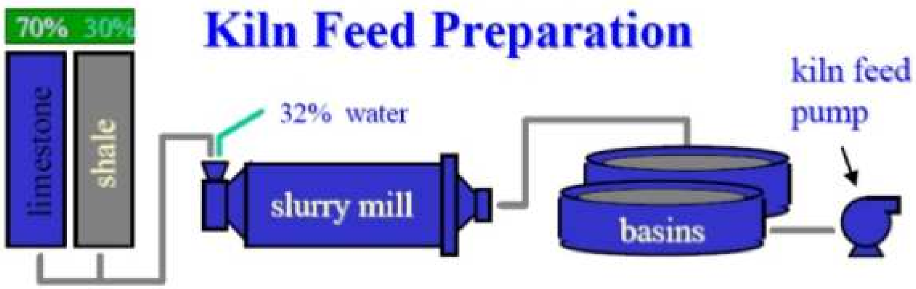
Thorium : only 1% dissolves,

U and Po: only 3% dissolve.

Pb- partly dissolves

FATE OF RADIONUCLIDES

Wet process:
components are mixed as a slurry and are pumped into the kiln



- Proportioning of feed stock.
- Size reduction to < 125μ.
- Control of moisture.
- Blending to reduce standard deviation.
- Uniform delivery rate of feed to the Kiln.

- **Radium is much more water soluble and much more mobile.**
- **Radium may leak, and vaporizes more easily with the water.**
- **Other radionuclides will remain in the cement (solid phase).**

QUESTION 3)
CONCRETE STRUCTURES MAY BE SEEN AS RADIOACTIVE SOURCES IN THE LONG RUN?

Preliminary results indicate:

1) **Surface beta-gamma radiation doses of blocks <u>with and without</u> phosphogypsum are not very different (<than 5%)**

2) **Radon emanation:**
   - **High from PG in powder**
   - **Low from concrete with low radium content**
   - **Comparable to radon emanation from blocks with no PG.**

3) **Long term water contact of concrete blocks (3 years) is underway to assess radionuclides leaching**

FINAL CONSIDERATIONS

- PG can be incorporated in cement without generating a product with significant radioactive content.
- If cements with PG are applied only in concrete for structures such as bridges and viaducts, with no prolonged contact/exposure, the radioactivity added to natural radioactivity in cement will be meaningless.
- However, the risk of exposure to radionuclides with higher implications to dose (226Ra, 210Po) is transferred to the cement manufacture. There, the potential accumulation of volatilized radionuclides in the kiln, and releases into the atmosphere would require careful control.
- NOTE: A cement manufacture producing 100 tonnes/day of cement, with 10% phosphogypsum, could release 10E10 Bq 210Po per day .

THANK YOU FOR YOUR KIND ATTENTION !