Radiological risk assessment to workers of a dicalcium phosphate industry

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INTRODUCTION
European phosphate production

European Phosphate Industry Map

- Located in Flix, North East Spain (South Catalonia)
- 98 km from the Ebro River mouth
- Extract fluorides
- Rise the mineral concentration
- Increase the biological availability

**INTRODUCTION**

The production and storage of dicalcium phosphate

- Extract fluorides
- Rise the mineral concentration
- Increase the biological availability

- 1000-1500 Bq kg\(^{-1}\) of \(^{238}\)U and its decay chain daughters

\[
Ca_3(PO_4)_2 + 4HCl \rightarrow Ca(H_2PO_4)_2 + 2CaCl_2
\]

\[
Ca(H_2PO_4)_2 + CaCO_3 + 3H_2O \rightarrow 2(CaH(PO_4) \cdot H_2O) + CO_2
\]
INTRODUCTION

The production and storage of dicalcium phosphate

- Extract fluorides
- Rise the mineral concentration
- Increase the biological availability

1000-1500 Bq kg\(^{-1}\) of \(^{238}\)U and its decay chain daughters

- PR imported from Morocco
- Stored in an outdoor deposit of 3000 m\(^2\)
- Transported to the DCP plant weekly
INTRODUCTION
Spanish legal framework in NORM

Established for the first time the need of performing studies in workplaces to determine if there exist a significant increment of the exposure to natural radioactivity to the workers and public.
Radiological characterization

- Characterize the raw material, products and by-products ($^{226}\text{Ra}$, $^{210}\text{Pb}$ and $^{210}\text{Po}$).

- Assess the temporal variability.

- Evaluate the radionuclide fluxes ($^{226}\text{Ra}$, $^{210}\text{Pb}$ and $^{210}\text{Po}$).
AIMS OF THE STUDY

to establish the radiological risks derived from the external and internal doses received for workers:

PR deposit in the Port of Tarragona

DCP production plant
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA SAMPLING

DUST SAMPLING
- 17 sampling points (June 2013)

TOTAL DEPOSITION SAMPLING
- 3 weeks (from July 2013 to August 2013)
- Containers of 60 L

AIR FILTERS SAMPLING
- Aerosols collected in July 2013
- Radeco vacuum-pump system collecting 40 m$^3$

$^{222}$Rn SAMPLING
- RAD-7 system (3 cycles of 30 min)
- Continuous monitoring for 95 h at R10
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA SAMPLING

- Portable gamma detector (Canberra Inspector 1000)
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA SAMPLING

- Air filters sampling (Radeco vacuum system)
- Personal Dose (Canberra Personal Dosimeters)
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA

RADIOACTIVITY MEASUREMENTS

- **Alpha spectrometry** (U/Th determination)
  - $^{238}\text{U}$, half-life $4.5 \times 10^9$ a
  - $^{234}\text{Th}$, half-life 24.1 d
  - $^{234}\text{Pa}$, half-life 1.18 m
  - $^{230}\text{Th}$, half-life $7.54 \times 10^4$ a
  - $^{226}\text{Ra}$, half-life 1600 a
  - $^{222}\text{Rn}$, half-life 3.83 d
  - $^{218}\text{Po}$, half-life 3.11 m
  - $^{214}\text{Bi}$, half-life 19.9 m
  - $^{214}\text{Pb}$, half-life 26.8 m
  - $^{210}\text{Pb}$, half-life 22.3 a
  - $^{210}\text{Po}$, half-life 138.4 d

- **Gamma spectrometry**

- **Alpha spectrometry** ($^{210}\text{Po}$ deposition)
  - $^{210}\text{Pb}$ in a second analysis via $^{210}\text{Po}$ after the first analysis cleaned the original $^{210}\text{Po}$

- **UTEVA resins**
- **PIPS detectors**
- **Coaxial HPGe detector**
\[^{238}\text{U}\] in equilibrium with \(^{226}\text{Ra}\) and \(^{210}\text{Pb}\) (6.6 – 1500 Bq kg\(^{-1}\))

Dispersion of the PR from the storage deposit due to the wind

Dust on the ground is low (up to 10 g m\(^{-2}\)) → efficient cleaning mechanisms

**REDUCE THE RISK FOR WORKERS**
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA

RESULTS: ATMOSPHERIC DEPOSITION

The rainfall plays a key role in regulating the atmospheric deposition.

Collected 5.8 L m\(^{-2}\) of rainfall

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dissolved fraction</th>
<th>Particulate fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>N.M ± N.M</td>
<td>N.M ± N.M</td>
</tr>
<tr>
<td>C-2</td>
<td>N.M ± N.M</td>
<td>0.25 ± 0.12</td>
</tr>
<tr>
<td>C-3</td>
<td>2.20 ± 0.45</td>
<td>31 ± 2</td>
</tr>
<tr>
<td>C-4</td>
<td>2.44 ± 0.34</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>C-5</td>
<td>0.40 ± 0.11</td>
<td>N.M ± N.M</td>
</tr>
</tbody>
</table>
PM5  por qué es importante lo de los 5.8 l?
Pere Masqué; 16.6.2014
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA

RESULTS: AEROSOLS PARTICLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{238}\text{U}$ (mBq m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-0</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>A-1</td>
<td>0.38 ± 0.02</td>
</tr>
<tr>
<td>A-2</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>A-3</td>
<td>0.32 ± 0.02</td>
</tr>
<tr>
<td>A-4</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>A-5</td>
<td>0.12 ± 0.01</td>
</tr>
</tbody>
</table>
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA

RESULTS: $^{222}\text{Rn}$ IN THE AIR

$0 - 6 \text{ Bq} \cdot \text{m}^{-3}$

$< 10 \text{ Bq} \cdot \text{m}^{-3}$ (UNSCEAR, 2000)
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA

RESULTS: EXTERNAL DOSE

Background: 0.03 – 0.05 μS·h⁻¹
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA

RESULTS: TOTAL DOSE

\[ E = E_{\text{external}} + \sum_i (\hat{h}(g)_{i,\text{inh}} \cdot j_{i,\text{inh}}) + \sum_i (\hat{h}(g)_{i,\text{ing}} \cdot j_{i,\text{ing}}) \leq 1 \text{ mSv.y}^{-1} \]

\[ E = f \cdot \hat{H}^*(10) \cdot t_{\lambda} + \sum_i (\hat{h}(g)_{i,\text{inh}} \cdot j_{i,\text{inh}}) \]

\begin{align*}
^{226}\text{Ra} & \quad \text{(In equilibrium with daughters)} \\
^{238}\text{U} & \quad \text{decay serie} \quad \text{(In equilibrium with daughters)}
\end{align*}
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA

RESULTS: TOTAL DOSE

Effective external dose rate

\[ E_{external} = f \cdot \dot{H}^*(10) \cdot t_A \]

\( E_{inh} = V \cdot t_A \cdot \left[ DCC_{i,inh} \cdot c_{i,inh} \right] \)

\[ C_{i,inh} = \text{Concentration of } ^{238}\text{U decay serie in air (Bq}\cdot\text{m}^{-3}) \text{ at each sampling point (secular equilibrium with its daughters)} \]

\( V = \text{Breathed rate at working place (1.2 m}^3\cdot\text{h}^{-1}) \)

\( t = \text{Residence time of employees at the workplace (9 h}\cdot\text{week}^{-1}) \)

\( DCC_{i,inh} = \text{Dose conversion factor for each radionuclide (AMAD of 5\,\mu m)} (^{238}\text{U, } ^{234}\text{U, } ^{230}\text{Th, } ^{226}\text{Ra, } ^{210}\text{Po, } ^{210}\text{Pb}) \)

Internal dose by inhalation

\[ < 0.01 \text{ mSv} \cdot \text{y}^{-1} \]
OUTDOOR DEPOSIT OF PR IN PORT OF TARRAGONA

RESULTS: TOTAL DOSE

\[ E = E_{\text{external}} + E_{\text{inhalació}} \]

Total dose to workers

\(< 1 \text{ mSv} \cdot \text{y}^{-1}\)
### RESULTS: PR LOAD IN TRAIN WAGONS

**Dosis received by workers**

0 µSv in 3 hours

#### PR LOAD IN TRAIN WAGONS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Internal dose by inhalation (mSv y⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP-0</td>
<td>0.0072</td>
</tr>
<tr>
<td>DP-1</td>
<td>0.179</td>
</tr>
<tr>
<td>DP-2</td>
<td>N.M.</td>
</tr>
<tr>
<td>DP-3</td>
<td>0.984</td>
</tr>
<tr>
<td>DP-4</td>
<td>0.0171</td>
</tr>
<tr>
<td>DP-5</td>
<td>0.0586</td>
</tr>
<tr>
<td>DP-6</td>
<td>0.261</td>
</tr>
<tr>
<td>DP-7</td>
<td>0.261</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Internal dose by inhalation (mSv y⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-0</td>
<td>0.00301</td>
</tr>
<tr>
<td>A-1</td>
<td>0.00763</td>
</tr>
<tr>
<td>A-2</td>
<td>0.00201</td>
</tr>
<tr>
<td>A-3</td>
<td>0.00643</td>
</tr>
<tr>
<td>A-4</td>
<td>0.00301</td>
</tr>
<tr>
<td>A-5</td>
<td>0.00241</td>
</tr>
</tbody>
</table>
DCP PRODUCTION PLANT

FLUXES OF RADIONUCLIDES

Casacuberta et al. 2011
Phosphate rock storage
DCP drying nº 3
Phosphate rock digestors/reactors
Decanters
DCP Precipitation tanks
DCP drying nº 1-2
Laboratory and offices
DCP packaging
DCP storage area
DCP Truck loading
F1
F2
F6
F7
F3
F4
F8
F5
Phosphate rock storage
DCP drying nº 1-2
Laboratory and offices
DCP packaging
DCP storage area
DCP Truck loading
F4
F6
F7
DCP Precipitation tanks
DCP Precipitation tanks

November 2011 and March 2012
DCP PRODUCTION PLANT

RESULTS: AIR FILTERS SAMPLING

- F1: Stairs close to reactor 2
- F2: Below reactor 2
- F3: Unloading PR
- F4: Packing area
- F5: Offices
- F6: Between Dorr-1 and Dorr-4
- F7: Between B-18 and B-20
- F8: DCP truck load

The graph shows the concentrations of isotopes 230Th, 238U, 210Po, and 210Pb in terms of (mBq·m⁻³).
DCP PRODUCTION PLANT

$^{222}$Rn SAMPLING

- P: Passive detector (Makrofols)
- A: Active detector (Rad-7 and AlphaGUARD)

Total: 9 indoor and 22 outdoor sites
RESULTS: $^{222}\text{Rn}$ MEASUREMENTS

- at points located in indoor areas
- the outdoor sampling point P15 located at the digestors outdoor area
- the boiling process that occur during the HCl chemical attack of the PR
DCP PRODUCTION PLANT
RESULTS: EXTERNAL DOSE

Ground floor

Scrap metal area
0.14 - 7.83 µS·h⁻¹

Digestion area
0.76 - 4.00 µS·h⁻¹

Accumulate ²²⁶Ra due to the scales formation

Decantion area
0.16 - 27.0 µS·h⁻¹

²²⁶Ra absorption on the ebonite that re-covers the internal part of the pipes

the storage of unused pipes with ebonite and scales with high ²²⁶Ra concentrations (100 kBq·kg⁻¹).
DCP PRODUCTION PLANT

RESULTS: EXTERNAL DOSE

1st floor

Digestion area
0.76-4.00 μS·h⁻¹

Decantion area
0.16-27.0 μS·h⁻¹
DCP PRODUCTION PLANT

RESULTS: TOTAL DOSE (EXTERNAL DOSE)

\[ E_{\text{external}} = f \cdot H^*(10) \cdot t_A \]

- **Loading & Packing ext**: 0.100
- **Laboratory ext**: 0.125
- **DCP precipitation ext**: 0.090
- **Digestion & Decantation ext**: 0.185

- \( f = 1 \) (Dose equivalent factor)
- \( H^*(10) \) = Mean value at each zone
- \( t_A \) = Hours of annual exposure at each zone

\((\text{mSv}\cdot\text{y}^{-1})\)
RESULTS: TOTAL DOSE (INTERNAL DOSE)

\[ E_{inh} = V \cdot t_A \cdot \left( DCC_{i,inh} \cdot c_{i,inh} \right) \]

- **Digestion & Decantation**
  - inh: 0.185

- **Laboratory**
  - inh: 0.125

- **Loading & Packing**
  - inh: 0.352

- **DCP precipitation**
  - inh: 0.090

\[ C_{i,inh} = \text{the different concentrations of the radionuclides of } ^{238}\text{U serie in air at each zone (Bq m}^{-3}) \]
\[ V = \text{Breathed rate at working rate (1,2 m}^3\text{h}^{-1}) \]
\[ t = \text{Annual residence time of employees at each area} \]
\[ DCC_{i,inh} = \text{Dose conversion factor for each radionuclide (AMAD of 5μm) } (^{238}\text{U}, ^{234}\text{U}, ^{230}\text{Th}, ^{226}\text{Ra}, ^{210}\text{Po}, ^{210}\text{Pb}) \]
Workers are reducing their exposure using mask in areas with dust and also limiting the time in high exposure gamma dose.
CONCLUSIONS

PORT OF TARRAGONA

1. There is a dispersion of the PR around the deposit that can be measured in the dust accumulated in some parts of the port. Dust accumulation is less important proportionally to the distance to the storage deposit.

2. Maintenance practices carried out in the Port, where the load of PR and the floor cleaning are done with cab loaders, are generally effective and reduce significantly the impact of the PR derived doses to workers.

DCP PRODUCTION PLANT

1. The dose assessment in the DCP production plant has revealed that the highest contribution to the total dose is due to the external dose produced by the $^{226}$Ra accumulated in pipes where doses can reach values up to $30 \mu$Sv·h$^{-1}$.

2. The locations where these higher values were obtained are characterized by low occupancy factors of workers in the plant.
CONCLUSIONS

Although the doses are lower than the limits of 1 mSv·y$^{-1}$, the concentrations of $^{238}$U chain are not negligible and several radioprotection norms are necessary to maintain the dose as low as possible.
Thank you for your attention