NORM wastes is a particular type of radioactive waste:

- Their radioactivity content is often relatively low, so that they can be immediately released to the environment.
- In many cases they are produced in huge quantities, requiring vast areas for their disposal.
- Significant environmental issues - not related to their radioactivity content - emerge from their disposal.
- Some types of NORM waste have very interesting properties.

At the same time, the depletion of energy resources and raw materials require a sustainable use of resources and energy. In this context, the reuse of (waste) residues – including NORM - is highly desirable.

In this presentation NORM wastes are considered as by-products having commercial value rather than wastes that have to be properly managed.
The term NORM is used to encompass all Naturally Occurring Radioactive Materials where human activities have increased the potential for exposure, in comparison with the unaltered situation. Concentration of radionuclides may or may not have been increased.

Any mineral processing operation can potentially produce NORM.

NORM residues can be classified in two groups:

- **Group A Residues**: materials produced in large amounts, containing moderate amounts of natural radionuclides (typically less than 10 Bq/g).

- **Group B Residues**: materials produced in small amounts containing high concentrations of natural radionuclides (typically $10^3$ Bq/g).
Typical Group A residues are:
- phosphogypsum produced in the production of phosphoric acid,
- coal ashes produced in coal burning thermal power plants,
- red mud from bauxite industry.

Due to their low activity concentration and the large amount produced, traditional disposal management strategies are applied.

Typical Group B residues are:
- scales enriched mainly in radium isotopes formed inside pipes,
- sludge accumulated in deposits of several NORM industrial processes,
- filter-clothes used in filtration processes in several NORM industries.

Due to their radionuclide content, the residues of this Group should be managed in many cases as low-level radioactive waste.
The IAEA in the revised Basic Safety Standards supports the valorization and recycling of NORM residues, after a detailed study of their impact. In fact, IAEA in the revised BSS recognizes that: “…concerning residues of moderate content of radionuclides, there is an increasing acceptance on the concept of use rather than disposal, being the recycling an emerging option.”

On December 2013, the Council of the European Union adopted the new Directive 2013/59/EURATOM (EURATOM Basic Safety Standards, EU-BSS) that specifically addresses the topic of the use of residues from NORM processing industries in building materials.

The EU-BSS sets the requirement of a radiological screening and further characterization of building materials that incorporate specific NORM residues, before they can be distributed on the market.
The ACI screening tool

EU BSS - ANNEX VIII: Definition and use of the Activity Concentration Index (ACI) for the gamma radiation emitted by building materials. The Activity Concentration Index I (ACI) is given by the following formula:

$$ACI = \frac{C_{\text{Ra-226}}}{300} + \frac{C_{\text{Th-232}}}{200} + \frac{C_{\text{K-40}}}{3000}$$

where $C_{\text{Ra-226}}$, $C_{\text{Th-232}}$ and $C_{\text{K-40}}$ are the activity concentrations in Bq·kg$^{-1}$ in the building material.

ACI is related to the gamma radiation dose in a building, in excess of the typical outdoor exposure.

ACI = 1 can be used as a screening tool for identifying materials that may cause the reference level of 1 mSv per year to be exceeded.

For ACI > 1 the dose must be determined.
In this presentation, the practice of giving value to NORM by converting wastes to by-products will be demonstrated. This valorization is beneficial to the environment as well as the company involved.

To this end:

- tradition uses in building materials industry,
- new materials production,
- extraction of elements from NORM residues,
- other uses,

will be presented.
Valorization of ashes produced from thermal power plants
During coal combustion the ash produced is enriched in all non combustible elements existing in the coal, including any existing radionuclides. The enrichment factor strongly depends - among others - on the ash content of the coal. The ash is therefore characterized as NORM and is divided in:

- Fly ash mostly captured in the ESP
- Bottom ash falling inside the boiler

About 400 $10^6$ tonnes of ashes are produced annually worldwide.
In 2011 about 50% of the globally produced fly ash was utilized, the rest was disposed in landfills.

Natural radionuclide concentration of fly ash is in most cases relatively low (>1Bq/g). Therefore in most cases fly ash utilization does not pose any radiological problem.
Coal fly ash is widely used as secondary raw material:
- in the production of Portland cement, concrete and hydraulic plasters,
- as raw feed for cement clinkers,
- as road sub base and mineral filler in asphalt concrete,
- as construction aggregate,
- in the roofing tiles and paints production,
- for the extraction of elements,
- for other uses
In 2006 the American Coal Ash Association reported that $\sim 72 \times 10^6$ t of coal fly ash were produced. Approximately $32 \times 10^6$ t (45%) of them were utilized.

http://rmrc.wisc.edu/coal-fly-ash/
Rare earths and strategic elements from coal ash

Coal contains a number of elements of interest, including rare earths and metals of strategic importance. Coal combustion results to the enrichment of these elements in the ashes produced.

As a result, metal recovery from coal ash may be more efficient than ore processing. However, metal extraction and recovery is a chemical intense process involving acids, which results to multiple waste streams, which should be properly managed.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentrations in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>151 - 1784</td>
</tr>
<tr>
<td>Dy</td>
<td>18 - 527</td>
</tr>
<tr>
<td>Eu</td>
<td>2 - 31</td>
</tr>
<tr>
<td>La</td>
<td>60 - 839</td>
</tr>
<tr>
<td>Nd</td>
<td>70 - 967</td>
</tr>
<tr>
<td>Pr</td>
<td>17 - 239</td>
</tr>
<tr>
<td>Tb</td>
<td>3 - 80</td>
</tr>
<tr>
<td>Y</td>
<td>94 - 3540</td>
</tr>
<tr>
<td>TREE</td>
<td>721 - 8426</td>
</tr>
<tr>
<td>Ge</td>
<td>&lt;10 - 1841</td>
</tr>
</tbody>
</table>

Valorization of slags
Slags: production and utilization

Slag is the glass-like by-product left over after a desired metal has been separated (i.e., smelted) from its raw ore. Slag is usually a mixture of metal oxides and silicon dioxide, which can also contain metal sulfides and elemental metals. There are many opportunities for using furnace slag as landfill material and as construction material.

**EUROSLAG statistics for 2012**

- Blast Furnace Slags use $27.6 \times 10^6$ t
- Steel slags use $24.7 \times 10^6$ t
A risk assessment may indicate the need for certain restrictions, particularly when the slag is used in buildings.

Furnace slag with a moderate activity concentration such as that from copper smelting, iron and steel smelting, scrap metal recycling and elemental phosphorus production can generally be used without restrictions, in the construction of roads and dams.

Furnace slag from the smelting of iron and steel, sometimes after recovering the residual iron content, may be diluted with low activity residue such as fly ash and used as a component of cement, concrete and bricks.

The physical and chemical properties of furnace slag are such that the radionuclide content is not readily leached by environmental media.
Valorization of phosphogypsum
Phosphogypsum (PG) is produced during the digestion of phosphate rock with sulphuric acid to produce phosphoric acid. PG consists essentially $\text{CaSO}_4$ as well as heavy metals and radionuclides. For every tonne of phosphoric acid produced, 4–6 tonnes of PG are produced.

According to a IAEA (2006) Safety report series No 49 up to 2006 around $6 \times 10^9$ tons of phosphogypsum were produced worldwide. The annual production of phosphogypsum worldwide, currently is estimated at about 160 million t.

Radioactivity level (mainly $^{226}\text{Ra}$ and its progeny) of PG strongly depends on the phosphate origin.
## Phosphogypsum: radiological aspects

<table>
<thead>
<tr>
<th>Country (source)</th>
<th>$^{226}\text{Ra}$</th>
<th>$^{238}\text{U}$</th>
<th>$^{210}\text{Pb}$</th>
<th>$^{210}\text{Po}$</th>
<th>$^{232}\text{Th}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA [183]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South and central Florida</td>
<td>507–1358</td>
<td>41–366</td>
<td>577–1853</td>
<td>437–1765</td>
<td>11</td>
</tr>
<tr>
<td>Europe [191, 192, 178]</td>
<td>15–1700</td>
<td>500</td>
<td>1300</td>
<td>900</td>
<td>10</td>
</tr>
<tr>
<td>South Africa [193]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Local rock</td>
<td>45–48</td>
<td>64–73</td>
<td>76–132</td>
<td></td>
<td>205–284</td>
</tr>
<tr>
<td>Togo rock</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td>61</td>
</tr>
</tbody>
</table>

Extent of environmental contamination by Naturally Occurring Radioactive Material (NORM) and technological options for mitigation, Technical Report Series No 419, IAEA.
Historically PG has been managed mainly in two ways:

- stockpiling in large containment structures or
- discharging to water bodies, usually large rivers, river estuaries or the sea (50%).

In addition to the PG itself, billion liters of highly acidic process water associated with the PG production are stored in the formed PG stacks. Restrictions posed by the EU and IMO have significantly reduced enormously the proportion of PG discharged to water bodies today.
Phosphogypsum: management and valorization

PG in agriculture for soil remediation
Addition of PG in saline and sodic soils reduced their sodium and aluminum toxicity and increased the water retention, as well as the calcium and ammonia content of the treated soils. The radiological impact of this use is negligible. PG agricultural applications are growing exponentially worldwide.

PG in building construction
PG is used as a raw material in cement, bricks, tiles, blocks production. Exposure to PG construction materials has been thoroughly studied and most studies have shown that the exposure levels are not likely to be of serious concern. Attention should be taken if PG is used in high amounts in the construction of structural panels.
Phosphogypsum: management and valorization

PG as road basement
Historically is one of the most widely tested uses of PG. PG mixed with cement or fly-ash as a road basement absorbs less water and presents high stability and little degradation over time.

PG in marine applications
PG is mixed with cement and fly-ash for the construction of blocks and structures used for coastlines stabilization. These blocks have shown little degradation in contact with sea water.

PG in landfill
Pilot studies have showed that PG has a very good potential to be used as a cover material in landfill disposal facilities.

PG as a bitumen modifier
When PG is activated with a small quantity of sulfuric acid (0.5 wt%), the addition of 10 wt% PG improves its rheological response at high temperatures.
Phosphogypsum: management and valorization

All scientific evidence suggests that the doses received as a result of the use of PG in agriculture, road construction, marine applications and in landfill facilities are sufficiently low that no restrictions of such use are necessary.

In most cases where the PG is used in home constructions (cement, bricks, tiles,...) the doses received by the occupants are also low.

Only if the PG is used in large quantities in the construction of structural panels the effective doses can reach values that may require a case specific risk assessment.
Valorization of red mud
Bauxite tailings (red mud) are produced by the digestion of bauxite in sodium hydroxide, as the first step in the production of aluminum. The production of 1 t of alumina results to the production of ~1.5 t of red mud. Annual red mud production worldwide is estimated to several million tonnes (>5 $10^6$ t). The red mud stockpiled today exceed 250 $10^6$ t.

### Radioactivity (Bq/kg) in bauxite and red mud.

<table>
<thead>
<tr>
<th></th>
<th>Bauxite</th>
<th>Red mud</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium series radionuclides</td>
<td>10–9000</td>
<td>100–3000</td>
</tr>
<tr>
<td>Thorium series radionuclides</td>
<td>35–1400</td>
<td>100–3000</td>
</tr>
<tr>
<td>Actinium series radionuclides</td>
<td>120–130</td>
<td>—</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>10–600</td>
<td>10–100</td>
</tr>
</tbody>
</table>

Extent of environmental contamination by Naturally Occurring Radioactive Material (NORM) and technological options for mitigation, Technical Report Series No 419, IAEA.
Red mud is historically stored in dams. However this storage poses a risk to the environment and significant accidents have occurred the last few years. The catastrophic failure at the Ajka red mud dam in Hungary in 2010 clearly demonstrated the red mud disposal problem. An alternative is the wet deposition.

Red mud is less commonly considered in the building materials sector. It is mainly used as secondary raw material in cement production of:

- ordinary Portland cement, replacing clays,
- raw mix of special cements as a source of iron oxide or alumina.

Other applications are:

- pig iron production,
- recovery of iron,
- soil conditioning.
Valorization of residues from metal industry
Residues from metal industry
The example of a TiO$_2$ industry in Spain

Waste management in the 70’s

In the 70’s a factory producing TiO$_2$ pigments operated in the SW of Spain. It was a typical NORM industry producing the following residues:

- sludge from the solid un-attacked material in the digestion step,
- strong sulphuric acid solution enriched in Fe,
- weak sulphuric acid solution from the washing of the TiO$_2$

In total, 25,000 metric tons of sludge and more than 300,000 metric tons of weak and strong acids were produced annually.

The sludge - enhanced in radium isotopes - was transported in wet form, to a treatment plant, before being disposed.

The acid solutions - enhanced in uranium and thorium isotopes - were stored in big tanks and periodically released in the open ocean.
A New Directive

In the beginning of 1990s the Council Directive 92/112/EEC established procedures for harmonizing the programs for the reduction and eventual elimination of pollution from existing industrial installations producing TiO$_2$. In this Directive dumping of any solid waste, strong acid waste, treatment waste, weak acid waste, or neutralized waste was prohibited.

In order to conform to the Directive and eliminate the discharges of acid effluents to the sea, huge technical modifications in the production process were carried out in the plant with a significant success. The production process was re-designed in order to overcome the problem associated with the management of the strong acid residue generated.
Residues from metal industry
The example of a TiO$_2$ industry in Spain

By products in the 90’s (no waste)

The strong acid solutions are now treated producing:

- iron sulphate heptahydrate, is used for the recovery of basic soils, as a component in animal feeding or as a flocculant in water treatment,
- iron sulphate monohydrate, used as a raw material in fertilizer production and for the treatment of soils with iron deficiency,
- strong acid remaining after the previous steps, which is recycled in the process reducing by 30 % the needs of “fresh” sulphuric acid.

Consequently, with the redesigned process no acid solutions residues are produced today.

The environmental and occupational radiological impact of the new by-products is quite limited.
New materials production
Geopolymers

Inorganic polymeric materials - Geopolymers

Geopolymers are formed through the alkali activation of solid materials rich in Si and Al to produce amorphous to semi-crystalline three-dimensional polymeric structures, consisting of Si-O-Al bonds.

The materials used for geopolymer production can be, calcinated clays, volcanic rocks, industrial residues like:

- Metallurgical Slag
- Fly ash

Some of the geopolymer characteristics are:

- Freeze-thaw and acid resistance.
- Thermal stability and low permeability.
- Fire and heat resistance (passive fire protection).
- High compressive, tensile and flexural strength.
- Long-term durability and great Mohs hardness.
Applications and advantages of geopolymers

Construction and building industries:
- Concrete, building materials, pre-cast materials.
- Fire-resistant and fire proof panels.
- Foamed composites for thermal and acoustic insulation.

Ceramics, for the chemical industry and metallurgy:
- Refractory materials.
- Molds for thermoplastics, metals casting, foundries.

Environmental applications:
- Waste encapsulation and solidification-immobilization of hazardous substances.

Geopolymers compared to ordinary concrete has low production cost since by-products from NORM industries are used as raw material and its production is energy-effective since the whole process takes place at low temperatures and pressure.
The NORM4Building COST Action
The main objective is the exchange of multidisciplinary knowledge and experience to evaluate and – if justified – stimulate the reuse of residues from the NORM processing industry in new tailor-made sustainable materials.

A holistic approach to risk assessment is applied to verify the safe reuse of these residues in construction materials with specify attention to the impact on external gamma exposure of building occupants and the indoor air quality.

The NORM4Building Research Network involves more than 90 researchers from 24 European countries.
The COST Action NORM4Building

- A three year project (2014-2017)
- Workshops and Conferences.
- Short Term Scientific Missions.
- 3 Training Schools (Hasselt, Rilem, Athens).
- Database for NORM.
- Scientific papers produced as a result of new collaborations.
- A Book to be published within the next few weeks.
- Web page: http://norm4building.org/
A NORM residue is not necessarily a waste. There are many opportunities for their safe use as by-products. Recycling of a NORM residue, or its use in other applications rather than disposing it as waste, should be therefore the first consideration and NORM residues should be regarded more as a resource than as waste.

Today, only a small part of NORM is utilized, mainly in construction industry, however:

- depletion of natural resources of raw materials,
- environmental issues related to air, soil and water pollution due to the waste disposal, energy consumption, CO₂ emissions, water and land use,
- more stringent environmental protection legislation,
- economic issues,

will increase this part in the future.
The opportunities for using NORM residues as by-products depend on various factors, including the type of residue, the rate at which it is produced, the location of the facility and local market conditions. Consequently, the approach to NORM residue management needs to be tailored to the particular industrial activity.

After the mining of the resource a well defined and integrated strategy should be established in order to obtain the maximum benefit of the raw material, reducing as much as possible the amount of wastes produced.

In this way while the occupational and public exposures associated to NORM activities is kept low, the pressure over other natural resources, including water and land are diminished as well.

In any case a critical step towards the increase of NORM utilization is to increase public acceptance.
Thank you very much for your attention

Any questions?


Towards a holistic approach for risk assessment when reusing slag with enhanced NORM content in building materials, Schroeyers W., Croymans-Plaghki T., Schreurs S., 4th International Slag Valorization.


