BRAZILIAN EXPERIENCE IN REMEDIATION OF NORM SITES

Dejanira da Costa Lauria
Institute of Radiation Protection and Dosimetry
Brazilian Nuclear Energy Commission (IRD/CNEN)
Monazite

- Monazite is basically an orthophosphate of Rare Earth Elements containing thorium and uranium.
- A typical Brazilian monazite contain around 0.3% of uranium oxide and 6% of thorium oxide.
- Monazite is processed aiming obtaining lanthanide elements, but during the chemical processing wastes and residues are generated.
- The chemical processing of monazite in Brazil stated in the forties years and the industry worked many years without regulation concerning radiation protection.

Ce, La (PO₄) ≈ 39 %
U₃O₈ ≈ 0.3 %
ThO₂ ≈ 6 %
Basic Steps of the Monazite Chemical Processing

MONAZITE 85-95% pure

Magnetic separation

MONAZITE Light fraction 99%

Alkaline Digestion

Filtration

Phosphate solution 99%

Hydroxide cake Th, U, Ra, REE

CAKE II Th and U hydroxide

Chloride solution Ra and REE

REE chloride

Mesothorium Cake Ba (Ra)SO₄

170-320 Bq/g

1820 Bq/g

4360 Bq/g

Careless handling of the solid wastes, releasing of liquid effluents and the use of mineral wastes as landfill contaminated two sites.
Legacy of the Monazite Processing

- Disposal sites had to be set to storage the monazite's wastes and residues, which were disposed in shallow ground silos, in rubber drums or buried in trenches.

Soil contamination during the filling of silos
The monazite was chemically processed in Santo Amaro mill (USAM) for obtaining of a solution of rare earth chlorides. The Mill was located in a densely populated residential district of São Paulo City, the largest city in Brazil, encompassing 16,503 m² area.
USAM Decommissioning

The decommissioning was carried out in four steps:

1. the suitable packaging and the removal of wastes remaining at the plant;
2. the second stage was the decontamination and dismantling of the equipment;
3. the third stage was the decontamination of floors and walls, followed by the demolition of the buildings (built area of 13,000 m²); and finally,
4. the radiological survey of the site and its cleanup.
REMEDIATION ACTIONS

1) Site Radiological Characterization

1.a) Identifying the main contaminants

- History of the site
- Soil analyses by gamma spectrometry

- Based on the ratio Ra-228/Ra-226, two different contamination materials were identified:
  - Ra-228/Ra-226 < 8 (80%) (light)
  - Ra-228/Ra-226 > 50 (10%)

(Cake II)
1) Site Radiological Characterization

1.b) A survey of radionuclides in surface and deep soil was carried out.

- Radiological Survey:
- grid: 2 x 2 m
- Field: Scintilometer detector
- Laboratory: HPGe Detector
- Alpha and beta total counting
2. Establishment of the allowable residual level

- Based on:
  - Dose limit of 1 mSv/y
  - Worst case scenario: Child stays indoors for around 5500 h/y and in the residential garden for about 700 h/y. The inhabitants did not consume water from the site, nor ingest any food grown on the site.
Allowable residual level

- The assessment was performed by pathway analysis (base of RESRAD):
- External exposure was the main exposure pathway, being responsible for ca. 80-90% of the total dose.
- The contribution of thorium-series radionuclides to the dose was higher than the uranium-series one, and it increased with the increasing of the ratio Th/U.
- $^{228}$Ra concentrations could be used as criteria for soil remediation.
- Considering the measured local background of $^{228}$Ra soil concentration of 0.1 Bq/g, the allowable residual level (ARL) of $^{228}$Ra was set to 0.65 Bq/g of soil.
3. Establishment of Methods for faster measurements

1 m$^2$ of soil surface and 3 cm of depth:

a) Measured in field: Scintillator close to soil

b) Soil sampling and measurement in laboratory by HPGe

Relationship between the scintillation readings and the $^{228}$Ra activity concentrations: $^{228}$Ra [Bq/g] = 0.0025 [cps] - 0.1012

Screening measurements for soil remediation: The value of 300 cps was chosen as a value representative for the limit (0.65 Bq/g of $^{228}$Ra).
Establishment of Methods for faster measurements

- The gross alpha and beta counting showed a good correlation with the activity concentration of $^{228}$Ra ($r_{total} = 0.86, r_{beta} = 0.93$).
- Based on these results the gross beta counting was chosen for the monitoring during remediation.
- Based on the original limit established for the site, an allowable limit level of 3.5 Bq/g of gross beta counting in the soil at the site was derived.
4. Protocol for soil Cleanup

- Radiological Survey
  - Scintillator
  - > 300 cps
  - < 300 cps

- Sampling of Soil
- Soil Removing
  - > 30 Bq/g
  - < 30 Bq/g
  - Storage in USIN-a temporary deposit
  - Transfer to a Municipal landfill

- Measurement by total beta counter
  - > 3 Bq/g
  - < 3 Bq/g
  - Transfer to a municipal landfill

- Checking by Regulatory Authority
  - Ra-228 < 0.65 Bq/g
  - Site releasing for unrestricted use
USAM SITE

Site after remediation

Envisioned exposure scenario

Actual scenario
Going on

The last phase of USIN remediation, the site cleanup, is ready to started.
Challenges- USAM and USIN remediation

- Public concern
- Need of storage site for low level wastes
- Change of exposure scenario:
  - Some years ago it was not allowed privately-owned wells in São Paulo city. However, nowadays the city inhabitants are dealing with problems regarding the amount of water to supply public and in consequence nowadays it is allowed to drill wells with the purpose to get tap water.

However, no technological challenge was faced in this kind of remediation.
The first uranium mining and milling facility of Brazil, CIPC, located at the Poços de Caldas plateau, in the state of Minas Gerais, has finished operation and is under preparation for decommissioning.

When the licensing process took place in the late 70’s - early 80’s, no previous planning was made for the decommissioning phase.

Actually, this site remediation is a technological and scientific challenge.
Main areas of concern include:

- the open pit mining area
- the waste rock piles
- the tailings dam

Acid drainage caused by pyrite oxidation is responsible for releasing of U, Ra, Mn, F, Al from the wastes rocks, mine pit and tailing dam.

\[
FeS_2 + 8H_2O + 14Fe^{3+} \rightarrow 2SO_4^{2-} + 15Fe^{2+} + 16H^+
\]
The water from the waste rocks and mine pit are neutralized with lime and then after solid settlement, the liquid effluent is released into two rivers of the region. One river flows to Poços de Caldas City (Antas river) and the other to Caldas city (Soberbo river).
WASTE ROCK PILES AT CIPC/MG

$\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} \rightarrow 2\text{SO}_4^{2-} + 15\text{Fe}^{2+} + 16\text{H}^+$

$\text{O}_2$

$\text{BaSO}_4 \downarrow$

$\text{Ba(Ra, Pb)SO}_4$

Acid drainage leaching U to solution

pH = 3.30

$^{238}\text{U} = 175 \text{ Bq/L}$

71 to 315 Bq/L

Fernandes et al. 2008

$\text{Al} = 96 \text{ mg/l, Mn} = 75 \text{ mg/l, F} = 99 \text{ mg/l}$
Drainage acid from waste rock piles is discharge into the mine pit.

Solution is pumped to the Chemical treatment plant: neutralization with lime.

Solid is deposited in the mine open pit.
Tailing dam AT CIPC/MG

Residues from chemical processing of the ore

Acid drenage
Tailing dam at CIPC/MG

21/9/2006
The liquid effluent from tailing dam is treated with barium chloride, $\text{BaCl}_2$, for Ra precipitation and then the precipitated is stored in two settlements ponds. The liquid effluent is released into the Soberbo river.
CHICANE AT CIPC FOR WATER TREATMENT, BEFORE RELEASE TO THE ENVIRONMENT
Remedial options

- Return the material back to the mine: very expensive
- Immobilization: Tailing dam
- Capping was suggested as the most appropriated remedial action. Capping the waste rocks piles and tailing dam, with a material with a lower oxygen diffusion coefficient, will decrease the pyrite oxidation, will reduce radon emission and will shield the exposure to gamma emission.

Fernandes et al. 2008
Summary

- Due to the lack of a careful initial planning, significant expenditures will have to put in place to remediate the site from an effectiveness and long-term perspective.

- The occurrence of pyritic material in the ore associated to a high precipitation rate led to the production of acid drainage, followed by leaching of radionuclides and metals from ore.

- There is a potential scenario which may lead to unacceptably high exposure to radiation not only in the present but also in the future.

- The long time scale required for the pyrite oxidation in the mining wastes (at least 600 years) implies the need to implement permanent remediation actions.

- It has been suggested that covering the waste rock piles and tailing dam with a material with low oxygen diffusion coefficient may decrease the contaminant releases to marginal levels.

- Nevertheless, a better understanding of the process that produces the acid drainage is necessary.
Poços de Caldas- References


