NORM in the production of tin at Metallo-Chimique NV, Belgium

EAN – NORM workshop
Dresden, December 2012

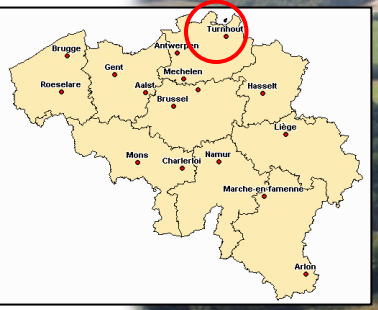
Content

- Company presentation
- Origin and distribution of radioactivity in the production of tin
- Radiation check at Metallo
- Health&Safety and other regulatory requirements

Company presentation

METALLO
The furnace of innovation

Metallo-Chimique NV, Belgium



metallum

Metallo-Chimique, key elements

Input : ca. 310000 ton / year

Output :

Cu	120000 t
Pb	20000 t
Pb/Sb	3000 t
Sn	11000 t
Ni	600 t
Metamix (slag)	180000 t
Zn oxide	3000 t
Ni-solution	10000 t
Anode slime	2500 t

- Recuperation of non-ferro metals (Cu, Sn, Pb, Ni) from "waste" and by-products (scrap, slags, ashes, …)
- All input materials are converted into new products of interest for others…
- "Zero waste" facility
- Positive contribution to save energy and primary raw materials

Metallo-Chimique, Raw Materials

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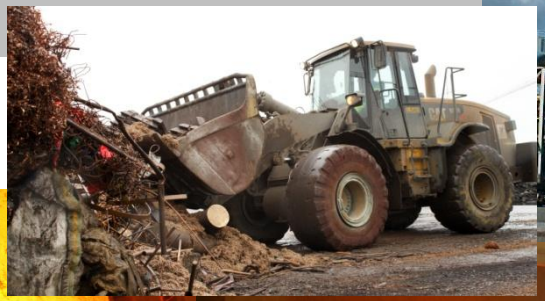
Production process









Metallo-Chimique, final products and by-products

Copper (anodes)

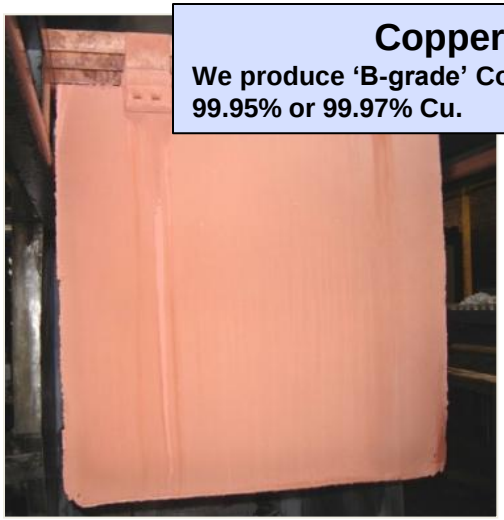
To customer's specifications in the specific format for tankhouse feed

Nickel

Nickel is recovered as electrolyte for the production of nickel sulphate or as metal in the form of briquettes with min. 90% nickel content for the stainless steel industry or as an alloy component.

Copper (cathodes)

We produce 'B-grade' Copper Cathodes with minimum 99.95% or 99.97% Cu.



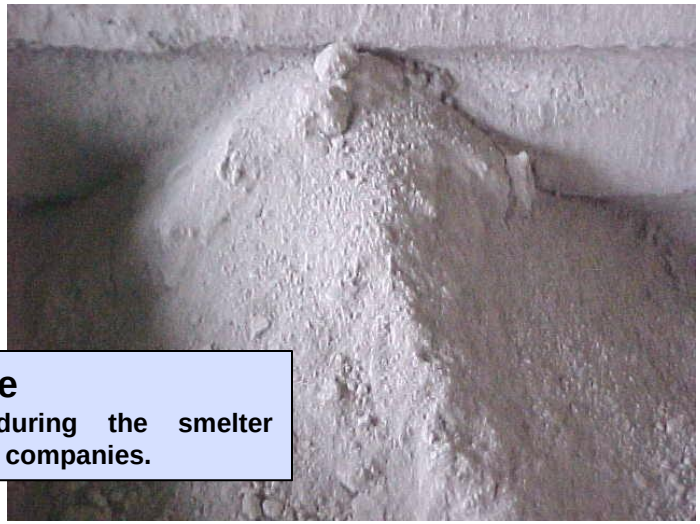
Tankhouse Slimes

The slimes generated in the tankhouse are sold for further refining of the precious metals in specialised industries

Metallo-Chimique, final products and by-products

Tin

Our high grade tin ingots with min. 99.93 or 99.95% Sn guaranteed are registered on the London Metal Exchange as the 'MC' brand and are well known for the low level of lead content , below 100 ppm or even down to 50 or 25 ppm.

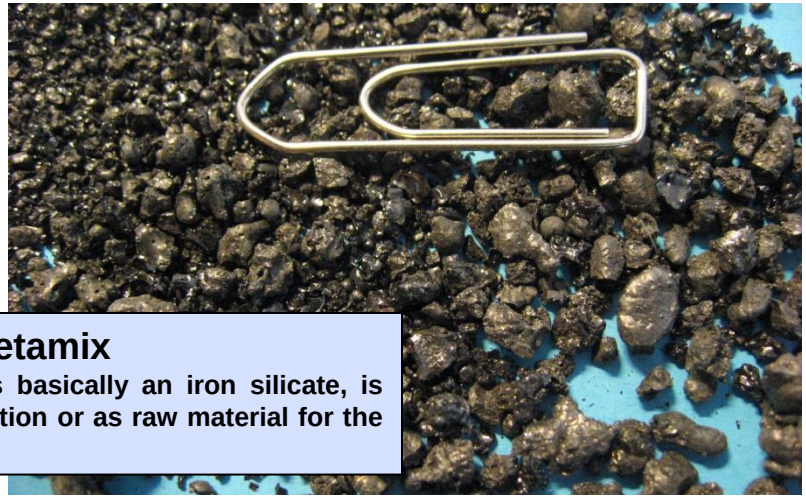


Zinc oxide

The zinc oxide generated during the smelter processes is sold to zinc refining companies.

Lead

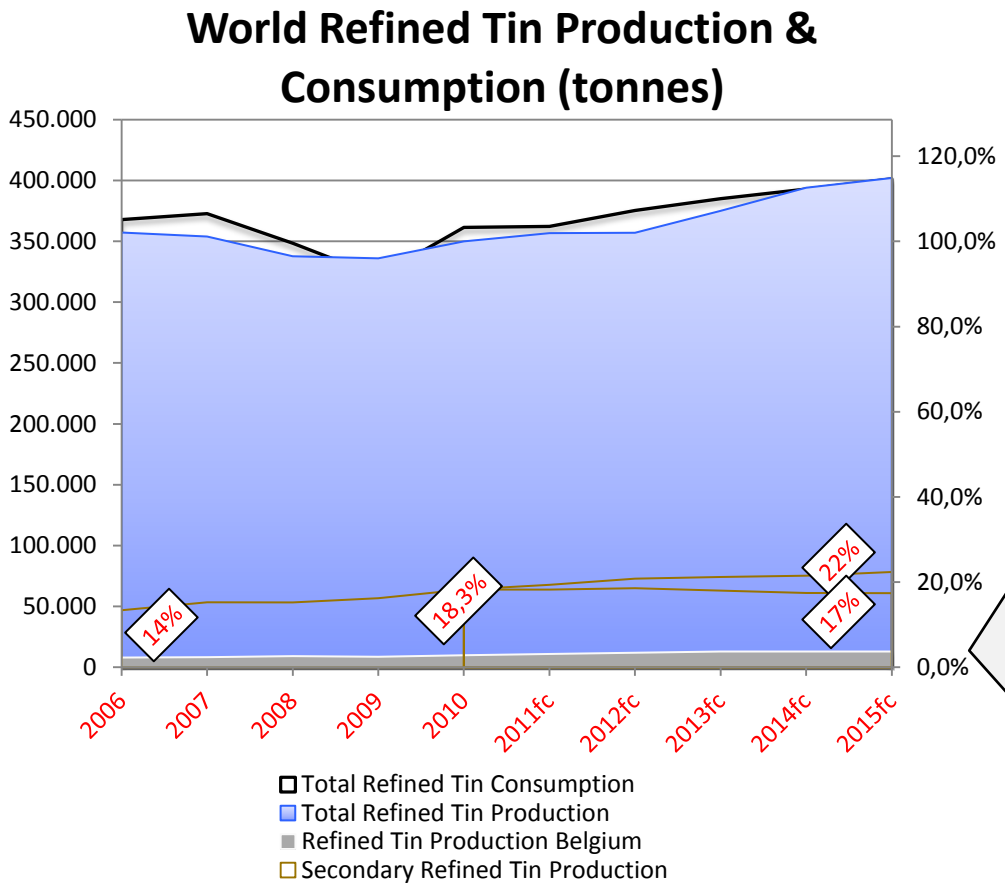
Soft lead ingots with min. 99.9% Pb content as well as hard lead ingots with varying contents from 3 up to 15% of antimony can be offered.

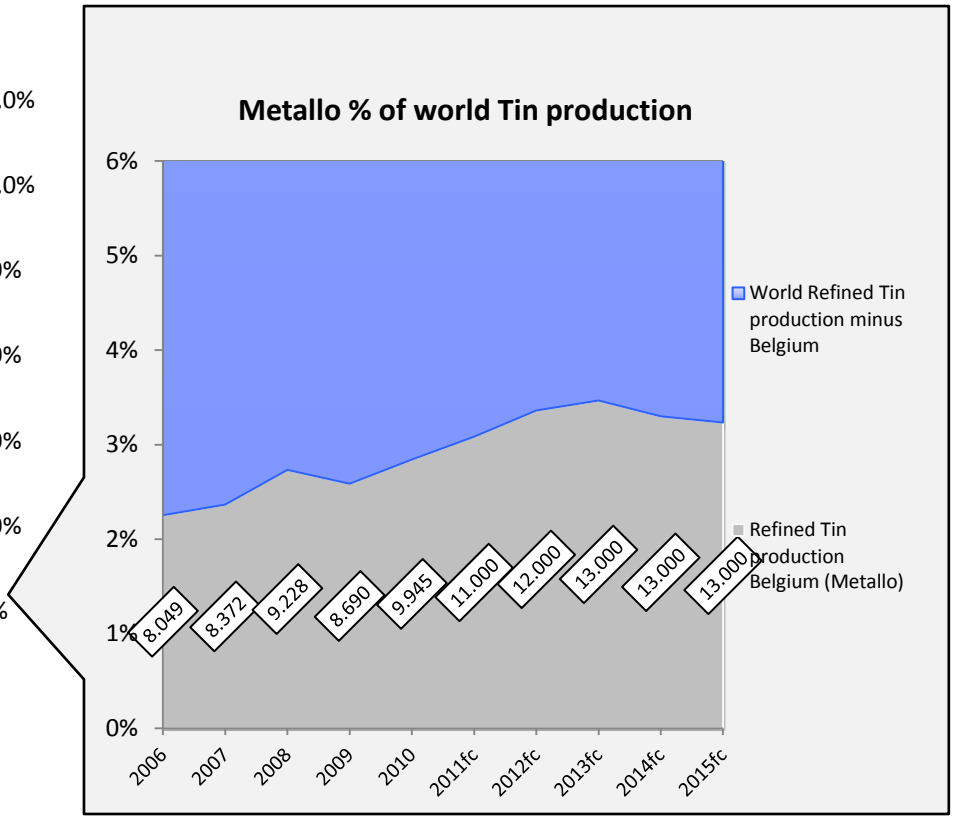


Metamix

The final slag, which is basically an iron silicate, is used mainly in construction or as raw material for the cement industry.

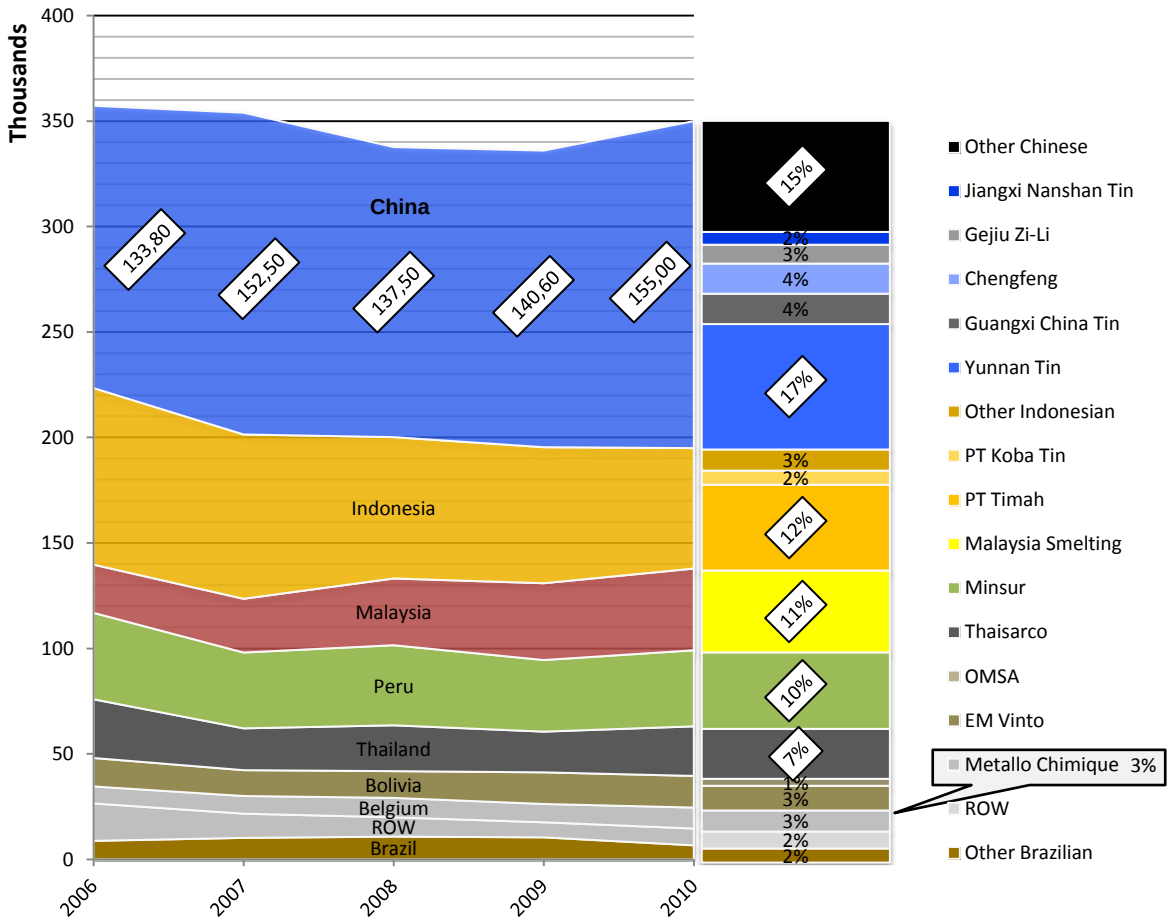
Tin : market size





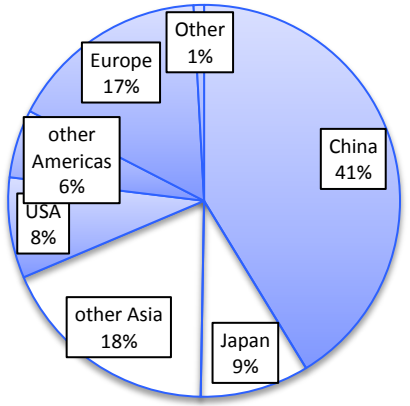
Tin : market actors

Top 13 Refined Tin Producers per country

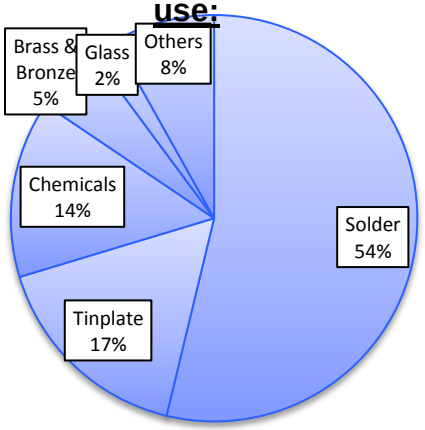


Consumers

World consumption per region:



World consumption per use:



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Origin and distribution of radioactivity in the production of tin

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Industrial tin minerals : cassiterite (= SnO_2)

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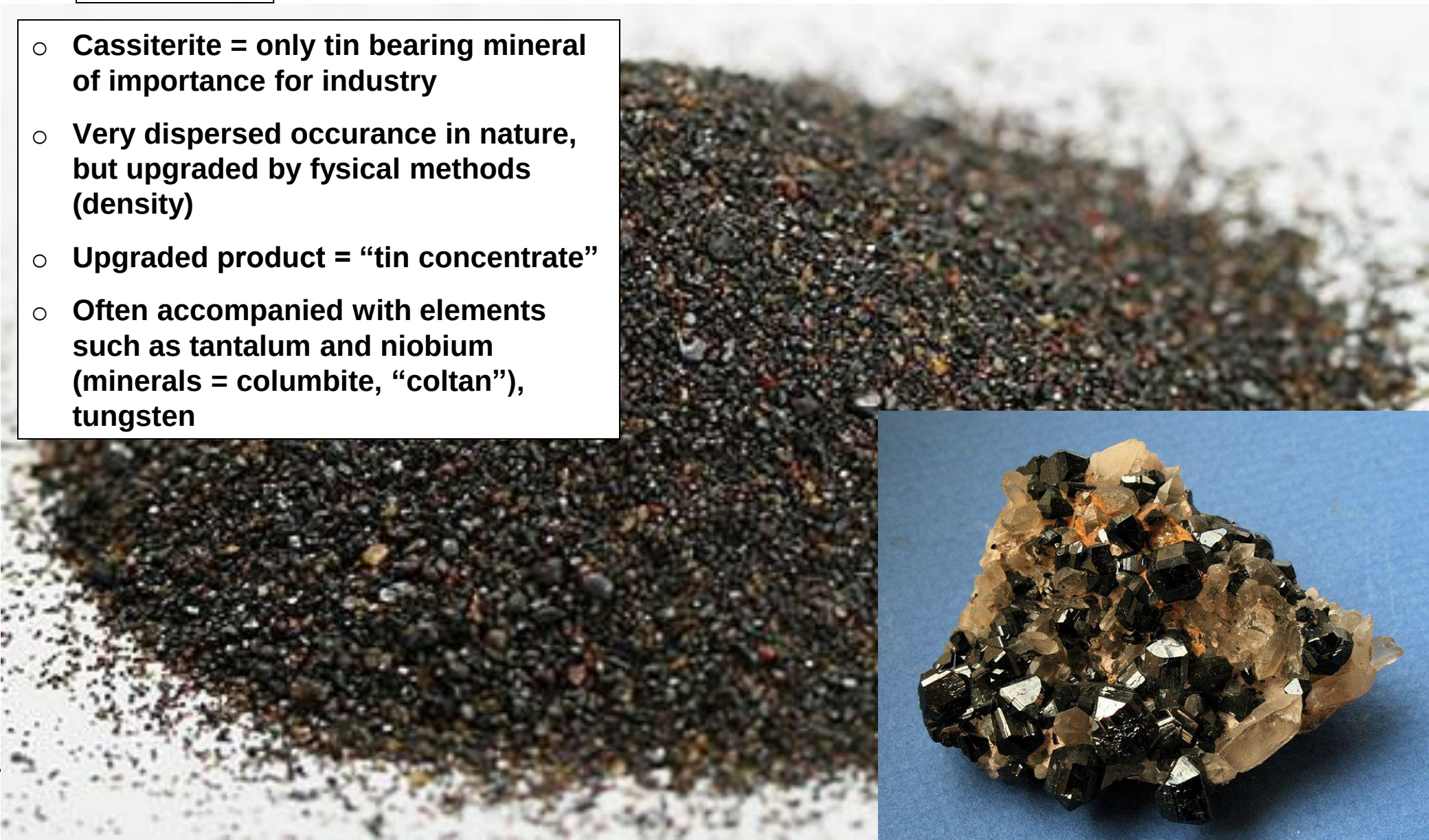
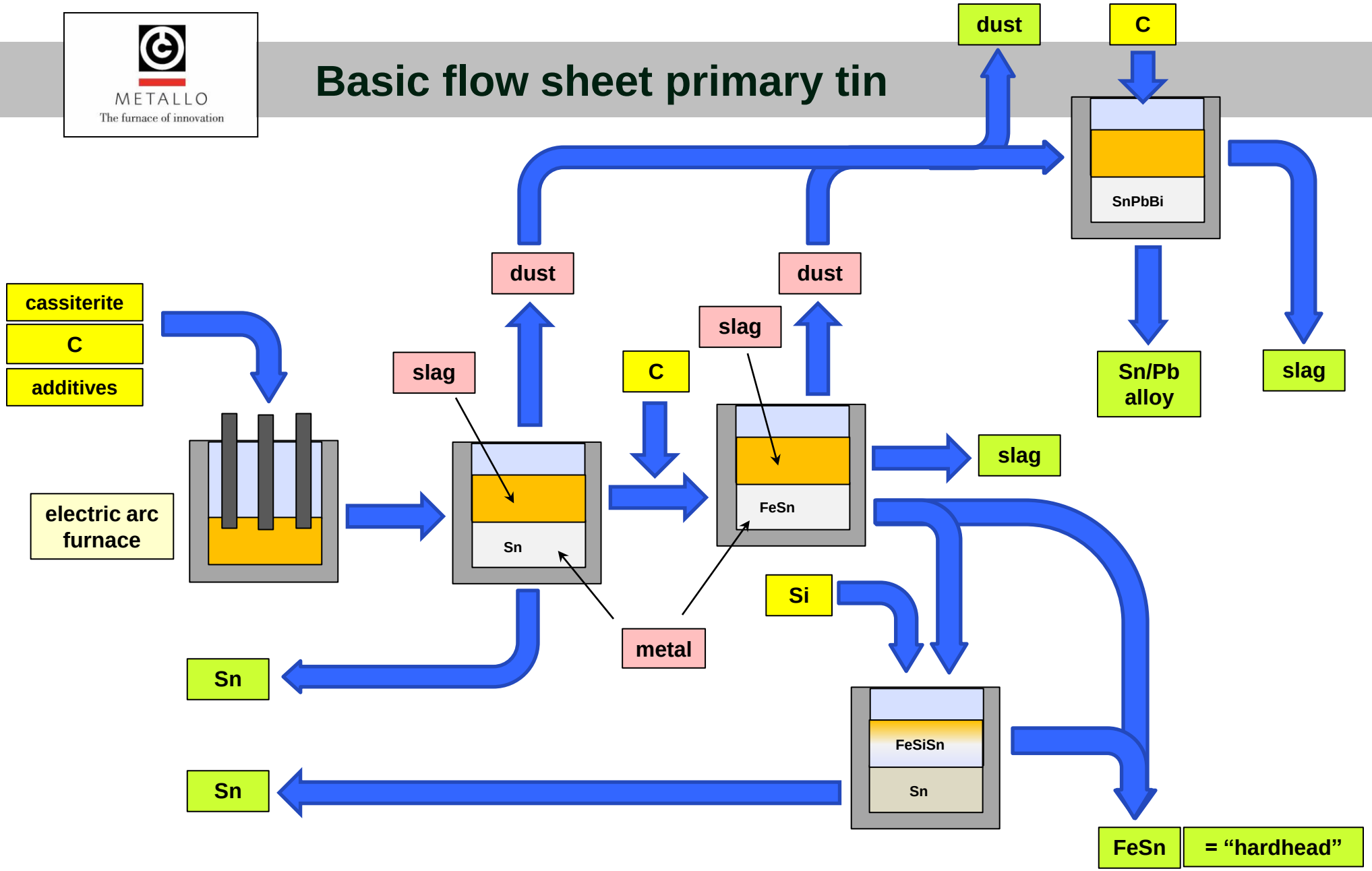
Industrial tin minerals : cassiterite (= SnO_2)

- Cassiterite = only tin bearing mineral of importance for industry
- Very dispersed occurance in nature, but upgraded by fysical methods (density)
- Upgraded product = “tin concentrate”
- Often accompanied with elements such as tantalum and niobium (minerals = columbite, “coltan”), tungsten



Basic flow sheet primary tin



Tin “concentrates”

- Can contain small amounts of uranium and thorium, and all decay products of U and Th
- Specific activity
  - U-238sec 0 – 50 Bq/g
  - Th-232sec 0 – 50 Bq/g

- Intermediates, by-products and waste generated during processing of tin concentrates can contain radioactive isotopes
- Examples :
  - Hardhead
  - Alloys
  - Slags
  - Dust

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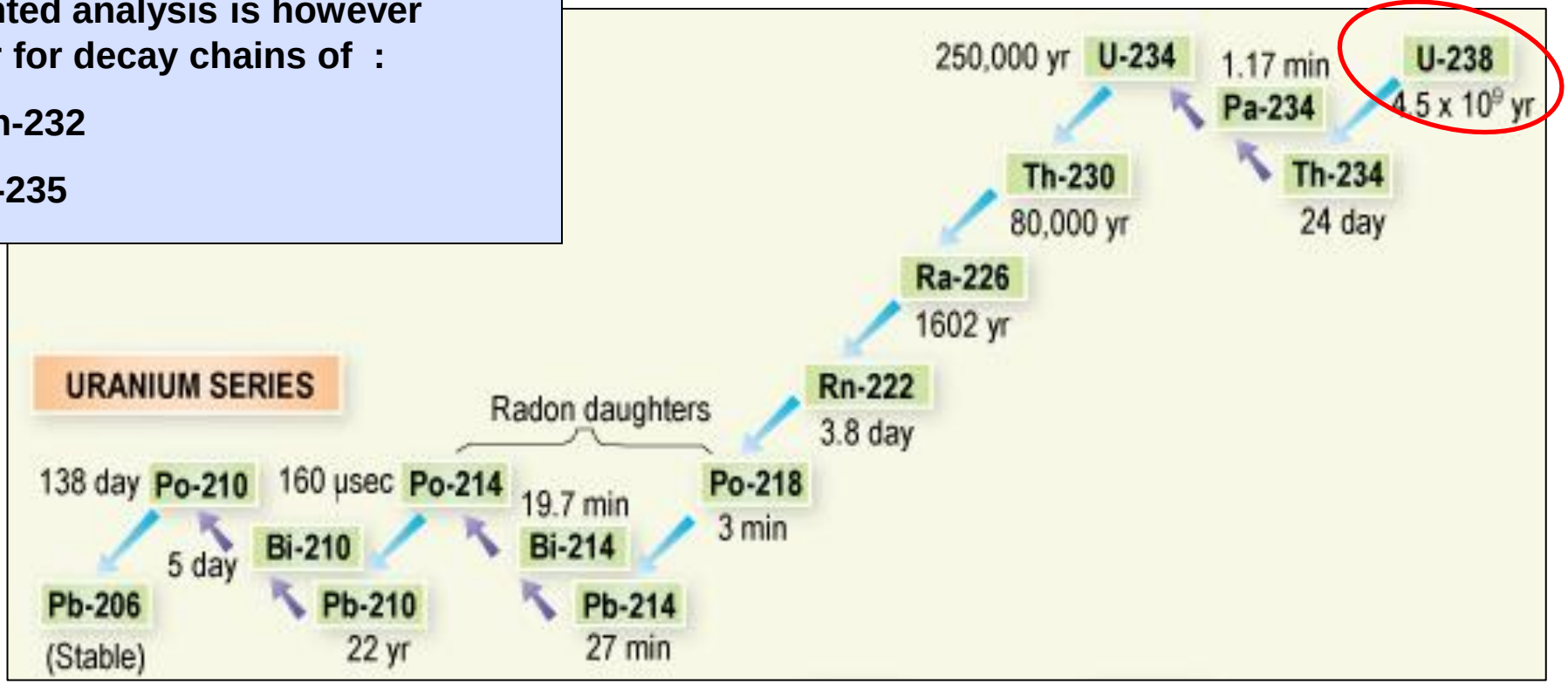
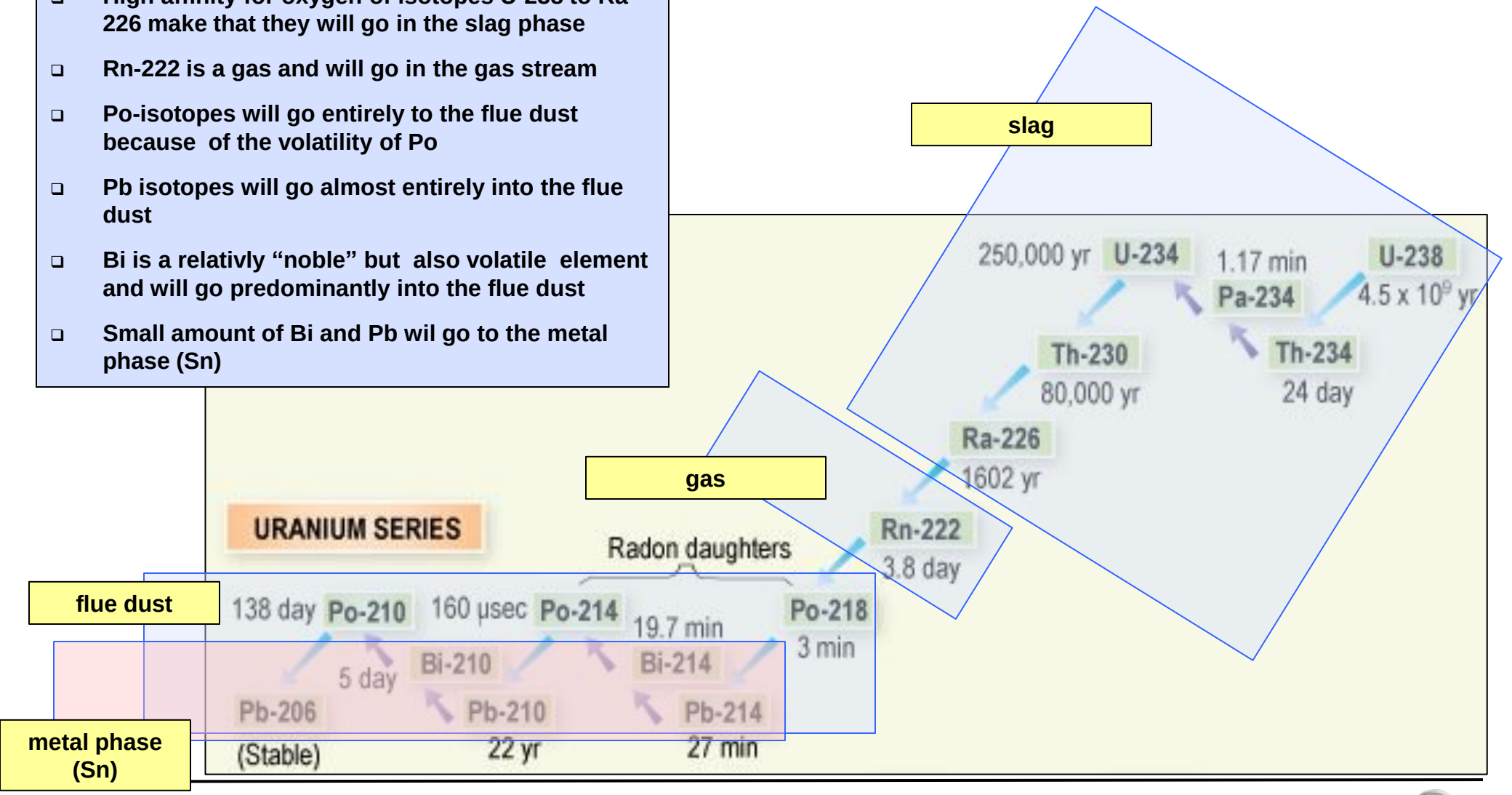
Relevant (natural) decay chain : U-238

- **Only the U-238 decay is taken into consideration because of its predominant importance compared to U-235 and Th-232**
- **Presented analysis is however similar for decay chains of :**
  - **Th-232**
  - **U-235**



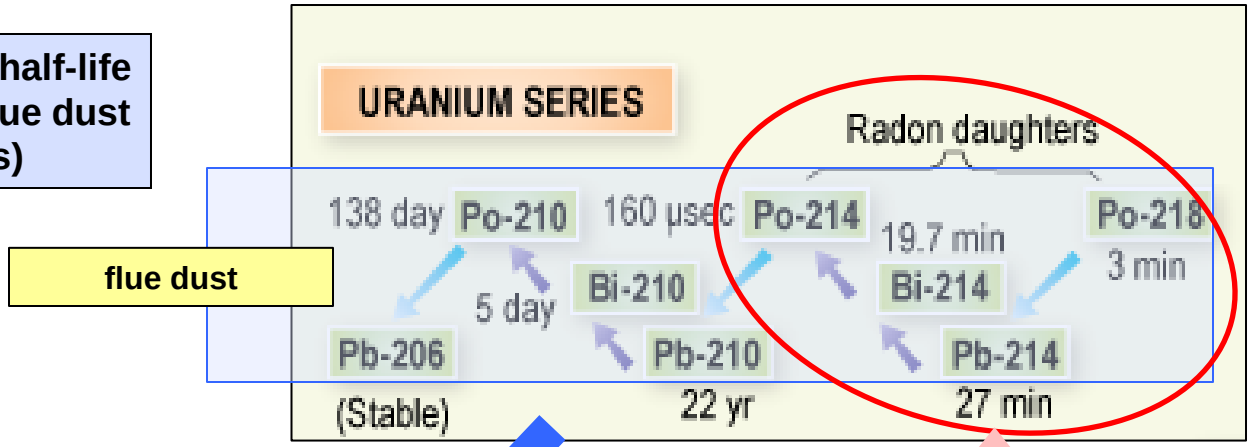
Smelting of cassiterite : behaviour of radionuclides (U-238 decay chain)

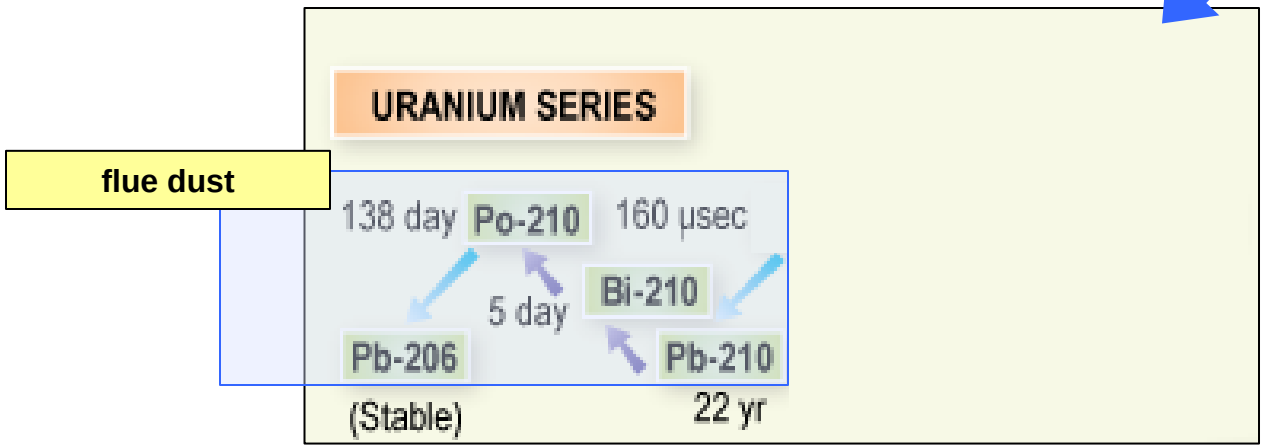
- High affinity for oxygen of isotopes U-238 to Ra-226 make that they will go in the slag phase
- Rn-222 is a gas and will go in the gas stream
- Po-isotopes will go entirely to the flue dust because of the volatility of Po
- Pb isotopes will go almost entirely into the flue dust
- Bi is a relativly “noble” but also volatile element and will go predominantly into the flue dust
- Small amount of Bi and Pb wil go to the metal phase (Sn)



Flue dust, behaviour of radionuclides (U-238 decay chain)

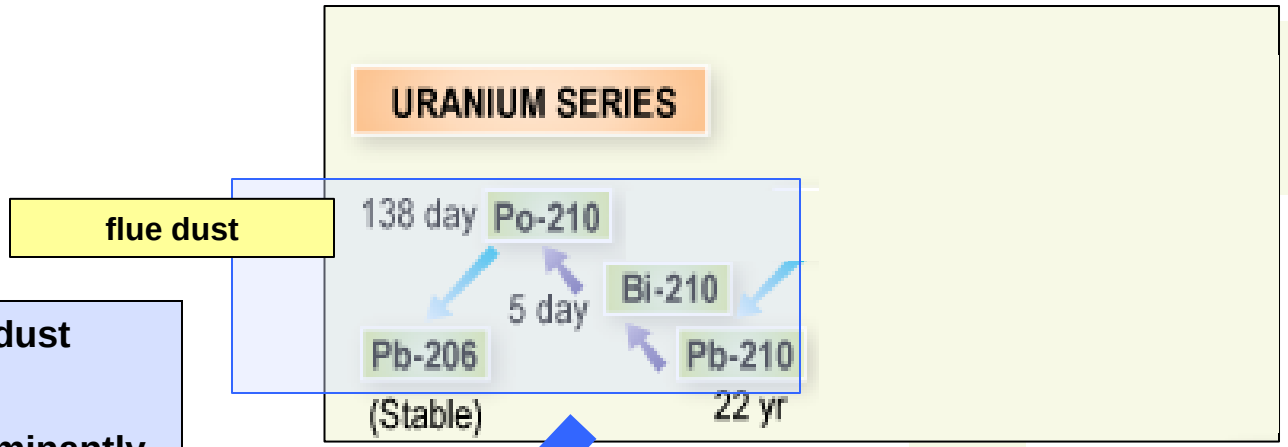
- **Po-218 to Po-214 have a very short half-life and will very fast dissapear in the flue dust (conversion to more stable isotopes)**



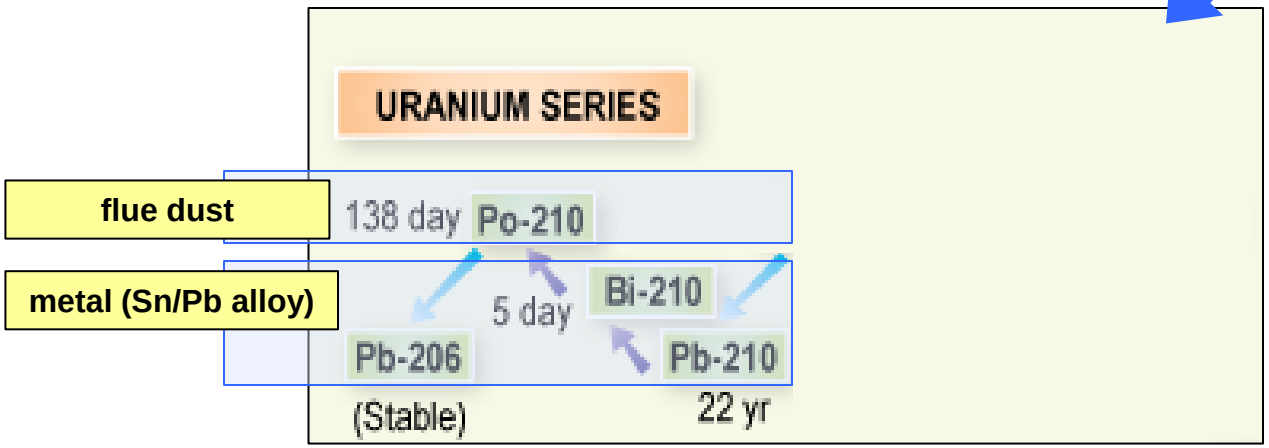


will soon disappear in the flue dust because of the short half-life.

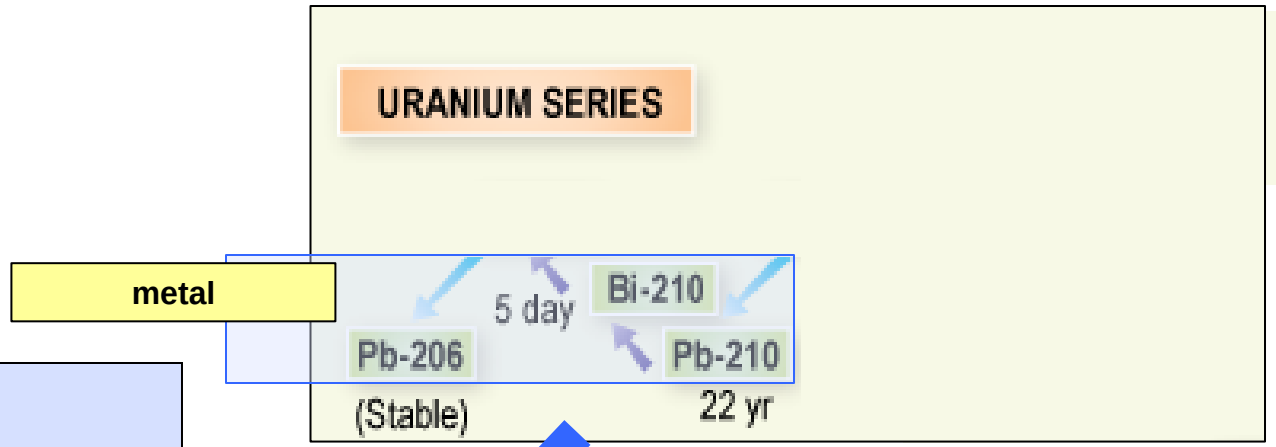
Processing flue dust, behaviour of radionuclides (U-238 decay chain)



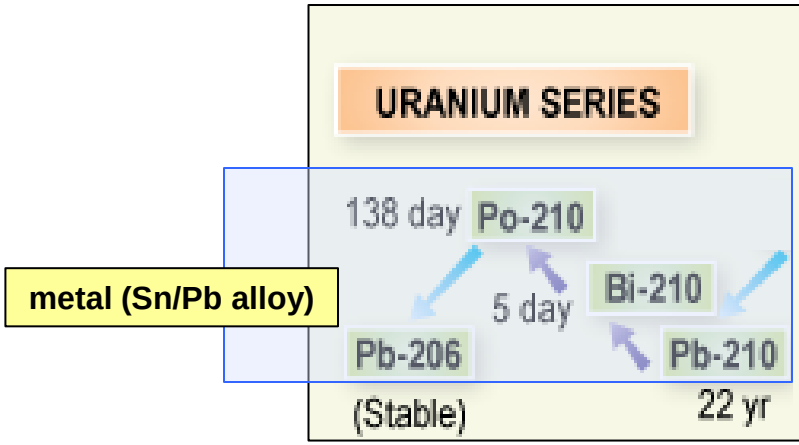
- Po-210 will go entirely to the flue dust because of its volatility
- Pb- and Bi-isotopes will go predominantly into the metal phase



Metal (Sn/Pb alloy), behaviour of radionuclides (U-238 decay chain)

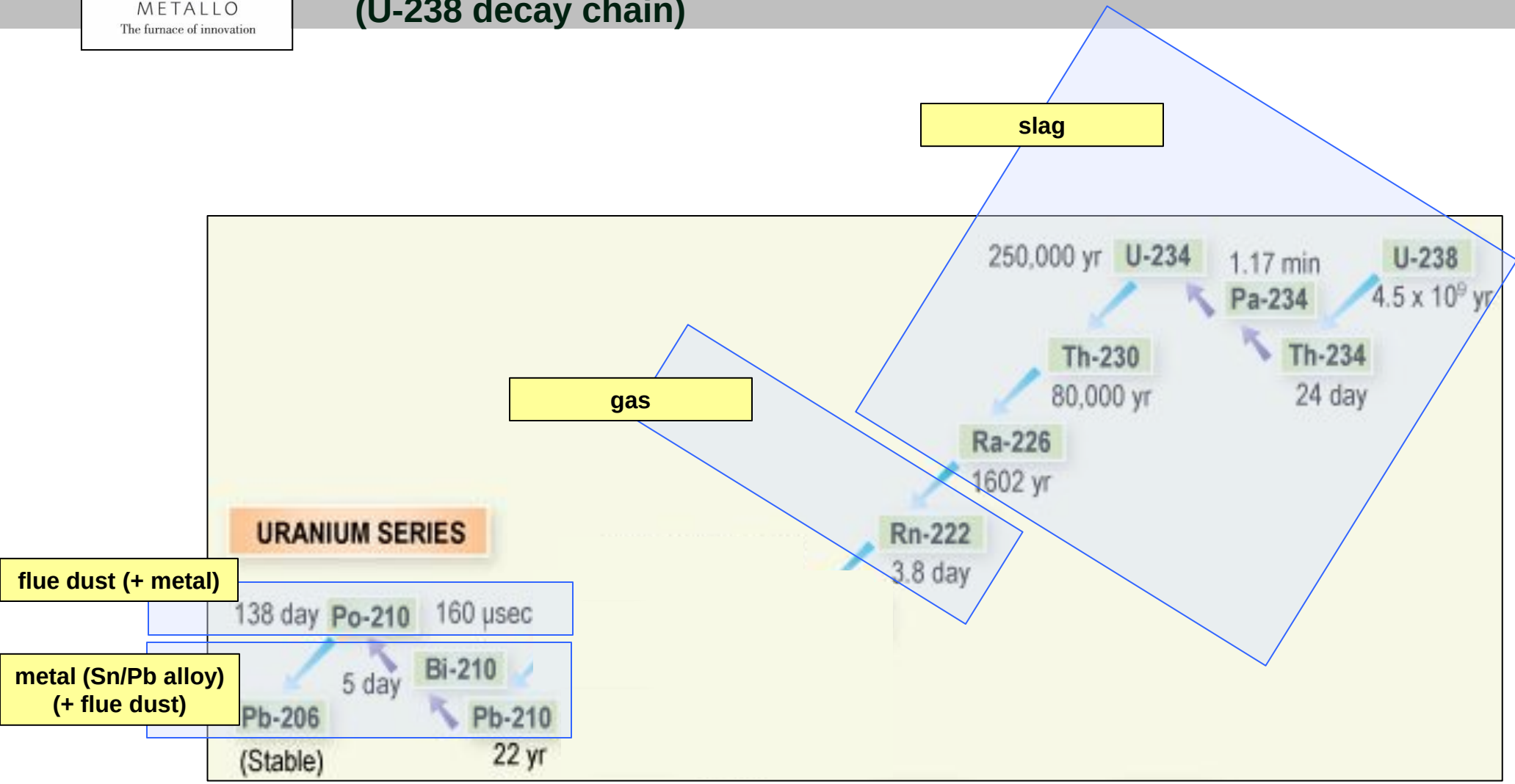


- Pb-210 will decay to Bi-210
- Po-210 is again created in the metal by decay of Bi-210

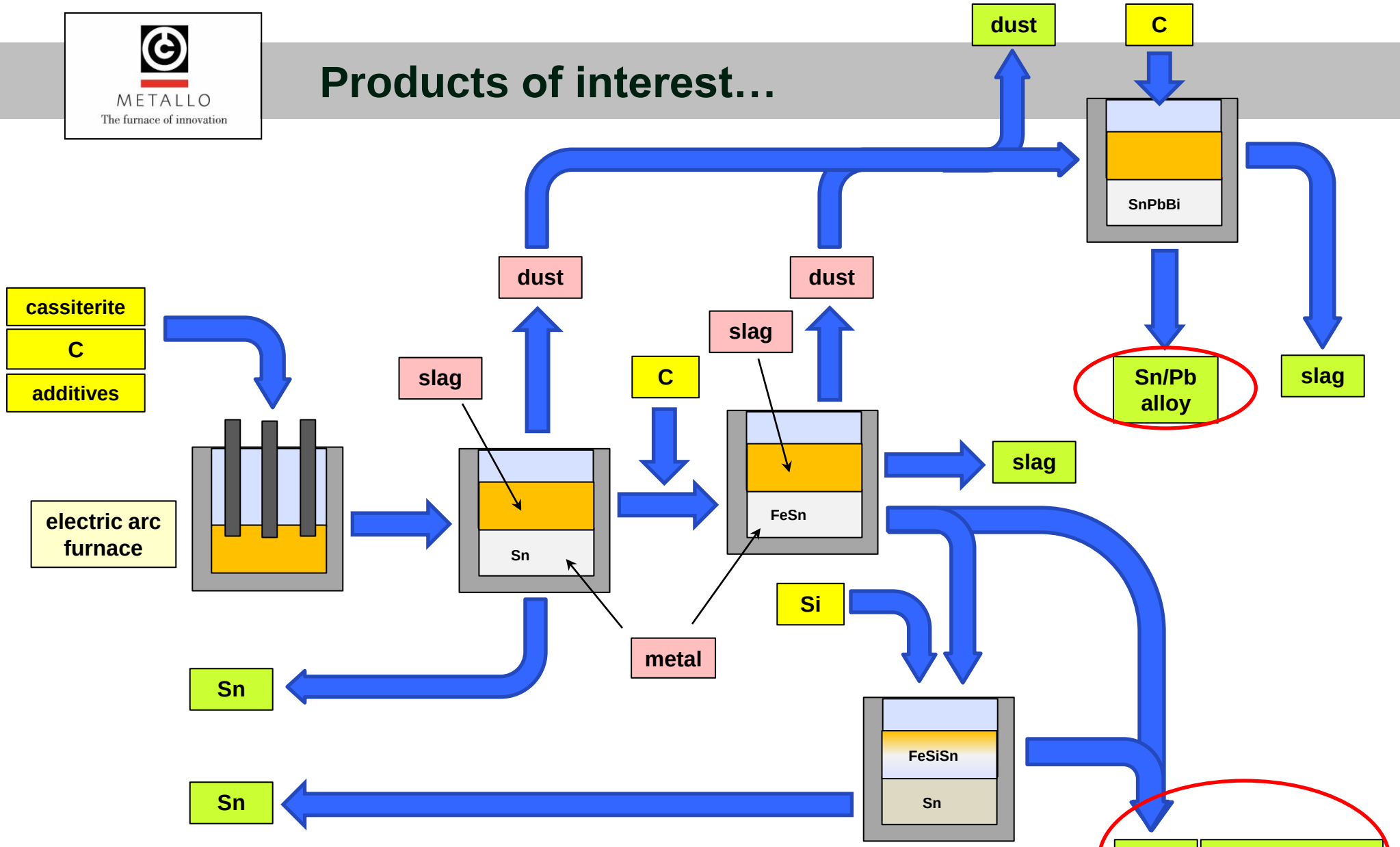


- Every time when this metal is processed at high temperature (>800°C) Po-210 will dissapear by volatilization …
- …and after a while created again in the metal due to the decay of Pb-210 to Bi-210 and the subsequent decay of Bi-210 to Po-210

Primary tin production, behaviour of radionuclides, global picture (U-238 decay chain)

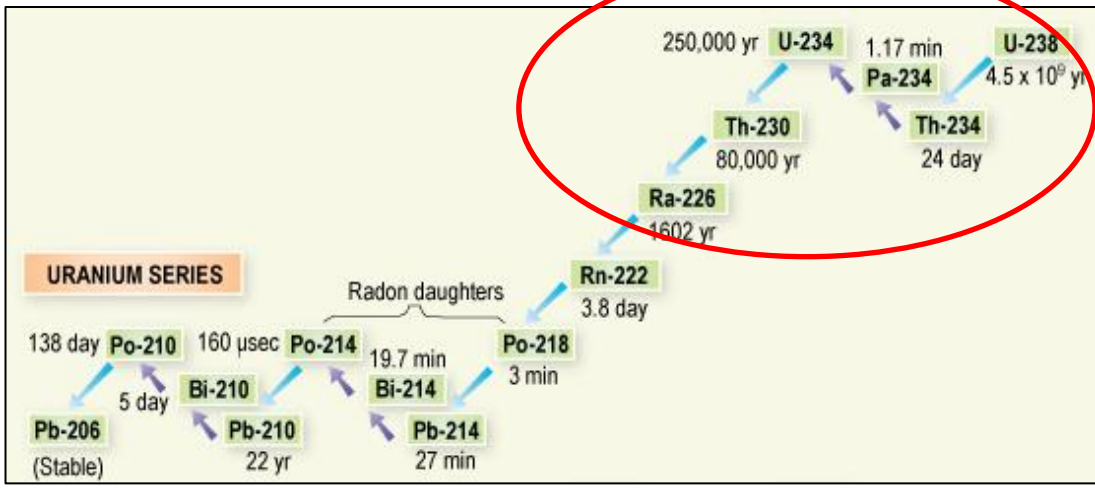


Products of interest…



Intermediates, by-products (1)

- **Hardhead**



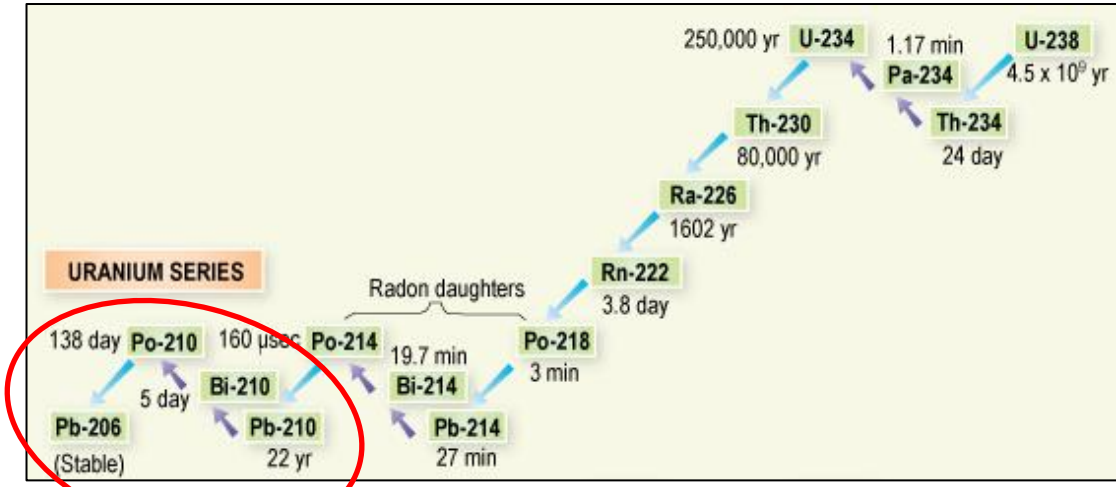
- By-product from the processing of tin concentrates
  - Mainly or entirely metallic state
  - Mainly iron
- Remark = hardhead is usually not radioactive on its own , the radioactivity is usually caused by the presence of slag
- Contains all decay products of U-238 and Th-232 with high affinity for oxygen

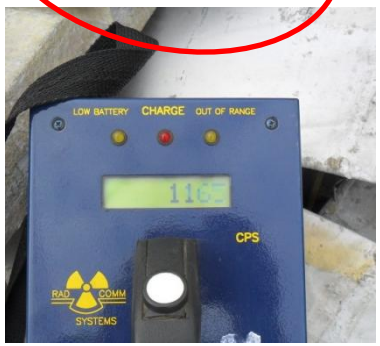
Nucleide(s)	low	high
U-238	0.30 Bq/g	11 Bq/g
Th-232	0.18 Bq/g	6 Bq/g

0,002 % U-238 0,004 % Th-232	0,088 % U-238 0,147 % Th-232

Intermediates, by-products (2)

- **Sn/Pb alloys**
  - **By-product from primary tin production**
  - **Quite different from the previous NORM because :**
    - **Does not contain isotopes that readily react with oxygen and end in the slag (U, Th, Ra, …)**
    - **Contains elements from the U decay chain starting from Pb-210**
    - **Shown example : ingots from primary smelter**
      - **Pb-210 : 81.5 Bq/g**
      - **0.32 µSv/h (contact)**
      - **1165 counts/sec (RC2)**





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- **Radiation check at Metallo**
- Health&Safety and other regulatory requirements

Radiation check at Metallo

Tin containing raw materials of interest …

- **In general : drosses, ashes, slags or other products from**
  - **primary Sn production**
  - **Nb/Ta production**
- **Typical examples :**
  - **Tin concentrates**
  - **Hardhead (Fe/Sn phase)**
  - **Sn/Pb alloys**
- **Sometimes radioactive !!**

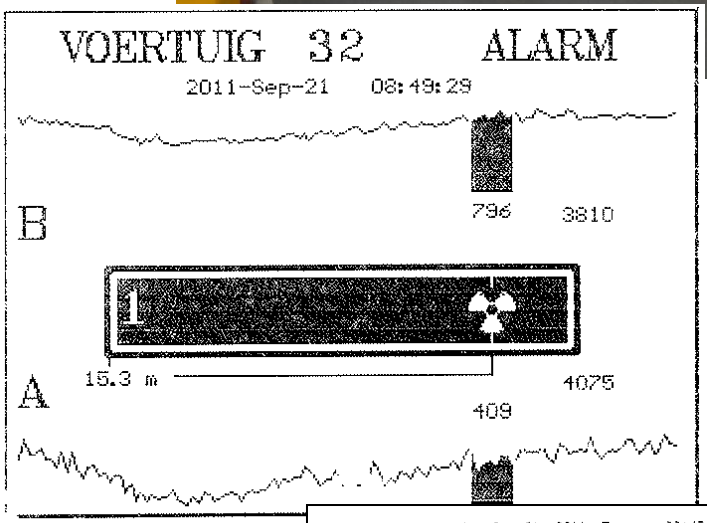
Radioactive ?

- **Facts :**
  - **You cannot see it …**
  - **You cannot smell it …**
  - **You cannot hear it …**
  - **You can't feel it …**
  - **You can't taste it … (not recommended anyhow)**
  - **Effects of exposure will be recognized usually (much) later …**

- **Don't forget :**

to measure = to know

Measuring radioactivity : full truck control



EXPLORANIUM AT-900S V 5.04 Ser#:

AT-900S Log File: Sep 21, 2011 First - 08:49:29 Last - 11:18:12

	Time	Vh/Se	Dir	Spd	Len	BG	IN	TH	HI	ALarm
*	08:49:29	32/1	out	3.83	1731	3810	3120	3508	3884	1B
	11:18:08	65/1	out	5.00	546	3801	3320	4107	4100	-
	11:18:12	65/2	out	6.21	311	3800	4110	4105	4320	2B

EXPLORANIUM AT-900S V 5.04 Ser#: 9453 21-09-11 11:16:11

- **Measuring device :**
  - **Exploranium AT-900S/6000**
- **Counting the number of particles flying through the detector :**

  counts / second
- **To be compared with natural background radiation**
- **Signal depending on :**
  - **Material characteristics : specific activity (Bq/g)**
  - **Equipment characteristics : sensitivity of the equipment**
  - **Size effects : amount of the material**
  - **Geometrical configuration :**
    - **Distance between emission source and detector**
    - **Distribution of material between the detectors**
  - **Shielding effects**

conclusion : it's radioactive !

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Measuring radioactivity : material inspection

- **Measuring device :**
  - **Rad Comm RC 2**
- **Counting the number of particles flying through the detector :**

  counts / second
- **To be compared with natural background radiation**
- **Signal depending on :**
  - **Material characteristics : specific activity (Bq/g)**
  - **Equipment characteristics : sensitivity of the equipment**
  - **Size effects : amount of the material**
  - **Geometrical configuration :**
    - **Distance between emission source and detector**
    - **Distribution of material between the detectors**
  - **Shielding effects**

conclusion : it's radioactive !

Measuring radioactivity : safety monitoring

- **Personal electronic dose rate meters**
- **Measuring device :**
  - **Canberra Mini-Radiac (since 2005 called : UltraRadiac™)**
  - **TRACERCO™ Personal Electronic Dosimeter T404**
- **Immediate reading of dose rate :**

  µSv/h
- **Acoustic signal when exceeding a treshold limit value**
- **Reading depends on :**
  - **Material characteristics : specific activity (Bq/g)**
  - **Size effects : amount of the material**
  - **Geometrical configuration :**
    - **Distance between emission sources and detector**
  - **Shielding effects**

conclusion : be carefull !

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Do you know what you need to know ??

legal requirements

Bq/g (per isotope)

material requirements

NORM / Artificial

transport requirements

NORM / Artificial

health&safety requirements

µSv / hour

conversion ?

relation ?

conversion ?

counts / second

radioactive or not-radioactive ?

dangerous or not-dangerous ?

natural or artificial ?

µSv / hour

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External check on radiation

- **Information from suppliers (very scarce !!)**
  - **Usually,**
    - they “don’t know”
    - they “cannot measure it”
    - it is “not harmfull”
- **“Port of Antwerp” control for containers**
  - **Communication when an increased and unexpected level of radiation is detected**
- **External measuring services**
  - **Case by case**
  - **Determining specific activity (Bq/g) per nuclide or series of nuclides**

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Health&safety and other regulatory requirements

NORM/TENORM processing

Compliancy with the regulatory requirements

can only be obtained

when NORM/TENORM is treated according to specific procedures,

ensuring that all precautions have been taken

to reduce human exposure to a minimum.

Special attention for :

- Permits and authorization
- Transport
- Unloading
- Storage and internal logistics
- Quality control (input)
- Processing
- Quality control (output)
- Specifications output products

Exposure measurements

- **Extensive investigation on occupational exposure : 2003-2004 (reported to FANC)**

- **General conclusion :**
  - **Very low exposure in general**
    - **Relatively low activity of materials**
    - **Relatively low tonnage treated**
    - **Very little workers are exposed to the material**
    - **Not much strictly “manual” activities**
    - **Automatisation of activities and processes**
    - **Distance to material usually at least several meters**

Example : treatment of hardhead

Example : stockpile of hardhead, ca. 200 ton

contact : 6 µSv/h
at 2 m distance : 1.5 µSv/h

Consumption : 500 ton/year

1 container = ca. 22 ton

• Reception check :	1 person (*)	5 min/container
• Unloading & sampling :	1 person (*)	35 min/container
• Sample preparation and assay :	1 person (*)	30 min/container
• Transport to furnace :	1 person (*)	5 min/1-5 ton
• Storage :	not relevant	
• Processing :	no exposure	
• Transport output products :	not relevant because of dilution factor of 50 – 100	

(*) many different persons involved…

Personal Protection

- **Personal Protection Measures :**

  gloves, working clothes, safety glasses, dust mask or …,

- **Personal Hygiene :**

  washing hands, showers, …

- **Personal Behaviour :**

  don't eat, drink or smoke on work place

Summary

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Questions ?

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Annex
Measuring equipment

Characteristics Exploranium AT-900S/6000

- **Properties :**
  - Large detector volume (2 x 49 litres)
  - 4 PVT scintillators, two in each detector box
  - Provided with test source
  - Very sensitive, easy to use, high reliability, low maintenance

- **Experience :**
  - Very high performance in detection and retrieving of radiation sources in “difficult” materials

Characteristics RadComm RC2

- **Properties :**
  - **Large internal, high grade PVT, plastic scintillation detector**
  - **Highly sensitive**
  - **Easy to use**
  - **Very robust design to whitstand the harshest evironmental situations (wheater, acciddental impact, dirt, …)**

- **Experience :**
  - **Very reliable**
  - **Excellent to retrieve radioactive pieces in metal scrap**
  - **Minor : battery life cycle**

Characteristics Canberra Mini-Radiac (UltraRadiac)

- **Properties :**
  - **Sensor : energy compensated Geiger Müller detector**
  - **Rugged design to withstand extreme environmental hazards (temperature, shock, humidity, dust, …)**
  - **Large display screen**
  - **Requiring standard AAA batteries**

- **Experience :**
  - **Slow response to changing radiation**

Characteristics TRACERCO™ PED

- **Properties :**
  - **Sensor : single, energy compensated Geiger Müller tube**
  - **Robust design, high tolerance to wet environments**
  - **Easy to use**
  - **Rechargeable battery**

- **Experience :**
  - **Very satisfactory**