Thorium applications in Spain

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Abstract. The Spanish Regulatory Authority — the Nuclear Safety Council — following the recommendations of European Directive 96/29 embarked on studies to assess the risk associated with non-nuclear applications of thorium in Spain. The work presented in this paper reflects preliminary results of a study aimed to check the traditional applications of thorium that are still in use and to assess the radiological impact of each one of them and the environmental impact of waste disposal. In this regard, several applications have been tracked through the Spanish market. The most important result obtained from the analysis of all these applications is that the vast majority of them have been abandoned as a result of the replacement of thorium by other elements, mainly yttrium, cerium and lanthanum. Nowadays the most important application is the manufacture and use of thoriated electrodes for tungsten inert gas welding. This is followed by the application in lighting, where thorium is used to coat tungsten electrodes in high intensity discharge lamps. The market for thoriated tungsten electrodes for welding involves 300 000–400 000 units per year, all of which are imported, mainly from China, so there is no manufacture of thoriated electrodes in Spain. The life of one of these electrodes has been tracked from its arrival in Spain to the disposal of the pieces remaining after use, assessing the radiological impact of storage, welding, sharpening and disposal as waste. Some of these tasks have been completed and some are still in progress.

1. Introduction

Following the recommendations of European Directive 96/29 [1], the Spanish Regulatory Authority — the Nuclear Safety Council (Consejo de Seguridad Nuclear) — embarked on studies to assess the risk associated with non-nuclear applications of several types of naturally occurring radioactive material (NORM) used mainly in industry. In particular, the study of thorium applications in Spain was entrusted to a cooperative research team from the University of the Basque Country and the University of Zaragoza.

The work presented in this paper reflects preliminary results of this study, aimed at checking which of the traditional applications of thorium still remain in use and finding out whether new applications have been developed, as well as to assess the radiological impact of each one of them and the environmental impact of waste disposal. In this regard, the uses reported in the European Commission reports Radiation Protection 95 [2] and Radiation Protection 107 [3], as well as in the United States Nuclear Regulatory Commission report NUREG-1717 [4], have been sought in the Spanish industry. It has been concluded that only the following applications should be tracked through the Spanish market: incandescent gas mantles, welding electrodes, lamps, aeronautical and aerospace thoriated alloys, vacuum tubes and optical lenses. The most important result obtained from the analysis of all these applications is that the vast majority of them have been abandoned as a result of thorium having been replaced by other elements, mainly yttrium, lanthanum and cerium.

Nowadays, the most important application is the manufacture and use of thoriated electrodes for tungsten inert gas (TIG) welding, followed by the application in lighting, where thorium is used to coat tungsten electrodes in high intensity discharge (HID) lamps. Aeronautical and aerospace thoriated alloys are used in aircraft engine parts, but only to a limited extent, if at all. The market for vacuum tubes is dominated by magnetrons for microwave ovens, but the activity content is only one hundredth of that of one welding rod and consequently the dose can be neglected. In optical lenses thorium was added to some optical glasses to improve their optical properties. It seems that safety and environmental concerns plus the availability of better optical manufacturing methods led to the decline in the use of thorium with production virtually stopping in the 1980s.

While external exposure is easily monitored, the radiation hazard arising from inhalation and ingestion of thorium or thorium contaminated dust during the various production operations such as the use of welding rods in many industries and the equivalent (but smaller scale) deployment in lamp technology requires a more elaborate assessment. In Spain there are no processes of sintering or pressing tungsten electrodes in the welding rod industry.

2. Thorium characteristics

Naturally occurring thorium is mainly the single isotope ^{232}Th, a radioactive alpha emitter with a half-life of 1.405×10^{10} a. The long radioactive decay chain headed by ^{232}Th contains another thorium isotope, ^{228}Th, with a half-life of only 1.9116 a. If radioactive equilibrium is achieved, both radioisotopes have the same activity. More information on the complete decay chain can be found in Table 1.

TABLE 1. MAIN CHARACTERISTICS OF THE ^{232}Th DECAY CHAIN [5]

Primary chain			Secondary chain		
Isotope	Half-life	Main decay	Isotope	Half-life	Main decay
^{232}Th	1.40×10^{10} a	Alpha			
^{228}Ra	5.75 a	Beta			
^{228}Ac	6.15 h	Beta			
^{228}Th	1.9116 a	Alpha			
^{224}Ra	3.66 d	Alpha			
^{220}Rn	55.6 s	Alpha			
^{216}Po	0.145 s	Alpha			
^{212}Pb	10.64 h	Beta			
^{212}Bi	60.55 m	Beta 64%	^{212}Bi	60.55m	Alpha 36%
^{212}Po	0.299 μs	Alpha	^{208}Tl	3.053m	Beta
^{208}Pb	Stable		^{208}Pb	Stable	

Natural thorium can be found in several minerals; nowadays, thorium is recovered commercially from the mineral monazite that contains 3–9 % ThO_2 along with rare-earth minerals. Thorium was discovered by Berzelius in 1828 who named it after Thor, the Scandinavian god of war. Its main properties are [6]: atomic weight 232.0381; atomic number Z = 90; melting point 1750ºC; boiling point 4788ºC; specific gravity 11.72. Pure thorium is soft and very ductile and can be cold-rolled, swaged and drawn, but is difficult to find — usually it is contaminated with oxide. When contaminated with the oxide, thorium slowly tarnishes in air, becoming grey and finally black Thorium oxide has the highest melting point of all oxides and is the chemical compound used in industrial applications of thorium. Its characteristics are: white odourless solid, molecular weight 264.04 g/mol, melting point 3220ºC, boiling point 4400ºC; specific gravity 9.86. Thorium oxide is alloyed with tungsten, which has a higher melting point of 3422ºC, to improve some of the properties of pure tungsten.

3. Incandescent gas mantles

Incandescent gas mantles, known also as Welsbach mantles, were the main application of ThO_2 up to the invention of TIG welding. They have been used for more than 100 years, since their invention by Baron Carl Auer von Welsbach in 1885. Thorium-containing mantles were available in a variety of designs and sizes, each intended to fit into one of the many different lighting devices in use. To function, the mantle must be heated to a temperature of 1870–2370ºC, which causes the thorium oxide in the mantle to incandesce. This is achieved by placing the mantle over, in or near a gas or kerosene flame that burns during the operation of the device. The greatest incandescence is obtained with mantles that consist of 99% thorium oxide plus 1% cerium oxide after pre-burning. The heat energy accumulates in thorium oxide and then the absorbed energy is transferred to cerium oxide, which emits strong visible light [7]. Without thorium oxide, the heat energy absorbed by cerium oxide is released mainly as infrared radiation. In view of the potential risks, the use of radioactive mantles cannot be justified and nowadays they have been substituted with non-radioactive mantles that contain yttrium instead of thorium to produce incandescence. Thorium is not an essential element of gas mantles, because non-radioactive mantles are as bright as radioactive ones.

The main problem with radioactive mantles is that they, and many other radioactive consumer products, are sold without any information concerning radioactivity, which is essential for consumers to be able to decide whether to purchase them. Furthermore, the general public should be educated so that they can understand the information concerning radioactivity. There is not much quantitative information about the thorium content of mantles. Nevertheless, in NUREG-1717 [4] it was assumed that a typical mantle contained 250 mg (1 kBq) for the purpose of dose calculations. They noted that some mantles contained up to 400 mg. In Europe there is no longer any fabrication of radioactive gas mantles and it is almost impossible to find them on the market. But it seems that there exists still some fabrication in the United States. Radioactive mantles could not be found in Spain.

4. Welding electrodes

Metallurgical industries present a high potential risk for workers due to the radioactivity of thorium, as thoriated welding rods probably represent the most extensive use of thorium among the non-nuclear industrial applications of this isotope. Thoriated welding rods used in TIG welding are tungsten electrodes with a 1–4% thorium oxide (ThO_2) content. This type of welding is used in industry for aluminium, stainless steel, thin sheets of metal and wherever a very good and reliable weld is required. TIG welding can be performed in any position, particularly in inverted and vertical positions. Thoriated TIG electrodes are 15 cm long, with a diameter of 1–4.8 mm. The role of the rod is to provide a high temperature plasma in a gas atmosphere, usually argon, produced by a continuous gas flow. The arc is about 1–2 cm long and thorium is added to the tungsten rods because it helps to strike the arc and maintain a better arc stability, avoiding fluctuations in the flame. Manufacturers have tried to substitute the thorium with other non-radioactive elements with similar electrical, metallurgical and thermal properties, such as lanthanum and cerium, but performance is not improved and the producers of tungsten electrodes for inert gas welding rely largely on thorium as the most effective additive. Sometimes, thorium is also added to the alumina grinding discs used for sharpening the tungsten electrodes.

In Spain the most widely used thoriated welding rods are those containing 2% ThO_2 and having a diameter of 1.6, 2.0 or 2.4 mm. Sometimes, 1 and 4 mm diameters are used. Measurements were performed on different rods from two large suppliers of welding electrodes in Spain. The Spanish market for thoriated electrodes involves 300 000–400 000 electrodes per year, almost all of which are manufactured in China.

4.1. Storage

The storage in warehouses of electrodes from different importers was considered and the radiation field was simulated using the computational code MCNP-4C [8]. The modelled scenario consisted of a set of shelves 2 m high, 2 m wide and 1 m depth, storing 2% ThO_2 welding rods 1.6, 2.0 and 2.4 mm in diameter. The rods were usually in PVC or polyethylene boxes containing 10 units. The exposure scenario is summarized in Table 2.

In order to standardize and avoid different criteria on the distribution of boxes in the shelves, a unique density of 2.22 g/cm^3 (1.75 g/cm^3 due to the welding rods) and a unique geometric distribution of boxes were assumed. The photon energies considered were those of all X ray and gamma emissions in the decay chain with an emission frequency higher than 0.1% [5], grouped in 30 keV intervals. In this way, the total final probability accounted for was 99.02% with a mean energy of 594 keV. Radiation doses were calculated at distances of 20 and 60 cm from the shelf.

TABLE 2. EXPOSURE SCENARIO FOR THE STORAGE SIMULATION

Rod diameter (mm)	Boxes					Total mass (kg)
	Quantity	Width (cm)	Length (cm)	Height (cm)	Volume (cm^3)	
1.6	850	4	18	0.5	36	64.5
2.0	300	4	18	0.5	36	37.5
2.4	850	6	18	0.8	86.4	153.5

The results for the central part of the front face of the shelf are summarized in Table 3 and illustrated in Fig. 1. The dose rates obtained in the adjacent corridor, 60 cm from the shelf and 1 m above the floor, are shown in Fig. 2. Considering now that a warehouse worker walks at a speed of 3 km/h along the corridor, the dose received by the worker would be 3.39×10^{-4} µSv. Assuming that the worker is exposed once per hour, the annual dose would be 1.97 µSv for a working year of 1700 h. Secular equilibrium in the decay chain is assumed — it is shown later in the paper that this assumption leads to an overestimation of the dose.

TABLE 3 DOSE RATES CALCULATED AT THE CENTRE OF THE FRONT FACE OF A SET OF SHELVES ON WHICH THORIATED WELDING RODS ARE STORED

Height from floor (cm)	Dose rate (µSv/h)	
	20 cm from shelf	60 cm from shelf
5	2.11	1.16
40	2.89	1.56
70	2.69	1.45
105	3.13	1.72
135	2.71	1.48
170	2.97	1.62
200	2.27	1.25

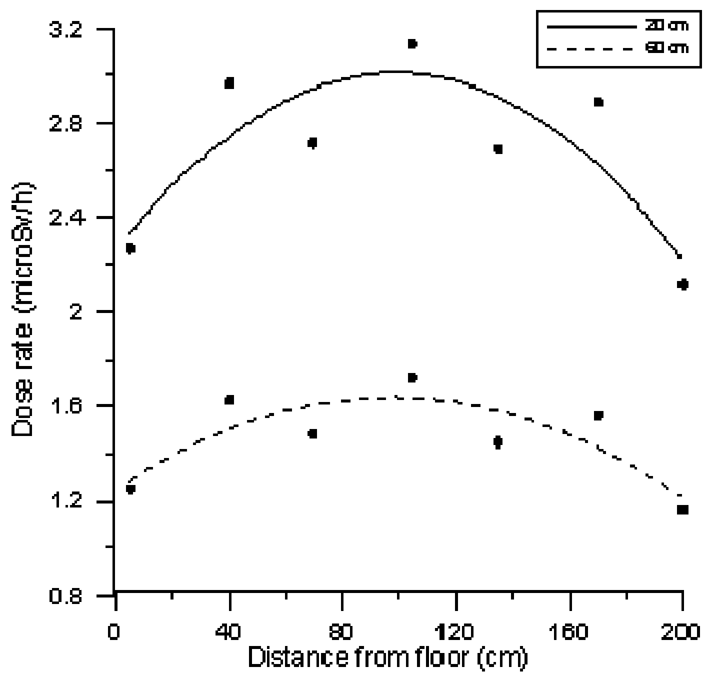

FIG. 1. Dose rate distribution beside a set of shelves storing thoriated electrodes

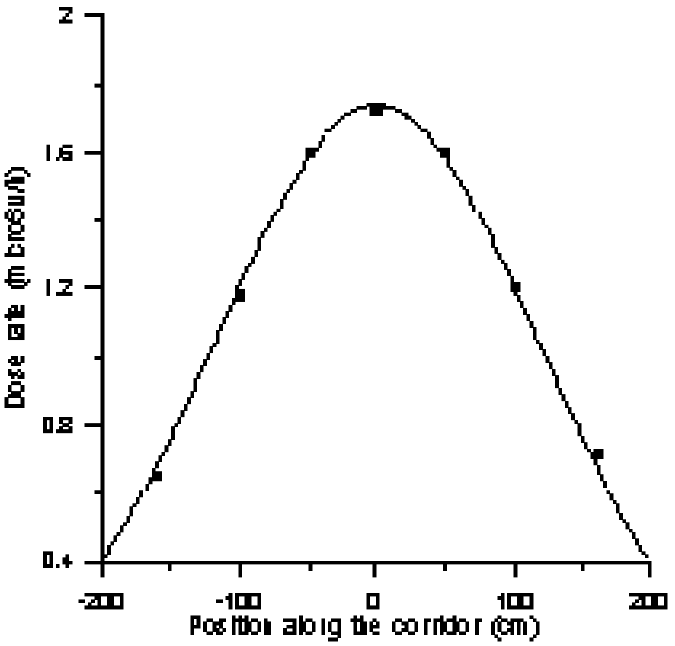

FIG. 2. Dose rate distribution along the adjacent corridor

4.2 Distribution of ThO_2 in the rods

Electrodes are made by sintering and eventually pressing a mixture of tungsten and ThO_2 powder. The homogeneity of the distribution of thorium in the rods was studied by measuring the activity of different segments by gamma and alpha spectroscopy and also by electron microscope analysis of the surface and of different cuts made at different places along the electrode perpendicularly to its axis. The results show that the ThO_2 particles are more or less homogeneously distributed both along the electrodes and in the radial direction, so it was concluded that the distribution could be considered homogeneous. The sharp end of the electrode where the electric arc is produced was the subject of particular study. Electron microscope photographs showed that fusion and sublimation of ThO_2 takes place at the surface, with the ThO_2 grains being almost absent from the external surface of the sharp end of the electrode after 1 h of continuous use.

4.3 Radioactive equilibrium of the ^{232}Th chain

To establish the equilibrium status of the different radioisotopes in the ^{232}Th chain, a quantitative determination of the thorium content was performed by alpha and gamma spectrometry. The aim was to define with some precision the source term of the radiation field and to know the radionuclide content generated in the diverse stages of the use of the electrodes as well as of the residues. The analysis of radionuclides was carried out by using intrinsic germanium low background reverse Canberra detectors GX4018 with 40% efficiency and, for the alpha spectroscopic analysis, Canberra passivated implanted planar (PIP) silicon detectors with 450 mm^2 of active area.

The electrodes studied had a ThO_2 content in the range 1.7–2.2%. Measurements of the content of ^{232}Th and its decay product ^{228}Th are summarized in Table 4, along with similar measurements conducted on lanthanated and ceriated electrodes for comparison. The uncertainty of the measurements is about 1% (k=1). The theoretical activity concentrations of ^{232}Th are 61.16 Bq/g for 1.7% ThO_2, 71.8 Bq/g for 2.0% ThO_2 and 79.22 Bq/g for 2.2% ThO_2.

If equilibrium conditions prevail, the activities of ^{232}Th and ^{228}Th will be the same. Extraction of thorium will cause the equilibrium to be broken and the parent isotope will start the reconstruction of the equilibrium. Then the ratio ^{228}Th/^{232}Th, initially with a value of unity, should diminish with time to a minimum of 0.422 after 39.855 h or 4.55 a. Should the ratio be below this number then at least a second thorium extraction has occurred. If this new extraction is performed precisely at the moment of the minimum, the new minimum $^{228}Th/^{232}Th$ ratio will fall to a value 0.178. The decay equations give the following expression for the ratio $^{228}Th/^{232}Th$:

$$\frac{A\left(^{228}Th\right)}{A\left(^{232}Th\right)} = 1 + \left[\frac{\lambda_4}{(\lambda_2 - \lambda_4)} e^{-\lambda_2 t}\right] + \left[1 + \frac{\lambda_2}{(\lambda_4 - \lambda_2)} e^{-\lambda_4 t}\right] \cong 1 + 1.4980\left[e^{-\lambda_4 t} - e^{-\lambda_2 t}\right]$$

The results in Table 4 suggest that at least two separations of thorium have been made, one of them is obvious — it was when thorium was extracted from the mineral — but a second one has been performed in the course of fabrication of the welding rods as the value of the thorium ratio is around 0.3, below the minimum value of 0.422 that would be obtained with only one extraction.

TABLE 4. Th-232 AND Th-228 CONTENT OF THORIATED, LANTHANATED AND CERIATED ELECTRODES.

Type of electrode	Diameter	Weight (g)	Activity concentration		
			^{232}Th (Bq/g)	^{228}Th (Bq/g)	Ratio $^{228}Th/^{232}Th$
2% ThO_2 (brand 1)	1	0.1431	78.23	20.95	0.268
	2.4	0.8652	64.40	20.40	0.317
	4	2.5675	60.53	18.46	0.305
2% ThO_2 (brand 2)	1	0.1169	51.40	19.17	0.373
	2.4	0.4521	63.00	24.29	0.386
	4	2.2371	62.86	23.74	0.378
2% La O_2	2	0.2452	0.45	0.13	0.289
2% CeO_2	2	0.2209	0.20	0.06	0.30

4.4. Radioactivity of airborne particulate and dust while welding

The workplace thorium air concentration was measured by taking samples of airborne particulate and dust components. To simulate the breathing conditions of workers in a representative way, low volume samplers were used [9]. Both the welding and the grinding operations were monitored, as well as the environmental radioactivity in the workplace. The welding intensities were 80–90 A for manual welding and 140 A for an automatic robot welding machine. Airborne particulate and dust samples were collected at a welding school run by a major Spanish welding electrode manufacturer. Nitrocellulose filters 47 mm diameter with a nominal pore size of 0.8 μm were used. Samples were collected at the working point while welding both manually and with an automatic robot welding machine. Also, samples of environmental airborne particulate were collected in the welding hall. The air flow rate was set at 30 L/min in order to simulate the normal breathing of a person. Some of the results are summarized in Table 5. Th-230 belongs to the ^{238}U family and was detected in manual welding, coming probably from the material being welded. Measurements conducted on deposits on hands while welding gave a negligible activity.

TABLE 5. ACTIVITY OF AIRBORNE PARTICULATE AND DUST WHILE WELDING

Welding operation	Volume of air sample (m^3)	Mass of deposit (mg)	Activity concentration (Bq/m^3)		
			^{232}Th	^{228}Th	^{230}Th
Robot trial 1	2.25	1.5	8.80×10^{-4}	2.77×10^{-4}	Not detected
Robot trial 2	3.96	4.6	3.65×10^{-4}	Not detected	Not detected
Manual Welding	2.272	4.8	3.00×10^{-3}	1.35×10^{-3}	4.27×10^{-4}

4.5. Radioactivity of airborne particulate and dust while sharpening the welding rods

Samples of airborne particulate were collected while performing the grinding operation on the electrodes. The sharpening operation of one electrode takes about 1–2 minutes and generally is performed manually, usually after having accumulated many electrodes, which are then sharpened together. Samples of dust deposited onto the hands (usually gloves have to be worn) and airborne particulate from the nose position of the worker were also collected. The activity collected on the filters was very low. Taking into account the short duration of the exposure, even when several electrodes are accumulated, a negligible dose can be assumed. The deposition on the hands, mainly in the left hand (for a right-handed person) could be more important if the obligatory gloves are not worn. The airborne particulate and dust, as well as the deposition on the hand while sharpening thoriated electrodes and pure tungsten electrodes, was measured. In one trial, involving a surface area sample of 31.5 cm^2, the activity concentrations were 6.00×10^{-3} Bq/cm^2 for ^{232}Th, 2.13×10^{-3} Bq/cm^2 for ^{228}Th and 1.08×10^{-3} Bq/cm^2 for ^{230}Th. Th-230 comes probably from the alumina grinding discs used for sharpening the rods.

5. Lamps

A variety of electric lamps used for illuminating purposes may contain thorium. In the past, thoriated-tungsten filaments were used extensively in incandescent lamps intended for general lighting purposes. However, most such lamps now use rhenium–tungsten filaments. Thorium has also been widely used in lamps requiring high electrode emissivity, in lamps that emit intense light such as lamps used in vehicles and in lamps emitting light with specific spectra. The most common type of outdoor and industrial lamps containing thorium appears to be HID lamps, including mercury vapour, metal halide, and mercury–xenon arc lamps. These lamps are constructed with thick-walled glass or quartz envelopes designed to withstand considerable temperature variations and rough use. In addition to general outdoor or industrial lighting, HID lamps are used for roadway lighting and for lighting in large indoor structures. The lamps are in different external forms but essentially all of them contain a quartz capsule about 1.5 cm in diameter and about 2.5–3 cm long. Electrodes coated or containing ThO_2 are located at both extremes of the central axis. Two electrodes in the form of rods each with a total mass of 0.1083 g were measured. The activity of these lamp electrodes is only 2×10^{-3} times the activity of a single 2.4 mm diameter thoriated TIG electrode. In addition the ThO_2 part of the lamp electrodes are encapsulated and so there is no ^{220}Rn emission and only gamma rays would need to be considered in any future dose estimation. The conclusion is that the dose contribution of lamps can be ignored.

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