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Environmental impact and risk assessment of a zircon mineral plant emissions

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Abstract

In this paper we present a study of the effects of particulate emissions of a zircon mineral processing plant on the air quality of an industrial area.
It is well known that zircon minerals contain significant levels of natural radioisotopes (500÷1000 Bq/kg for ^{232}Th and 1000÷5000 Bq/kg for ^{238}U). For this reason, the industrial processes of these minerals require specific impact analysis of the health effects and potential risk for people living near by the plant.
The case study we analysed is located in an industrial area in the North-East part of Italy. The plant mills zircon sands reducing them to a size lower than 5 μm, for foundry or ceramic industrial uses. Sands come from Australia, South Africa and Ukraine and their natural radioactivity is in the range of 1800÷3200 Bq/kg for ^{238}U. The presence of many other industrial plants in the area of concern requires particular attention in evaluating the environmental effects of this kind of mill process, as a consequence of new European and National legislation (Directive 29/96/EURATOM [1], Italian Legislative Decree n. 241/2000 [2]), too.
The analysis we describe in this paper has been performed using gaussian models to simulate the dispersion and deposition of radioactive particulate on the neighbour sites. The results of the simulation models have been used as guide-lines for a monitoring sampling campaign to verify the long term effects of the mill process. The radioactivity concentration has been determined by gamma-ray spectrometry using HPGe detector connected to a multi-channels analyser. The simulation models results have been used to make a risk evaluation of the effective absorbed dose, too.

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1 Short introduction to the problem

In 1975, Gesell e Prichard [3] proposed a new category for human radiation exposure called TENR (Technologically Enhanced Natural Radioactivity) to define exposures to truly natural sources of radiation which would not occur without some technological activity not expressly designed to produce nuclear materials. In the following years, a growing attention has been devoted to the problem connected with the enhanced exposures from industrial activities that utilised raw materials containing natural radionuclides.
Numerous industrial activities use many different raw materials that contain Naturally Occurring Raw Materials (NORM). The release into the environment of radionuclides during these industrial processes can lead to the exposure for humans. The exposures generally included in the category of enhanced exposures are those arising from mineral processing industries and from fossil fuel combustion.
Recently, Italy has been adopted, with Legislative Decree 26 May 2000 n. 241, the Directive 96/29/Euratom that recommended to Members States the regulation of work activities involving a significant increase in exposure due to natural radiation sources. The limit established by legislation for the effective dose for the members of the public is 1 mSv in a year.

2 Description of the studied case

The case study concerned a mineral processing industry located in the industrial area of Ravenna (North-East of Italy). Its activities consist of warehousing and milling raw material, mainly zircon sands, packing and distribution the end product. Zircon sands are imported from Australia, South Africa and Ukraine; respective end products have a very wide range of industrial applications. The most usual application is in the ceramic production, mainly in ceramic tiles and porcelain stoneware where zircon is used as opacifier.
Zircon sands are originated by weathering, alluvial, and gravitational processes and zirconium silicate, $ZrSiO_4$, is their mainly compound. These sands contain a significant concentration of natural radioactivity (1000÷5000 Bq/kg of ^{238}U and 500÷1000 of ^{232}Th [4]), generally one or two orders of magnitude higher than the average value in the earth's crust. The relatively high level of radioactivity can be explained on the basis of the following considerations: during formation and growth of zircon crystals by cooling of melted magma, atoms of uranium and thorium become trapped in the crystalline structure. Indeed, even though much less abundant than zirconium in the earth's crust, uranium and thorium can substitute for zirconium in the crystalline structure, because of the similar dimensions of their atomic radii and similar chemical properties. Furthermore, zircon ores undergo enrichment during sand processing which produces almost pure zirconium silicate. These are the reasons why zircon minerals are usually included in the category of sources of TENR. The level of radioactivity concentration depends by zircon sands origin and it changes according to the original country.

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The aim of the present work is the evaluation of the radiological impact of the radionuclides released in the atmosphere by zircon sand grinding procedure and the related estimation of the risk assessment for neighbour population. The estimation of the effect for the workers can be considered outside the aims of this specific work. In fact, it depends on many other aspects, quite different from air concentration of suspended radioactive particulate emitted from the smoke-stack (e.g.: particulate produced by the material process, indoor concentration, storage of the sands, etc.).

3 The experimental methodologies

In this study, the activity concentration measurements were performed by γ-ray spectrometry, using a high-purity germanium detector connected to a multichannel analyser. The high resolution of this type of detector is particularly useful for activity measurements of the uranium and thorium chain members, which present peaks very close one to each other. The detector is covered with 10 cm thick Pb shield, internally lined with a cadmium-copper coating. The gamma-ray spectrometer is equipped with software Silena GammaPlus for data acquisition and analysis.
Table 1 summaries the main characteristics of the detector we used for our measures.

Table 1. Basic features of the HPGe detector used.

Type	Silena
Geometry	coaxial
Material	HPGe n-type
Crystal radius	27 mm
Crystal length	48.5 mm
Crystal volume	109 cm^3
Relative efficiency (NaI)	22.6%
FWHM	1.9 keV (at 1332 keV)

The spectrometer calibration was made by using as source a water solution of ^{57}Co, ^{60}Co, ^{85}Sr, ^{88}Y, ^{109}Cd, ^{113}Sn, ^{139}Ce, ^{137}Cs, ^{241}Am emitting gamma-rays with energy ranging between 59.5 and 1836.1 keV. The solution was prepared and certified by LMRI (Laboratoire de Mesure des Rayonnements Ionisants). Quality control of the measurements was performed by measuring the reference material IAEA-375 certified by International Atomic Energy Agency.
Determinations of radioactivity content were carried out on samples of raw materials, end products (sands and flours produced from grinding of raw materials) and soils. Four of these latter were collected in the area of maximum deposition indicated by ISC-LT model application described in the following paragraph.
All samples were dried to 105 °C, grinding and sieved (when necessary), and placed in 0.45 litre Marinelli beakers. The samples were kept in these containers at least three weeks before measurements, so the radium, radon and its short-lived decay products were in radioactive equilibrium when measured.

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The ^{238}U and ^{232}Th concentrations were obtained by measuring the activities of their daughter products and assuming secular equilibrium conditions, hypothesis supported by other studies [5, 6]. The ^{238}U concentration was determined from the 351.92 keV gamma line of ^{214}Pb, the ^{232}Th concentration as a mean value of the results from 338.40 keV, 911.07 keV and 968.90 keV gamma lines of ^{228}Ac, the ^{235}U concentration from its 143.76 keV gamma line, and the ^{40}K concentration from its 1460.83 keV gamma line. Gamma line values and relatively yields used for the calculation are those recommended by CEA (Commissariat À l'Énergie Atomique) [7].
The activity concentration of particulate matter emitted to air was assumed the same of zircon materials involved in the industrial process. In fact, the processes performed by the industrial plant are mainly dry grinding operations that, probably, do not modify the activity concentration and do not disturb the secular equilibrium of radionuclides.

4 The applied models

In this work, we used the ISCLT3 (Industrial Source Complex Long Term, Version 3) model to estimate the concentration of suspended radioactive particulate in the atmosphere and its deposition on the neighbour soil [8, 9]. ISCLT3 model is a gaussian plume model, that can perform Long Term (or "climatological") simulations of the diffusion and deposition of pollutants emitted from many different kind of sources (e.g.: point, area, volumetric type). The simulations can range from some hours to one year in time and can be performed using either hourly specific meteorological data, or site specific Joint Frequency Functions (JFF).
In our work, we used the JFF of the meteorological station of "Marina di Ravenna", some kilometres only far from the investigated industrial plant, and we used the Briggs rural type sigma coefficient. The model can also estimate the deposition of the particulate emitted from the sources, on the base of the meteorological data of the area of concern and of the physical characteristics of the particulate, like its density, roughness and granulometry. The ISCLT3 model can also takes account of the building downwash, that represent a very important phenomenon, for the correct evaluation of the exposition of receptors near the plant.
We applied the above mentioned model for estimating the annual average of hourly concentration and annual deposition. These kind of data, obtained from the simulation model, have been used to locate the sampling position for monitoring activity concentrations of soil nearby the plant and to estimate the dose absorbed by inhabitants living near the industrial complex.

5 Analysis of the results

5.1 Activity concentration of zircon materials

The activities of ^{238}U, ^{232}Th, ^{235}U and ^{40}K in Bq/kg (dry weight) in raw material and end product samples are given in Tables 2 and 3, respectively. As it is possible to observe, two samples were analysed for each material. The

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uncertainty of the measurements was lower than 10% for ^{238}U, ^{232}Th, ^{235}U and about of 15% for ^{40}K.

Table 2. Activity concentrations in zircon sand raw materials.

Sample	Origin	Activity concentration (Bq/kg)			
		^{238}U	^{232}Th	^{235}U	^{40}K
N. 1	Australia	2400±200	520±40	110±10	34±5
N. 2	Australia	2200±200	480±40	100±10	33±5
N. 3	South Africa	3200±300	520±40	140±10	32±6
N. 4	South Africa	2900±200	450±40	130±10	32±5
N. 5	Ukraine	1800±200	370±30	84±7	26±4
N. 6	Ukraine	1900±200	380±30	87±8	32±4

Table 3. Activity concentrations in end products.

Sample	Activity concentration (Bq/kg)			
	^{238}U	^{232}Th	^{235}U	^{40}K
Zircon flour n. 1	2300±200	450±40	100±10	32±5
Zircon flour n. 2	2300±200	470±40	100±10	42±11
Zircon flour n. 3	2700±200	550±50	150±10	33±6
Zircon flour n. 4	2800±200	540±50	160±20	< dl
Zircon flour n. 5	2800±200	510±40	160±10	27±7
Zircon flour n. 6	2700±200	520±50	160±20	< dl
Zircon flour n. 7	2600±200	480±40	150±10	< dl
Zircon flour n. 8	2800±200	500±40	170±20	< dl
Zircon flour n. 9	2500±200	470±40	130±10	29±6
Zircon flour n. 10	2600±200	490±40	140±10	< dl

The activities of the ^{238}U series and ^{232}Th series in zircon sands are of the same order of magnitude and within the range reported by United Nations Committee on the Effect of Atomic Radiation [10] and National Radiological Protection Board [4]. The above results indicate that the South Afrika zircon sands have the highest radioactivity content, as reported in other works [11, 12]. The ^{232}Th: ^{238}U activity ratio (0.16÷0.22) is in agreement with the results reported by other authors [13] and indicates the better crystallographic affinity between zircon and uranium, than between zircon and thorium. From the point of view of radiation protection, the most relevant observation is that the main radioactivity content of samples is due to ^{238}U and its decay products.

As we can observe from the above reported tables, the end products activities from the different decay chains are quite similar to those ones of the original radioactive sands. These results confirm the above assumption that the industrial process does not change the secular equilibrium and the activity concentration in the natural decay chains.

Paper from: *Risk Analysis III*, CA Brebbia (Editor).
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5.2 Particulate concentration and deposition

The ground level air concentration and soil of the particulate matter has been estimated by using the ISCLT3 model. Building down-wash effects have been taken into consideration, too. The simulation results indicate that the maximum concentration (4.1 $\mu g/m^3$) and maximum deposition (114 mg/m^2-year) occur near the emission point, at about 160 m far from the stack. These results can be explained through the relative high frequency of occurrence, in the area of concern, of high instable atmospheric classes of dispersion (classes A and B) that give rise to this typical diffusion and deposition patterns from high emissions like the ones taken into account. These results are lower of about two orders of magnitude than the Italian threshold values for these kind of pollutants and point out that the effects on the environment out from the industrial plant can be considered absolutely negligible, too. In Figure 1 and 2, just on the purpose of explaining, we present the estimated iso-concentration and iso-deposition levels in the area near by the plant

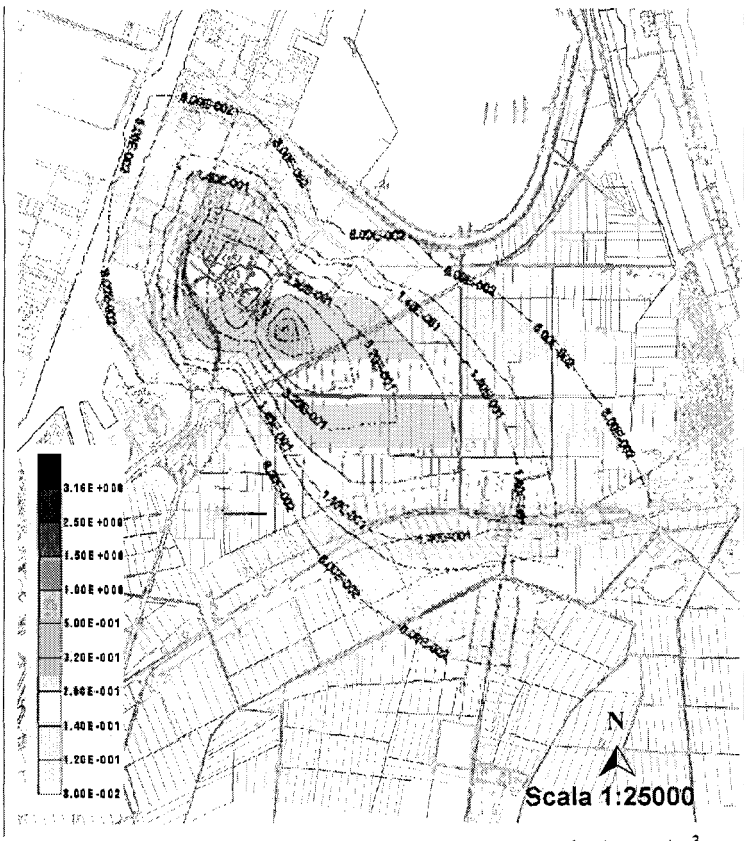

Figure 1: Annual PTS iso-concentration levels, in mg/m^3

Paper from: *Risk Analysis III*, CA Brebbia (Editor).
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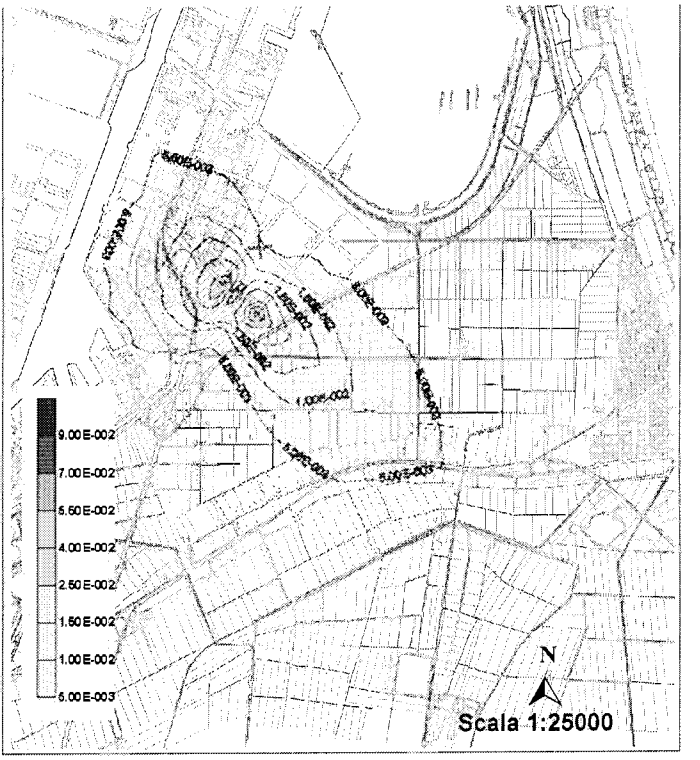

Figure 2: Annual PTS iso-deposition levels, in mg/m^2

5.3 Measurements of activity concentration of soil

The activities of ^{238}U, ^{232}Th, ^{235}U and ^{40}K in Bq/kg (dry weight) in soil samples are given in table 4. Four samples have been collected, just around the point of maximum deposition, estimated by ISCLT3 model at about 300 meters south-east from the emission stack.

Table 4. Activity concentrations in soil samples.

Sample	Activity concentration (Bq/kg)			
	^{238}U	^{232}Th	^{235}U	^{40}K
1	15±1	16±1	< dl	450±40
2	24±2	23±2	< dl	470±40
3	23±2	22±2	< dl	460±40
4	16±1	15±1	< dl	450±40
World average	35	30		400
World range	16÷110	11÷64		140÷850

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Comparison between soils collected in the area near by the plant and soils collected far by the plant show a negligible effect due to the deposition of radioactive particulate matter emitted by the plant.
Our results have been compared also with those ones reported by UNSCEAR. For the world average soil concentration the value quoted by UNSCEAR [14] is referred in table 4. The activity concentrations of soil near to the industrial plant are located in the lowest part of the radioactivity concentration range of the world. It is evident that the natural radioactivity concentration in the maximum deposition area is not distinguishable by natural background. We can conclude that the radiological impact due to particulate matter deposition is negligible.

5.4 The estimation of the absorbed doses

An estimation of the dose resulting from the exposure of member of the public to ionising radiation due to the investigated industrial plant has been performed. For the calculation of the total absorbed doses E we applied the following formula reported in [2]:

$$E(g) = E_{est} + \sum_i h(g)_i^{ina} j_i^{ina} + \sum_i h(g)_i^{ing} J_i^{ing} \quad (1)$$

where:
$E(g)$ is the effective dose incurred by an individual in the group of age g;
E_{est} is the relevant effective dose from external exposure;
$h(g)_i^{ina}$ and $h(g)_i^{ing}$ are the committed effective dose per unit-intake for ingested or inhaled radionuclide i (Sv/Bq) by an individual in the group of age g;
J_i^{ina} and J_i^{ing} are, respectively, the relevant intake via ingestion or inhalation of the radionuclide i (Bq).
The only significant path of exposition for the population near by the plant is represented by:

$$\sum_i h(g)_i^{ina} j_i^{ina} \quad (2)$$

In fact, the radioactivity air concentration is very low and doesn't produce significant exposure due to external radiation and ingestion.
The effective dose due to inhalation has been evaluated using the results of the concentration estimated by ISCLT3 gaussian model.
The estimate of the effective dose inhaled by the receptors (people living neighbour the plant) has been done using the following formulas from the EPA Risk Based Corrective Action (RBCA) methodology for the outdoor inhalation dose evaluation [18]:

$$ADD = Pa \cdot IRa \cdot ET \cdot EF \cdot Rf \quad (3)$$

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Where:
ADD is the Annual aDsorbed Dose from inhalation (mg/y),
Pa is the maximum concentration of particulate in air ($\mu g/m^3$), obtained from ISCLT3 model
IRa is the inhalation rate = 0.89 m^3/hr
ET is the daily outdoor exposure time = 8 hr/day
EF is the exposure frequency = 365 days per year
Rf if the fraction of breathable particulate =1

Through this calculus we have estimated an effective absorbed dose, via inhalation, of $4.41 \cdot 10^{-3}$ mSv/a. This value is about 3 order of magnitude less than the threshold limit 1 mSv/a reported in the Italian Legislation (D.Lgs.241/2000).

6 Conclusion

In this work we have analysed the potential impact on the population of the grinding of zircon sand performed in one plant of the Ravenna area. The measure of the radioactivity in the soil nearby the industrial plant and the estimation of the absorbed dose, performed using world wide accepted procedure, points out that the radiological impact on the environment and on the population is negligible. In the next future, the authors are going to extend their health and environmental analysis to the workers and to the quality of the air indoor and in the industrial just near the sites where the industrial process take place.

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