Environmental Science Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Most ^{210}Po radionuclide activity present in crude coal after its combustion is attached to particles with diameters lower than 1 µm. Such small particles are not efficiently separated by classical filters, cyclones, or electrostatic precipitation systems. Coal combustion processes can thus generate a significant amount of ^{210}Po, which is released to the atmosphere mostly in the winter season. Even 50% of ^{210}Po escaping through vent systems increases the aerosol activity in the region of local power plants. In such areas, ^{210}Po activity should be carefully monitored in the air as well as in all types of environmental samples, including soil, water, and locally produced food.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Excess of Polonium-210 activity in the surface urban atmosphere. Part 2. Origin of ^{210}Po excess

Magdalena Długosz-Lisiecka

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The presence of significant ^{210}Po activity, unsupported by its grandparent radionuclide ^{210}Pb, in the surface atmosphere of industrialized regions can originate from human technical activities. In urban air, the activity ratio of ^{210}Po to ^{210}Pb might increase as a result of natural condensation and coagulation processes of relatively volatile ^{210}Po-containing species emitted during coal combustion processes. The excess of ^{210}Po cannot be explained by its in-growth from radioactive decay of the ^{210}Bi. Up to about 50% of ^{210}Po radionuclide released during coal combustion processes can be emitted into the air as gaseous or ultrafine products. Subsequently these products are quickly attached to the surface of fine particles suspended in the air. As a result, an excess of ^{210}Po activity in aerosols has been reported. As much as 11 GBq of ^{210}Po per year can enter the urban air from the local coal power plants in Lodz city, Poland, in this way.

Introduction:

As a result of high temperature processes like fossil fuel burning, three types of conversion are observed: vaporization, secondary chemical reactions, and solid waste production.

It is well known that investigated radionuclides in the form of either pure elements or their derivatives are relatively volatile and can easily evaporate under conditions typical for high temperature processes[1]. Barton[2] reported that the temperature of fossil fuel combustion (~1300 °C) strongly affects the fate of metallic elements which are present in trace amounts in natural fuels. Besides the gaseous ^{222}Rn, the long lived radionuclide ^{210}Pb and its two progenies, ^{210}Bi and ^{210}Po, are the main radioactive isotopes released from power plants and domestic furnaces. The final distribution of the metallic elements between fly ashes and gaseous or slag phases depends on the physicochemical properties of their burning conditions.

In the air, elemental polonium starts to sublime at 700 °C, while at 900 °C it should evaporate completely from matter. However, at combustion temperatures in the presence of oxygen, polonium and its parent lead isotope as metals can react rapidly to form slightly less volatile oxides. Polonium oxides such as PoO_2 with a sublimation temperature of 885 °C are the products most likely to be present in the hot exhaust gases generated in fossil fuel combustion processes. It is not possible to remove these gaseous oxidation products using standard ash recovery systems. As is evident from Fig. 1, elemental polonium exhibits higher vapour pressure compared with bismuth and lead. At the temperature of 1200 °C typical for the coal combustion process, the Po/Pb vapour pressure ratio is equal to 220. In comparison, the Bi/Pb vapour pressure ratio at this temperature is equal to only 5. The boiling points are equal to 960, 1740, and 1559 ºC for Po, Pb, and Bi respectively. These data suggest that the dust and off-gas products of the thermal processes should be enriched in Po relative to Pb or Bi[3,4,5].

In some technological processes carried out at temperatures above 1000 °C (for example, during energetic coal combustion, iron sintering, or pelletizing plants or in phosphorous or cement production), an additional portion of ^{210}Po, unsupported by its parent radionuclide ^{210}Pb, can be released into the atmosphere. A certain part of the ^{210}Po freely discharged with exhaust gases through the vent system might be subjected to adsorption on the walls of the system. Condensation on ultrafine particles with diameters lower than 0.1 µm escaping through the electrostatic filter zone is another process that can be assumed to be effective and important.

The aim of this study was to investigate the fate of ^{210}Po radionuclides emitted in high temperature processes.

Material and methods

Fly ashes and exhaust gases generated in domestic heating systems were collected by the simple sampling kit. In the above mentioned sampling method, two washer kits (both with 100 ml of 2M HCl) have been installed between a one-stage Andersen impactor and the pump (Fig.1). The ^{210}Po radionuclide activity in both washers can be considered as a gaseous form of ^{210}Po not captured on the nitrocellulose filter.

The samples of solid particulate matter collected from the dedusting installation at three coal power plants and domestic heating systems were analyzed according to the method applied in the radiochemical analysis of alpha-emitting radionuclide ^{210}Po.

The ^{210}Po analytical procedure was similar to that used in the previous study[6].This method is based on the spontaneous deposition of radionuclide on silver discs in a Teflon container at a temperature of 80 °C for at least 8 hours. The activity of the sample with deposited polonium was then measured using an alpha spectrometer[7] (PIPS detector by Canberra, Inc.) with a mean chemical yield equal to 90%.

Yield of polonium separation[6,8] by this method has been calculated by use of IAEA reference materials: IAEA 300 (sediment) and IAEA 327 (soil). For ^{210}Pb accuracy and precision determination IAEA 327, IAEA 434 and soil material used in laboratory inter-comparison test (IAEA 2006-03 code) have been applied (Table 1).

Table 1. The ^{210}Pb measured and certified activity in reference materials.

Reference material	^{210}Pb measured activity concentration [Bq/kg]	^{210}Pb certified activity concentration [Bq/kg]	Standard deviation %
IAEA Soil 327	58.8	61.7±3.3	4.9
IAEA	680	688±48	1.2

Phosphogypsum 434			
IAEA Soil 2006-03	259.5	262.8±15.8	1.3

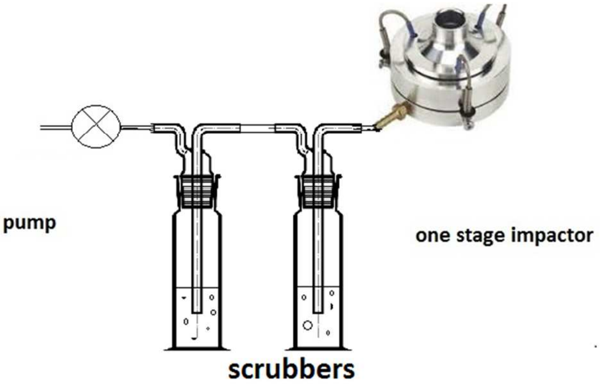

Fig. 1. Diagram of the sampling kit for the analysis of ^{210}Po in the attached and unattached forms.

In the first step of the analytical procedure, solid particles generated during combustion were collected on the nitrocellulose filter and then analyzed after standard radiochemical preparation. The attachment rate λ of radon decay products to solid particles is based on the diffusion process and can be estimated using Equation (1)[9]:

$$\lambda = 4\pi r^2 N\alpha \sqrt{\frac{RT}{2\pi M}} \tag{1}$$

where:

N – number of condensation nuclei in 1 m^3 of air,
r – radius of nuclei,
α – accommodation coefficient,
R – Boltzmann's gas constant (8.617 $*10^{-5}$ eV/K),
M – molecular weight of decay products,
T – the absolute temperature (K).

Results

In the coal-burning processes, most radionuclides such as ^{222}Rn and its decay products evaporate in the hot gases phase. Some of them return to the solid phase mostly by deposition on the surface or within pores of fine (< 2.5 μm) or ultrafine (< 0.1 μm) particles in the post-combustion zone.

The coal combustion process starts by fast drying of the crude coal. In the next phase, organic matter is pyrolysed.

Polonium reacts efficiently with oxygen, leading mainly to the formation of PoO_2 and other polonium oxides. In the gaseous form, polonium compounds displaced into the cooler zone initiate the condensation process. Only a small portion of ^{210}Po radionuclide material appears to remain non-volatilized in the bottom ash. Gaseous polonium compounds can be involved in the surface condensation on cold parts of the installation or attached to the surface of small particles. Alternatively they can still stay in the gaseous phase. In this form, polonium can be transported through the whole vent system and released to the atmosphere.

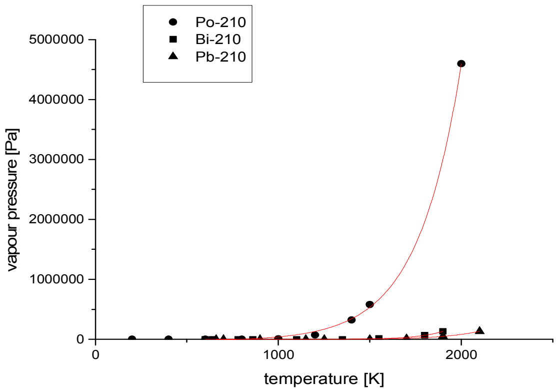

Fig. 2 The vapor pressure for metallic Po, Bi, and Pb.

Condensation on solid particles

At high temperature (T > 1000 ^{o}C), a large number of particles are generated and therefore they preferably and rapidly coagulate into soot cluster aggregates. As a result of such efficient coagulation (Equation 1), polonium activity of fine and ultrafine particles increases. Under these conditions, polonium activity grows, probably due to the additional filtration layer.

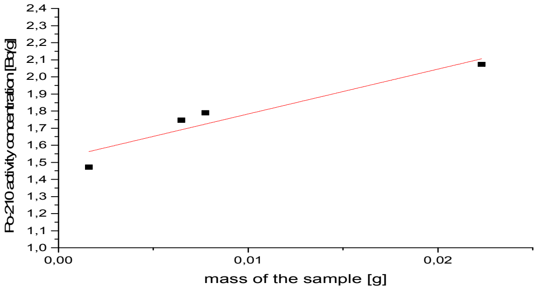

Fig. 3 ^{210}Po activity concentration measured at T = 150 ^{o}C in the stream of particles emitted in the domestic coal combustion process.

Because of the high concentration of solid particles in the zone close to the combustion chamber, ^{210}Po and other long-lived ^{222}Rn decay products very likely attach to the particulate matter. It has been found that ^{210}Po specific activity is proportional (R^2 = 0.998) to the mass of the collected dust (Fig 3.).

At lower temperatures of flue gases, the condensation rate decreases due to the lower kinetic energy of the particles and gas mixture. In the open air, the condensation process proceeds very slowly.

It is well known that the attachment rate is proportional to the surface area of the condensation nuclei. The activity concentration reaches a maximum for particles with a large specific area generated in coal combustion processes. Fly ash aerosols up to 10 μm in diameter are efficiently captured by the electrostatic precipitation field. Decreasing the diameter of the aerosol also decreases the efficiency of their uptake. Particles with diameters lower than 1.45 μm leaving the electrostatic zone can be emitted with flue gases into the atmosphere[10]. Particles with aerodynamic diameter lower than 1.45 μm represent 66% of the dust escaping from the electrostatic zone. Most of the polonium is thus not captured in the precipitation system but carried in the stream of exhaust gases. This fraction of ^{210}Po has been proposed as the main source of increased activity of air and soil in the region of the emission source in Lodz city. Similar enhanced activity of ^{210}Po was observed in Silesia region in Poland[11].

Lignite-burning plants usually generate very large quantities, even thousands of tonnes per year, of fine and ultrafine aerosols. Only the use of an electrostatic dust collection system with multi-electrostatic zones turned out to be effective for polonium and lead element capture. Escaping fine aerosols smaller than 0.1 μm and gases with high ^{210}Po activity concentrations are called the unattached fraction. They can carry as much as several becquerels per gram[1]. Immediately after escaping, ^{210}Po polonium and other radionuclides condense on fine particles. Part one of this study presented the results of observations of atmospheric aerosols collected during one full year[12].

The quantity of the dust emission flux to the atmosphere will depend on the efficiency of the off-gas purifying systems, additionally installed electrostatic precipitators, and high-pressure water scrubbers. The flue gas desulfurization system additionally captures fine and ultrafine components of particulate matter and effectively adsorbs polonium and other metal compounds. The particles with diameter < 0.5 μm can be separated from the flue gases by the mechanism of diffusion based on Brownian motion and thermal or pressure diffusion in the gas mixture[10]. Condensation occurring as a result of adiabatic expansion of the exhaust gas is caused by the change of particle velocity and cooling to a temperature lower than the dew point for the polonium compounds[1] (Mora et al., 2011). The process of dedusting which is realized in the desulfurization system depends on the dust concentration in the hot gases, the exhaust gas velocity, and the pH of the mixture. Analyzed samples of the final product indicate the efficient uptake of the volatile compounds of polonium and lead.

^{210}Po and ^{210}Pb activity concentrations have been measured in crude coal samples, in solid particles of fly ashes escaping from electrofilters, and in the solid fraction after desulfurization processes. Analysis of all data makes it possible to estimate the fraction of ^{210}Po released to the atmosphere in the unsupported form.

Table 1. ^{210}Po mass balance for coal (CPP) and lignite power plant (LPP) and domestic heating system.

	CPP in Lodz* 2600 MW	CPP in Chorzów 1000 MW	LPP in Bełchatów 5350 MW	Domestic heating system ~ 25 kW
^{210}Po in coal – total activity per year	21.0 GBq	14.0 GBq	787.5 GBq	112.5 kBq
^{210}Pb in coal – total activity per year	21.0 GBq	14.0 GBq	900.2 GBq	128.6 kBq
Estimated ^{210}Po activity in cached fractions	10.1 GBq	6.8 GBq	489.8 GBq	60.0 kBq
Estimated ^{210}Pb activity in cached fractions	20.1 GBq	13.6 GBq	804.5 GBq	120.0 kBq
^{210}Po deficit of the activity per year	10.9 GBq	7.2 GBq	297.6 GBq	52.5 kBq
^{210}Pb deficit of the activity per year	0.9 GBq	0.4 GBq	95.7 GBq	8.6 kBq
^{210}Po defect/^{210}Pb defect activity ratio	12.11	24.50	3.11	6.10
^{210}Po activity deficit/^{210}Po total activity	48.1%	51.0%	37.7%	46.6%
^{210}Pb activity deficit/^{210}Pb total activity	4.28%	2.86%	12.15%	7.64%
Typical temperature of burning [^{o}C]	1100–1300	1100–1300	1000–1200	550–950
Annual Po-210 activity release per watt [Bq/W]	4.19	7.20	55.62	2.10

*(sum of all stations in the city)

In the tested heating systems, disequilibrium between ^{210}Po and ^{210}Pb activities in escaping fly ash has been observed (Table 2).

Mass balance estimation indicates the absence of activity for both radionuclides in the captured ash compared with fossil fuel total activity. This confirms the hypothesis on the free release of a certain portion of radionuclides in the vicinity of power plants. Polonium, being a more volatile element than its precursors, Bi or Pb, evaporates more easily from the burning coal containing equilibrium activities of ^{210}Po, ^{210}Pb, and ^{210}Bi[13,14]. This process leads to ^{210}Po and ^{210}Pb disequilibrium (Table 2), which can confirm the activity deficit in fly ash emitted from local power plants and domestic heating systems.

The portion of fly ashes, that is, ultrafine particles that escape filtration and are released from a stack, generally has a higher enrichment factor. For ^{210}Po, this factor depends on the coal type, ash content, and power plant design. The enrichment factor can reach values up to 31, defined as the ratio of radionuclide concentration in the ash to that in the feed coal[15].

As a result of mass balance, as much as about 50% of ^{210}Po and 3–12% of ^{210}Pb activity present in the coal can be released directly into the urban air. During one full year, energetic and power generation power plants can combust about 933 000 tons of coal in Lodz city. As a result, 24 000 tons of slag and 130 000 tons of fly ash would be generated. Although very efficient dedusting systems have been installed, some amount of fine fly ash escapes into the atmosphere. Even in the case of a dedusting process with 99% efficiency, about 210 tonnes of fine particles are emitted annually into the atmosphere. The total activity of ^{210}Pb and ^{210}Po in secular equilibrium in coal combusted in power plants during a full year was 21 GBq .

Simple calculation (Table 2) confirmed that as much as 11 GBq of ^{210}Po per year can be freely released to the atmosphere in Lodz city centre from three local coal power plants. Similar results were obtained for Skawina Power Plant, located in Chorzów, where the total emission of ^{210}Po was estimated to be about 7 GBq per year. Vrecek and Benedik[16] (2003) estimated the annual emissions of ^{210}Pb and ^{210}Po in the escaping fly ashes in Slovenia to be 13.4 and 3.25 GBq, respectively. A study by Mora[1] in Spain confirms emissions of as much as 140 GBq of ^{210}Po activity, which represents around 40% of the total amount. The value of escaping ^{210}Po activity is equal to 17.5 GBq per year[17] was measured in Seoul, Korea. Is should be noted that the lethal dose for ^{210}Po inhalation is 2–15 MBq[18]. Due to the strong dilution of ^{210}Po after emission from the stock, the radiological hazard for the local inhabitants is quite low and was estimated to be 20 and 4 μSv/year for children and adults, respectively, in Lodz city, Poland.

By comparison, at the Lignite Power Plant (LPP) located in Bełchatów city, annual ^{210}Po emission was estimated to be about 300 GBq. ^{210}Po activity release per watt was in the range from 4.2 to 10 Bq for coal-fired power stations and as much as 55 Bq for lignite-fed power plants. Usually, the release of ^{210}Po and other radionuclides is reduced by the use of desulfurization systems.

The flue gas desulfurization process efficiently reduce emissions of polonium and lead to the atmosphere. In the current study, a small increase in the content of ^{210}Po in the final product was found but it was not possible to precisely assess the adsorption level. Most of the coal power plants in Poland still do not use a desulphurization system or use it temporarily in the winter season. The power plants mainly use standard installations for purification of exhaust gases. As a result, polonium, other metals, dioxins, furans, and acids are freely discharged to the atmosphere.

Attached and unattached fraction of polonium-210

It is well known that the activity concentration of ^{210}Po and ^{210}Pb depends on the square of the radius of particle matter. Most ^{210}Po and ^{210}Pb activity is connected with fine and ultrafine particles. As much as 77% of ^{210}Pb and 70% of ^{210}Po activities of solid particles were measured in size-fractionated aerosols smaller than 0.7 µm in Japan[19]. In the present study, 72% ^{210}Pb and 82% ^{210}Po activities were measured in aerosol fractions in the particle size range of 0.1–0.3 µm.

^{210}Po, which is more volatile than its parents ^{210}Pb and ^{210}Bi, leaves the boiler with the flue gas in gaseous form and condenses as the temperature of the flue gas drops. In coal burning condition, condensation of the attached Po element on aerosols is very effective. Some activity of Po in non-adsorbed form has also been traced and measured.

During energetic combustion, a large amount of gaseous products and solid particles are generated. The distribution of discharged polonium between gaseous products and ultrafine and fine particles depends on the element and the physical conditions of the combustion.

The activity of ^{210}Po in attached and unattached forms in flue gases has been measured in the stream of flue generated in a domestic coal combustion boiler.

The ^{210}Po quantity in attached and unattached form depends on the equilibrium between vaporization and condensation processes. ^{210}Po activity in the unattached fraction depends strongly on the particles concentration. Analysis of the coal combustion products carried out with Whatman filter and double washer kit confirmed the presence of 8 to 30% of ^{210}Po in the unattached, escaping form. A higher ^{210}Po contribution in the unattached phase was reported in a shorter sampling period. Longer aspiration and larger mass of the dust deposited on the filter reduced the ^{210}Po activity concentration.

The efficient escape of ^{210}Po and possibly its parent ^{210}Pb from the power plant stack was confirmed. An American study found that 32% of ^{210}Pb from the input coal activity was still in a volatile state upon release from the stack into the atmosphere[20]. In Slovenia Power Plant, the portion of gaseous ^{210}Pb released from the stacks can reach 8%[21]. Papastefanou[9] established that at least 60% of radioactivity is in a gaseous phase in the case of Greek power stations.

To investigate the fate of ^{210}Po in the open air, a similar test was done in the open air in the vicinity of a local power plant at a distance of about 200 m from the stack and in a suburban area for comparison. To measure the activity of ^{210}Po in attached and unattached forms in the air, a one-stage impactor equipped with a double washer kit was applied too. The obtained results are presented in Table 3.

Table 3. ^{210}Po activity concentration in the attached and unattached forms in the open air near a local coal power plant.

Location	Sampling date	Po-210 attached [mBq/m^3]	Po-210 unattached [mBq/m^3]	$\frac{A_{Po-210}\,unattached}{A_{Po-210}\,attached}$
Lodz city centre	May 2013	0.066	0.196	2.97
Lodz city centre	September 2013	0.146	0.275	1.88
Lodz suburban area	September 2013	< LD[1]	0.005	–

[1] LD – Detection Limit

As is evident from the above table, the majority of polonium present in the air is in the unattached form. These data suggest a higher natural ^{210}Po contribution from ^{222}Rn emanation in comparison with artificial coal combustion. Po element tends to stay longer in the ultrafine clusters and attached to the fine or coarse particles, which are more efficiently scavenged from the atmosphere. In the open air, at various diffusion rates of free ions and neutral atoms and in different particle concentrations in the summer and winter seasons, the ^{210}Po activity distribution between the attached and unattached forms is not yet fully understood. In the summer season, ^{210}Po contribution in the unattached phase is almost three times higher than in the attached form. In the summer period, the growth rate of particles is faster and more homogenous nucleation occurs[9]. Because of the escaping fly ashes contribution and humidity in the winter season, the rates and mechanism of aerosol particle growth seem to be more complicated in the analysis.

The ^{210}Po activity distribution in fractionated dust and in the unattached phase might change dramatically depending on the meteorological conditions and local particle concentration. Therefore, in urban air ^{210}Po activity in both phases and other alpha-emitting radionuclides should be monitored more preciously.

Conclusion

Most ^{210}Po radionuclide activity present in crude coal after its combustion is attached to particles with diameters lower than 1 µm. Such small particles are not efficiently separated by classical filters or electrostatic precipitation systems. Coal combustion processes can thus generate a significant amount of ^{210}Po, which is released to the atmosphere mostly in the winter season. Even 50% of ^{210}Po escaping through vent systems increases the aerosol activity in the region of local power plants. In such areas, ^{210}Po activity should be carefully monitored in the air as well as in all types of environmental samples, including soil, water, and locally produced food.

Acknowledgments

This research programme is supported by a SONATA grant (UMO-2012/07/D/ST10/02874) from the National Science Centre.

The author give thanks for Prof. H. Bem and dr S. Karolczak for their keen interest and consultancy in this work.

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[a] Technical University of Lodz, Institute of Applied Radiation Chemistry, Wróblewskiego 15, 90-924 Łódź *Fax: +48 42 631 31 05; Tel: +48 42 631 31 67; E-mail: mdlugosz@mitr.p.lodz.pl*

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