Phosphorus Production and Natural Radionuclides: Consequences for the operators concerned

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1. Abstract

Thermphos International BV in Vlissingen (Netherlands) manufactures elemental phosphorus out of phosphate ore ($Ca_3(PO_4)_2$). In the production of phosphorus, phosphate ore is milled and then pelletised in a granulator using a clay suspension. Natural radionuclides are released to the workplace.

In 1994, a monitoring program in the workplace was carried out. Conclusions on the pathways of exposure were drawn.

Since 1998, 60 PAS (Personal Air Sampler) measurements are carried out annually based on the new ICRP-66 lung model. It was expected that this new measuring technique overestimated the dose because all the dust in the air at the place of work is used to estimate the dose and the size diameter distribution of the dust particles is not taken into account.

To deal with this problem several dust measuring devices were tested such as cyclones with respirable and thoracic separation properties in agreement with EN-481.

With a cascade impactor, the particle size distribution of the dust cloud was determined. However, cascade impactor measurements are complex and difficult to perform.

As an alternative to the cascade impactor a thoracic cyclone in combination with a conservative DCC can be used to make an acceptable dose estimation. This conclusion is based on dust measurements and a theoretical approach. In a EU-project (SMOPIE) this method is confirmed. Two important issues in this conformation are to comply with the ICRP's lung model and the availability of practical measurement devices.

In 2004, the first measurement program was carried out with this new thoracic sample device approved by the Dutch labour/factory inspectorate.

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The results of this monitoring program are presented and compared with the measurement results from the period 1998-2003. Based on the results from the period 1998-2003 the operators involved are receiving an average dose of approximately 1 mSv per year due to inhalation of radionuclides and are therefore classified as exposed workers (under Dutch law). The consequences of this classification are presented.

2. The Phosphorus Production Unit

Thermphos International BV in Vlissingen (Netherlands) manufactures elemental phosphorus out of phosphate ore ($Ca_3(PO_4)_2$). In the production of phosphorus, phosphate ore is milled and then pelletised in a granulator using a clay suspension. The pellets are calcined in kilns at temperatures up to 1000 ^oC. The calcined pellets are fed, together with cokes and gravel, to electric furnaces in which the elemental phosphorus is liberated as a vapour (P_4) together with carbonmonoxide. A slag ($CaSiO_3$) is formed, which is used as building material in civil works (roads and dikes).

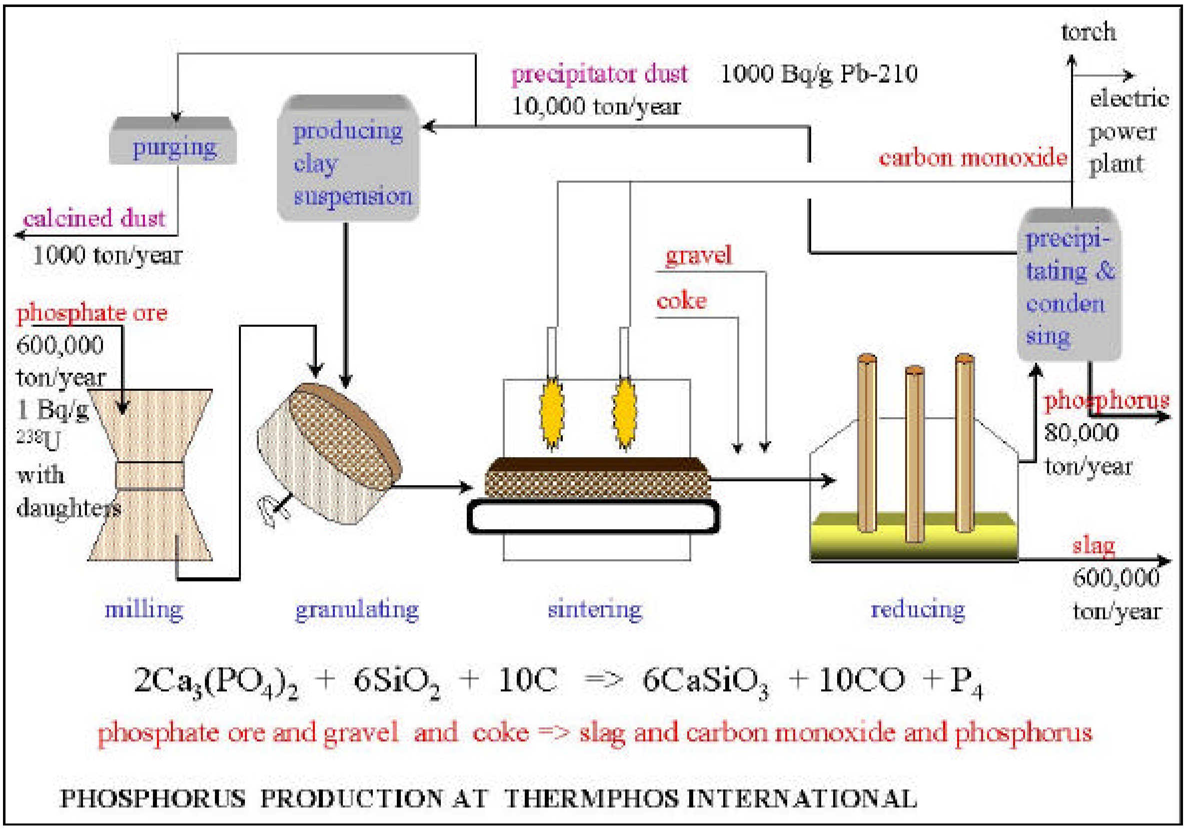


Figure 1. The elemental phosphorus production at Thermphos.

3. Radioactivity problem

Impurities such as heavy metals and radionuclides are present in sedimentary phosphate ore. Uranium-238 is the main radionuclide found in sedimentary phosphate ore, which can have an activity ranging from 0.5 to 2 Bq/g (in equilibrium with daughters). During the electrothermal phosphorus production process, the radionuclides are unintentionally enriched. At the high temperatures prevailing in the furnace, volatile inorganic substances, metals and radionuclides evaporate and condense on dust particles. The dust is trapped in the electrostatic precipitators and is recycled via the clay suspension into the pellets. When they reach the furnace for the second time, the volatile inorganic substances, heavy metals and radionuclides evaporate again. In this way these substances are enriched in the precipitator dust cycle. High concentrations of these substances cause instability in the operation of the furnaces, so the system has to be purged to control the concentration. The purge unit produces calcinate (calcined precipitator dust) with enhanced concentrations of radionuclides (up to 1000 Bq/g ^{210}Pb), which is, therefore, radioactive waste. During the manufacturing of elemental phosphorous dust enriched with ^{210}Po and ^{210}Pb is emitted to the air in the workplace.

4. Workplace problems

4.1 Introduction

Operators involved in the production of phosphorus are exposed to radionuclides (mainly the enriched ^{210}Pb and ^{210}Po) from the precipitator dust cycle. In practice, these nuclides are alpha- and beta-emitters and do not cause an external dose. To cause a relevant dose, there must be an intake of these radionuclides into the human body. In workplaces, such intake occurs predominantly by inhaling dust.

4.2 Dust characteristics in the lungs

The leaching properties of the dust from the plant were examined by carrying out tests on simulated lung moisture. The results showed that the relevant radionuclides (^{210}Pb and ^{210}Po) are leached out of the inhaled dust very poorly and must therefore be assigned to the ‘slow’ lung retention class. This means that the radionuclides are retained in the lungs for several years on average. The resulting dose is, therefore, received predominantly by the lungs.

5. Measurements

Personal Air Sample (PAS: see Photo 1) measurements were carried out to determine the dose to which workers in the phosphorus production plant are exposed.

Photo 1. Air pump and IOM filter holder with filter.

The personal air sampler consists of an air pump connected by a tube to a filter in a filter holder. It is carried by the operator in such a way that a continuous sample of the air (120 l per hour) surrounding the operator passes through the filter in the filter holder. The filter is positioned close to the mouth and nose. As the air is drawn through the filter, the dust containing the radionuclides collects on the filter. The operator carries the personal air sampler for the working period of 8 hours. The filter is measured for alpha- and beta-counts in a proportional counter tube. The inhalation of radionuclides can be calculated from the measured activity on the filter, the amount of air that flows through the filter and a worker's assumed breathing rate. The inhalation dose is calculated from this inhaled radioactivity with the help of a Dose Conversion Coefficient (DCC) (Sv per Bq).

5.1 Measurement effort

In the period 1984 to 1993, approximately 30 PAS measurements were carried out annually on workers most likely to inhale radionuclides. This number increased during the years to approximately 60 at this moment. By taking more measurements at the same time at different places in a working area and comparing them with earlier measurements, taking the process conditions into account, it was possible to determine the exposure pathways by which the radionuclides from the process reach the workers involved. As a result, a number of measures (see optimisation and ALARA considerations in the workplace) were taken in order to reduce the dose. In general, it can be concluded that workers involved in the production of phosphorus at the Thermphos site were exposed to an average dose of 1 mSv per year. This dose is not constant from day to day. There were days when the dose, extrapolated from one workday (the measuring period), yielded an annual dose of 5 mSv. On the other hand, there were also days that yielded an extrapolated annual dose of 0 mSv. The variations depend on the determined process conditions and working methods (exposure pathways).

5.2 Improving measurements and changing from the ICRP30 to the ICRP66 model

From 1984 to 1997, the measurement system was based on the ICRP30 (1979) model.

From 1998 to 2003 the system was based on the ICRP66(1993) model with the IOM inhalable device .

In 2004, the inhalable device was replaced by a thoracic device.

The PAS measurement method has been improved in response to stricter legislation in combination with the implementation of the new "Human Respiratory Tract Model for Radiological Protection" (ICRP66). The ICRP characterises the dust in a dust cloud in terms of 2 parameters: the AMAD (Aerodynamic Median Activity Diameter) and the GSD (Geometric Standard Deviation) of the dust particles on or in which the activity is located. When the GSD is equal to 1, the term AMAD cannot be used, as the distribution is monodisperse rather than polydisperse. AMAD must then be viewed as the particle size.

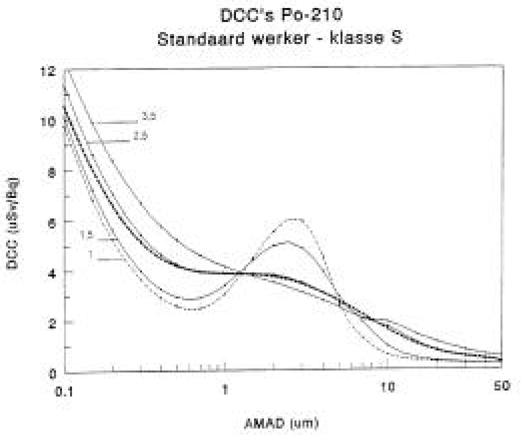


Figure 2. DCC as a function of the particle size (AMAD and GSD).

NRG determined the DCC's for ^{210}Po and ^{210}Pb as a function of the size of the particles on which the activity is located (AMAD), the geometric standard deviation of the distribution of the particles (GSD) and the lung retention class. This relationship for ^{210}Po is shown in Figure 2. Under conditions of normal logarithmic distribution, the DCC does not significantly change over a range from approximately 0.5 to 5 µm. The lower DCC of the larger particles is attributable to their inability to reach the deeper parts of the lung. Particles of a few µm reach the deeper parts of the lung where they are deposited easily. Smaller particles of approximately 0.5 µm have a smaller DCC because after inhalation a significant fraction is exhaled and not deposited. The high DCC of the very small particles is due to the increased deposition of these particles in the deeper parts of the lung as a result of Brownian motion.

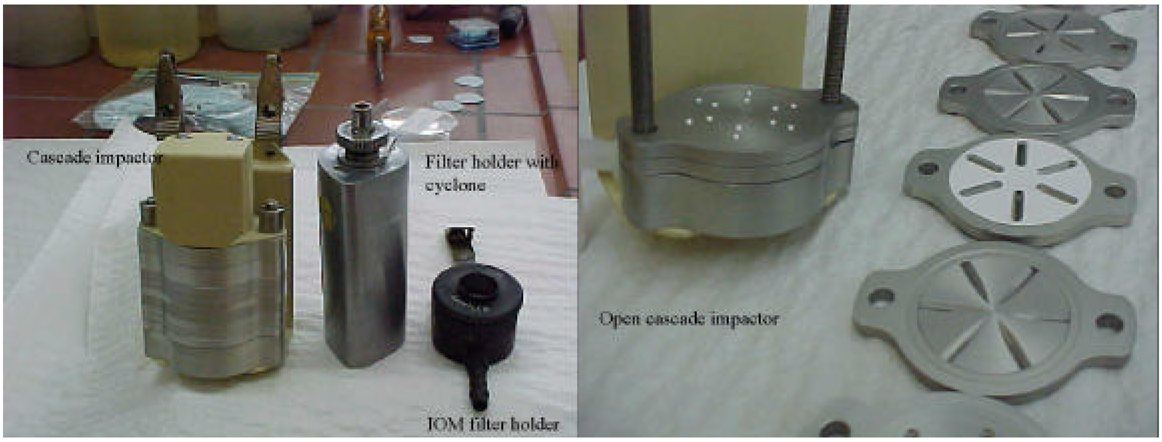
During the period 1998 to 2003, Thermphos used a simple sampler head (IOM filter holder for inhalable dust: see Photo 2) and conservative DCC's (average for the range from 0.1 to 5 µm) of 4.2 µSv per Bq for ^{210}Po (see Figure 2) and 5.8 µSv per Bq for ^{210}Pb for the dust collected on the filter. If the measured activity originates from particles larger than 5 to 10 µm, it follows that the estimated dose is too high. In particular, when operators produce dust during cleaning work, it is likely that a considerable part of the activity comes from particles that are larger than 5 µm.

5.3 Cascade impactor measurements

To determine activity distribution as a function of particle size measurements with a cascade impactor were carried out.

This cascade impactor, which was specially made for workplace measurements, consists of a number of stacked plates with openings that are displaced by 30^{O} from one plate to the next. Filters are inserted between the plates. The filters have the same openings as the plates. The larger particles in the airflow cannot make the 90^{O} turn needed to reach the openings of the next plate and therefore impact, as a result of centrifugal force, on the underlying filter. The first holes are relatively wide slots. The size of the holes gradually decreases from plate to plate. The airspeed therefore increases and the size of the particles that can pass through to the following plate becomes steadily smaller.

Photo 4 shows the filter of plate 3 after loading. Figure 3 gives the separation characteristics as a function of the particle size of the various plates of the cascade impactor.



Photos 2 and 3. Filter holders and open cascade-impactor.

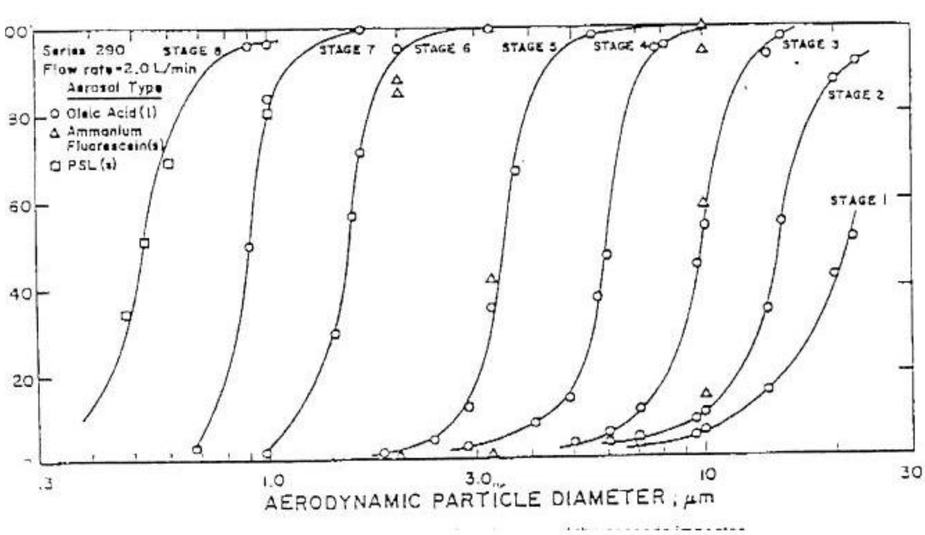
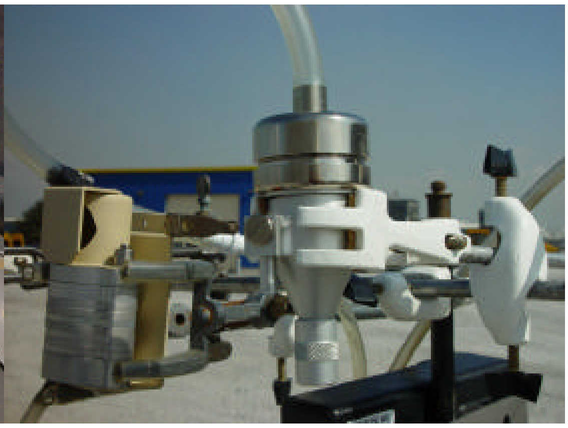


Figure 3. Separation characteristics of a cascade impactor.

Photo 4. The filter of the third plate after measurement.

5.4 Result of measurement with cascade impactor

A PAS measurement, obtained while cleaning work that produced fresh dust was being carried out, showed that the dose was overestimated by a factor of 2 if no correction was carried out to compensate for the particle size. A large proportion of the particles was larger than 5 µm, and therefore had a lower DCC. This conclusion was drawn from the data from an IOM sampler head and a cascade impactor, which were worn simultaneously.



Photos 5 and 6. On the left is a joint measurement setup comprising various measuring devices. On the right is the assembled cascade impactor and a thoracic cyclone.

The available dust separating equipment used in the field of the industrial hygienist must conform to an international convention. Figure 4 shows the separation diagrams for the thoracic, respirable and inhalable convention. The ICRP bases its calculations of the DCC's not on one of these 3 curves but on the total amount of dust in the air. This is in fact a straight line extending to the right from 100%.

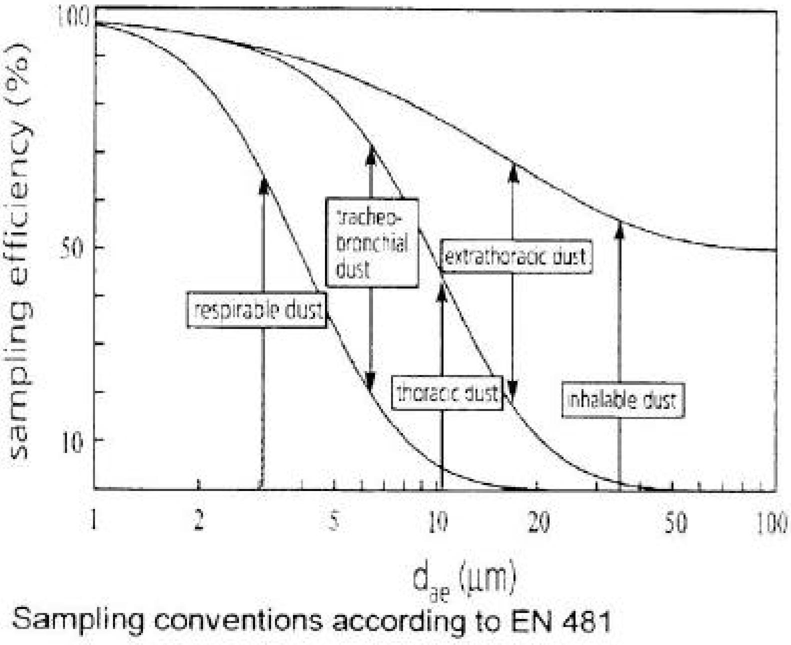
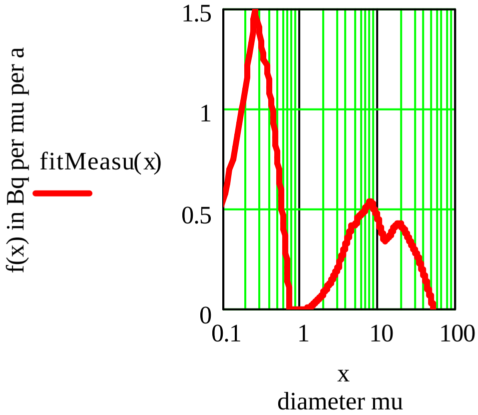


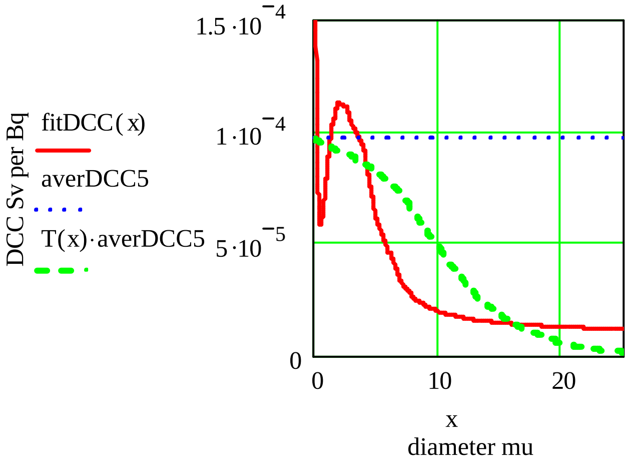
Figure 4. The international convention to which sampling equipment must conform.

5.5 A thoracic cyclone as an alternative for a cascade impactor

In the dose assessment based on the old lung model used by Thermphos before 1998, the relationship between the DCC and the particle size had a greater influence on the measurement results than in the ICRP66 model. This is why, when these measurements were carried out, the dose was determined using the dust fraction that remained after passing through a respirable cyclone. Based on the old model, this was justifiable. With the use of the ICRP66 model, this was no longer the case. Therefore, from 1998 the dose was determined on the basis of the inhalable dust fraction rather than the respirable fraction (see Figure 4). For dust that contains a significant fraction of large particles (> 5 µm), the method gives an overestimate for the dose, given that the DCC for the total dust is based on the fraction with particle sizes between 0.1 and 5 µm. A cascade impactor could be used to overcome this problem. However, cascade impactor measurements are complex and difficult to perform.

As an alternative to the cascade impactor a thoracic cyclone in combination with a conservative DCC can be used to make an acceptable dose estimation. This conclusion is based on dust measurements during a warm summer day without clouds (maximum heat input to the earth's surface) with just above wind-still conditions, and as a result of these circumstances, an extreme production of dust by lorries (112 vehicle movements) driving on an unpaved road of phosphorus slag with approximately 1 Bq per gram ^{238}Us. In a EU-project (SMOPIE) this method is confirmed. Two important issues in this conformation are to comply with the ICRP's lung model and the availability of practical measurement devices. The measurement results of a thoracic cyclone and a cascade impactor were compared and it was found the results were nearly the same. In Figure 5 this approach is demonstrated. The activity distribution as a function of the dust particle size (actually 2 distributions were found) the curve fitMeasu in Figure 5 should be multiplied with the DCC as a function of the particle size (monodisperse DCC: GSD is 1). What we should have, to make the right correction, is a device with the separation properties of the monodisperse DCC-curve. This device, however, is not available. The best approach to this DCC curve (fitDCC(x) is the thoracic device, which is the curve T(x), which 100% point is convert to the conservative DCC in the range from 0 tot 5 µm (averDCC5) by multiplying. The calculations show that the result of calculating with the monodisperse DCC curve or using the separation properties of a thoracic cyclone, gives nearly the same result. In this calculation the thoracic curve even gives a slight overestimation of the dose.





The calculation of the dose from the distribution and the monodisperse DCC $int := 50$

$$DoseMeasu := \int_0^{int} fitMeasu(x) \cdot fitDCC(x)\,dx \qquad DoseMeasu = 0.343 \cdot 10^{-3}$$ Sv per a

The calculation from the distribution and the thoracic separation curve:

$$DoseCorTH := \int_0^{int} fitMeasu(x) \cdot T(x) \cdot averDCC5\,dx \qquad DoseCorTH = 0.382 \cdot 10^{-3}$$ Sv per a

Figure 5. Comparing the monodisperse DCC with the separation properties of a thoracic cyclone.

fitMeasu is the activity distribution as a function of particle size inhaled by a person, which is a working year (1600 hours) exposed to air with a dust distribution caused by lorries. The dose is the dose received by this person. The DCC is the DCC as a function of the particle size for ^{238}Us (monodisperse: GSD1) with all daughters in equilibrium (no radon exhalation assumed) and was calculated with LUDEP. For more details on this subject, see InhalDoseNormEn.pdf.

Thermphos proposed that the PAS measurements should be carried out with a thoracic cyclone and started to do this in 2004 approved by the Dutch labour/factory inspectorate.

6. Measurement results

In Table 1 de measurement results are given. The dose is the average value from N (number) measurements. The 90% confidence interval is also given. This interval is the average value plus or minus the CI90% value. Between brackets is the data for the cleaning operator. Because these employees produce dust during working activities, their dose was significantly above the dose of other employees. However, it is expected that the dust produced by a cleaning operator has many particles above 5 µm. Therefore this dose is overestimated without taken the particle size into account. The 2004 measurements indicate (based on 5 and 4 measurements) that with a thoracic cyclone, taken the particle size into account, the measured dose for this operator is reduced.

Table 1.

Method	Dose Sinter plant	N	CI90%+/-	Dose Furnace plant	No	CI90% +/-
ICRP30 (1993-'97)	0.4 (1.6)	20	<0.2	1.3 (1.8)	68	<0.2
ICRP66 IOM (1998-2003)	1.14 (2.29)	71 (24)	<0.2	0.8 (1.71)	100 (25)	<0.2
ICRP66 Thoracic 2004	0.44 (0.45)	21 (5)	0.27	0.34 (0.38)	30 (4)	0.28

From these results, it is clear that the dose determination is an estimate. If the ICRP model changes the dose estimate results can change significantly. Furthermore the dose reduction measures taken by Thermphos during the last 15 years will have a significant influence on the amount of activity in the workplace and therefore on the dose estimation as well. Thermphos is convinced that the measures taken have reduced the dose to which workers in the plants are exposed. However, model changes and improvements in the measurement devices have apparently overruled these effects. The changes to more or less active phosphate ores are another complication in this matter.

7. Safety procedures and protection measures

The policy of Thermphos is aimed at dose reduction. The measures taken go beyond the essential minimum based on ALARA considerations and a CBA value (see optimisation). Thermphos applies safety regulations aimed at preventing excessive doses. If a vessel, sintering disk or furnace has to be opened for inspection or repair work, the surface contamination has to be measured first. If the contamination is below 0.25 Bq per cm^2, operators can enter without protective equipment. From 0.25 Bq per cm^2 to 10 Bq per cm^2, a FFP3 half mask must be worn. This mask has a very high theoretical (laboratory) protection factor (50). This is due to the sturdy construction and broad, flexible sealing edge. On the basis of BS 4275 BS EN 149, a protection factor of 20 is assigned. The Dutch labour/factory inspectorate specifies a value of 10, which is therefore also used by Thermphos in dose reduction calculations. Above 10 Bq per cm^2 a full-face mask with overpressure breathing air is prescribed. These limiting values for the surface contamination are conservatively derived from the results of the measurement programs. They apply to incidental work that does not produce excessive dust. If excessive dust is produced, a full-face mask with overpressure breathing air must be worn.

Photos 7 and 8. FFP3 half mask.

Photos 9 and 10. Full-face mask with remote air supply.

8. Optimisation and ALARA considerations in the workplace

About 200 operators and technical staff work in phosphorus production. The collective dose that this population receives in 25 years is 5 man-Sv. Assuming that an investment in improved working conditions would avert that collective dose, reasonable investment costs are about 750,000 €, based on the CBA value of £50,000 per saved man-Sv, as specified by the NPRB for occupational exposure. Higher values are also mentioned in literature.

The measures that have been taken are:

- Large-scale cleaning activities. New floors in the phosphorus plant with a top layer that is easy to keep clean. (Cost: 300,000 €).

- Central vacuum cleaning system (vacuum pipes through the plant with vacuum tube connection points) to simplify the work and to make the task of repeatedly emptying the vacuum cleaners unnecessary and avoiding the creation of more dust when full vacuum cleaners are emptied.

- Process automation to avoid work during which a dose is received and to prevent vessels from overflowing.
- Breathing air protection measures in situations where the creation of concentrations of radionuclides in the surrounding air is unavoidable.
- Continuous cleaning operations carried out by several cleaning operators.
- Improved ventilation, as in the vicinity of the ferro-phosphorus tapping point.
- The slag beds have been relocated from their position immediately beside the phosphorus plant to their current position well away from the plant.
- Measuring and monitoring programs.
- In 2002, a breathing air network was installed in the sintering plant. There has been one in the phosphorus plant for a number of years.

In view of the fact that it is impossible to eliminate all exposure, the dose reduction due to these improvements is not the complete 5 man-Sv mentioned above but only a fraction of it. It is therefore evident that the improvements carried out are based more on considerations of “good housekeeping”, “best available techniques” and “responsible care for the operators concerned” than on strict ALARA considerations with a CBA value.

9. Legislation exposed workers

Since 2002 (based on directive 96/29/EURATOM and Dutch legislation implementing this directive), workers must been designated as exposed workers category B if they can receive a dose of more than 1 mSv per year. Above 6 mSv per year they must been designated to category A. Under Dutch law, it is not necessary to carry out an additional medical examination for a category B worker. The normal medical examinations prescribed by the working circumstances law are sufficient. Thermphos must have a monitoring system to obtain the dose the workers receive. This dose must be reported to the National Dose Registration and Information system, which the Dutch government informs regarding to occupational exposure.

Based on the legislation Thermphos has designated the workers of the Elemental Phosphorus Plant to exposed workers (200 persons) category B. This also applies to workers employed by contractors. However, they are not designated as exposed workers if they work for less than 3 months in the phosphorus production plants. From the figures in Table 1, it can be deduced that such workers do not receive a dose in excess of 1 mSv per year. Approximately 90 workers employed by contractors are designated as exposed workers. Thermphos informed the operators involved about their designation in a letter where the dose assessment is also given.

This information did not give unrest by the operators concerned.

The measurement results of the monitoring system were communicated with the operators working in the phosphorus production plant and information over the (natural) radioactivity is given them for a period of more than 15 years. The dose-related risk is compared with "accepted real risks" associated with activities such as:

- Going to work every day, associated with a risk equivalent to a dose of 1.5 mSv per year.
- Working activities
- Smoking 20 cigarettes per day, which is associated with a risk many times higher.

This comparison is carried out to put the exposure risk into perspective in comparison with other "risks" associated with "accepted" activities.

This information is given to them in a paper as an annex to the mentioned letter. This information is also available on the intranet pages.

10. Conclusion

Natural radioactivity in processes like our elemental phosphorus production cause problems in the workplace, which cannot be ignored from a dose point of view.
However: These problems are manageable

11. References

ICRP 30

ICRP 66

NRPB,4 No.2 75-80 1993

InhalDoseNormEn.pdf : this is a more comprehensive paper on this subject than this extended abstract and is available from erkens@thermphos.com,

NRG (Nuclear Research & consultancy Group)