4.3

Electrothermal phosphorus production, radioactivity in the environment and workplace

W.H.H. Erkens

Thermphos International BV

The Netherlands

ELECTROTHERMAL PHOSPHORUS PRODUCTION
RADIOACTIVITY IN THE ENVIRONMENT AND WORKPLACE

W.H.H. Erkens[1]

Summary:

The phosphate ore processed by Thermphos International in Vlissingen to produce elemental phosphorus contains approximately 1 Bq/g uranium 238 with daughter nuclides in near equilibrium ($^{238}U+$).
During the production process, radionuclides are emitted into the environment. One of the residual products of the process is calcined precipitator dust, which has to be disposed of as radioactive waste. Slag is formed as a secondary product. This is used in road and hydraulic engineering, and causes a slight increase in external radiation. Operators concerned with the production of phosphorus receive a dose due to inhalation of radionuclides. This paper analyses the above mentioned situation in the light of current and proposed legislation (policy) and implementation of the adopted EU-directive.

CONTENTS

GENERAL BACKGROUND AND HISTORY

Hoechst Holland N.V. (referred to below as HHNV) began to produce elemental phosphorus from phosphate ore in April 1968. Since December 1971 three phosphorus furnaces have been in operation. Elemental phosphorus is used to produce a high grade (thermal) phosphoric acid. As well as the phosphorus division, installations have been built at the Vlissingen site for the production of DMT, TAED and alkane sulphonate and for supplying energy. In July 1997 HHNV was divided into several independent companies. Thermphos International BV (referred to below as TIBV) is continuing the phosphorus production. For readability reasons, in this paper the name HHNV is replaced by TIBV as the legal successor carrying on the (phosphorus) practices of HHNV.

In March 1983 the monitoring network, situated in the Sloe area to watch over the nearby nuclear power plant, detected radionuclides that appeared to come from TIBV. This was discussed for the first time with government representatives in May 1983. This meeting resulted in a request, which was submitted on 5 July 1985, for a licence under the Dutch Nuclear Power Act. The first such licence was granted on 30 December 1985. In 1984 the RIVM carried out emission/dose calculations. A recalculation took place in 1988.
In 1993 KEMA carried out another recalculation, based on the latest policy principles propagated by

---

[1] Thermphos International BV, Vlissingen site (former Hoechst Holland NV), Radiation safety department

VROM (the Dutch Ministry of Public Housing, Planning and the Environment). After publication of the risk management policy, as applied by VROM to radiation, TIBV applied for an updated licence in 1994. The licence was granted on 28 December 1994. In this paper the effect of radiation is expressed only in terms of dose instead of the formerly used risk.

The problem of radioactivity covers both the environment and the workplace.

THE PRODUCTION PROCESS

Introduction

The phosphorus production process consists of various stages, which are described below in sequence.

Sintering plant

The phosphate ore is milled to a fine powder in this plant. The powder is brought onto a rotating granulator disk, together with a binder (clay suspension). Due to the rotation of the disk granules (pellets) are formed. The unsintered pellets are transported onto the front end of the slowly rotating sintering grid roaster. They pass through a drying zone (temperature up to 300 °C) and are then sintered to hard spheres under two large burners at temperatures around 800°C. The pellets then pass through a cooling zone. The heat that they release is re-used in the drying zone.
The pellets are then conveyed to an intermediate storage facility, where they are stored in large silos before being fed into the electric furnaces.
There are three sintering roasters.

Slurry station

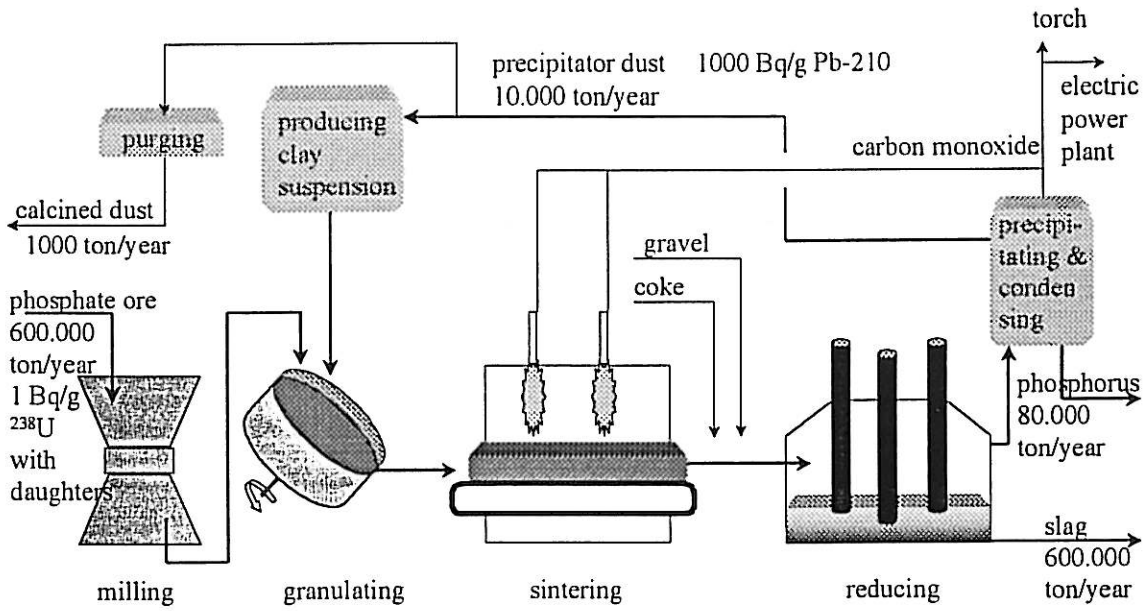
In the slurry station clay is suspended in water to produce the clay suspension used for granulation. Furthermore, precipitator dust, a return flow from the electric furnaces, is also added to the binding suspension.
There are two slurry lines.

Purging unit

The slurry station also houses the purging unit. This is the discharge from the precipitator dust cycle that is formed in the production process (see 3.2). By discharging more or less of the precipitator dust, the concentration of volatile inorganic matter, metals and radionuclides in the precipitator dust cycle can be controlled. The purging unit consists of a high-pressure filter-dryer and a rotating calcining kiln where the pressed, lumped precipitator dust is calcined at temperatures of up to 750 °C.

Phosphorus plant

There are three electrothermal phosphorus furnaces in the phosphorus plant. The pellets are fed into the furnaces together with gravel and coke. In each furnace there are three electrodes, which draw electrical energy from a triangular arrangement of transformers and channel it into the furnace for heating the furnace contents. At temperatures higher than 1500°C a reaction takes place, in which phosphate ore is reduced to elemental phosphorus (P_4). The chemical reaction is shown in the Figure 1.



$$2Ca3(PO4)2 + 6SiO2 + 10C \Rightarrow 6CaSiO3 + 10CO + P4$$

phosphate ore and gravel and coke => slag and carbon monoxide and phosphorus

PHOSPHORUS PRODUCTION THERMPHOS INTERNATIONAL

figure 1

A calcium silicate slag is formed, which flows continuously from the furnace. The elemental phosphorus leaves the furnace as a gas, together with the carbon monoxide formed during the reaction. Entrained dust is separated from the gases in an electrostatic precipitator. This dust is collected in the slurry tanks, where it is mixed with water. The resulting precipitator slurry is pumped to the slurry station, where it is re-used in the granulator binder. The now dust-free gases are subsequently cooled, causing the phosphorus to condense to a stream of liquid phosphorus. The carbon monoxide (CO) is used as fuel in the sintering roaster. The excess gas is compressed and piped to a nearby electric power plant as a fuel.

RADIOACTIVITY PROBLEM

Introduction

The added mix of sedimentary and magmatic phosphate ore contains approximately 1 Bq/g of uranium with atomic number 238: ^{238}U. This nuclide has a half-life of $4.4*10^9$ years. All daughters of the ^{238}U decay chain are in a state of (approximate) equilibrium with the parent nuclide. This means that all daughter nuclides (see Figure 2) are also present with an activity of 1 Bq/g. The symbol for the radionuclide with daughters is $^{238}U+$.

Enrichment mechanism

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, metals and radionuclides evaporate again. In this way these substances are enriched in the so-called precipitator dust cycle. High concentrations of volatile inorganic matter and metals cause instability in the operation of the furnaces. To control the concentration there is a purge on the system. This purge produces calcined dust with radionuclides and is regarded as radioactive waste under the existing legislation (see 2.4).

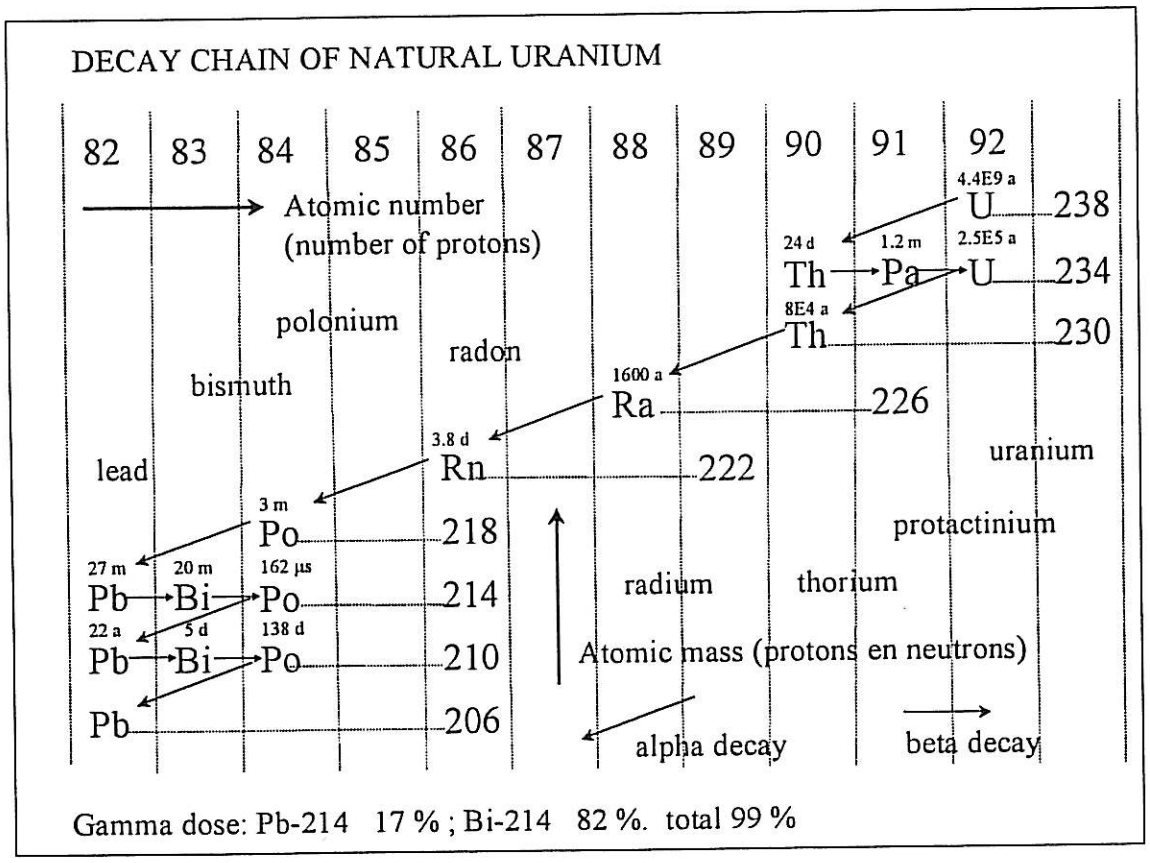


figure 2

The uranium 238 chain (see Figure 2)

The radionuclides with an atomic number greater than that of radon remain in the furnace and therefore become part of the slag. Approximately one ton of slag is formed per ton of phosphate ore. Due to this fact the natural radionuclides in the ore are not enriched in the slag. Radon is an inert gas and therefore escapes along with carbon monoxide. The nuclides with an atomic number less than that of radon escape from the melt and therefore end up in the precipitator dust cycle. The short lived nuclides with atomic numbers of 214 and 218, decay within a few hours. The problem nuclide is ^{210}Pb (lead), which has a half-life of 22 years and is therefore relatively long-lived. Moreover, most of the ^{210}Pb remains in the pellets in the sintering roaster. ^{210}Po, with a half-life of 138 days, is more volatile then ^{210}Pb and therefore leaves the pellets during the sintering process, passes both scubbers (see 4.1) where the sinter gases are washed and is emitted into the environment. Consequently the activity of ^{210}Po in the precipitator dust is lower then the activity of ^{210}Pb.

The daughter nuclides formed from ^{210}Pb, {^{210}Bi (bismuth) and ^{210}Po (polonium)} have half-life times of 5 and 138 days. This means that, after about 4 half-life periods, these daughter nuclides exhibit nearly the same activity as the parent nuclide ^{210}Pb.

The activity of ^{210}Pb in the precipitator dust and in the calcined dust is approximately 1000 Bq/g. This nuclide has therefore been enriched by a factor of 1000.

Recognition of the problem

From the very start of TIBV in Vlissingen it was known that the phosphate ore contained enhanced concentrations of radionuclides. The problem of enrichment of radioactivity and the associated emission was not recognised until 1984, when the monitoring network of the nearby nuclear power station detected activity emitted by TIBV.

Measurement effort

TIBV's own environmental sampling team takes 200 samples of the air and water discharges each year.

TIBV has set up a C-laboratory to enable the emissions of radionuclides to be determined. The measurements needed for compliance with the environmental and workplace regulations, imposed by the Nuclear Power Act licence, are carried out here.
See Table 1 for the emissions during the period from 1987 to 1993.

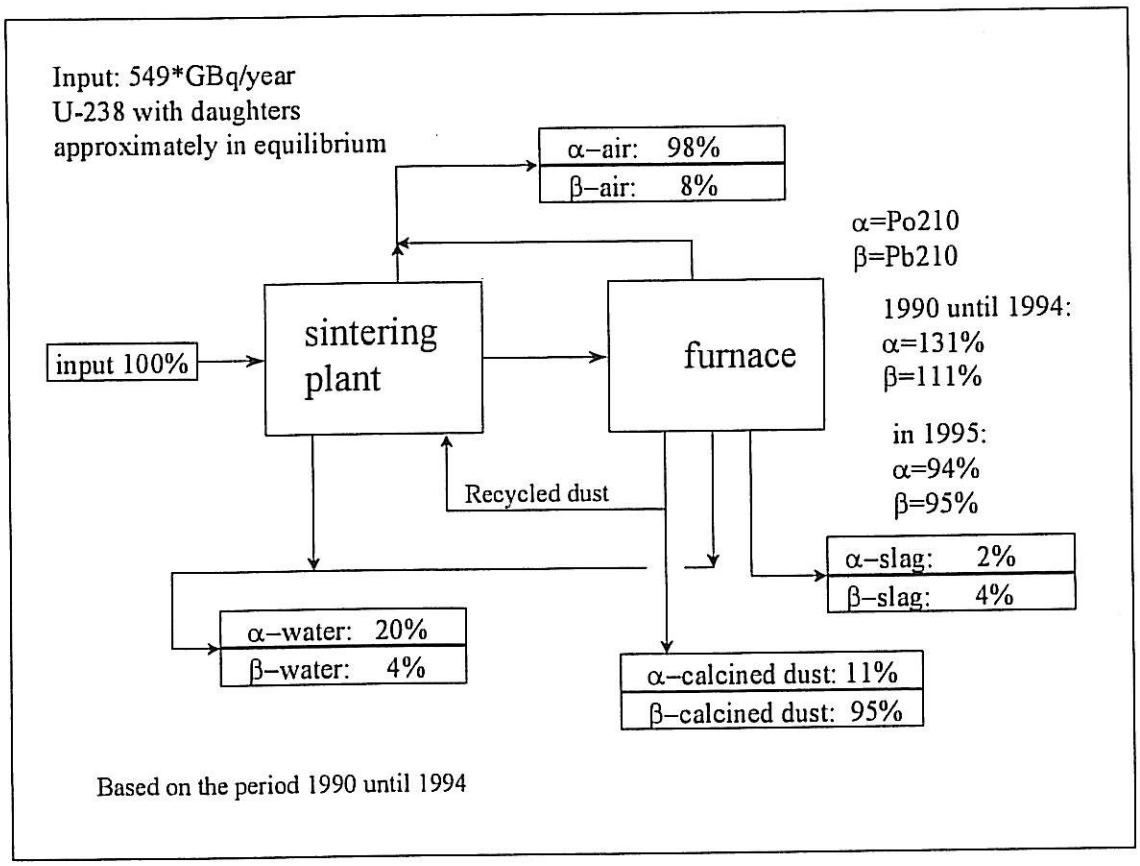
Table 1 Emissions to air and water

Year	α to air ^{210}Po GBq/y	β to air ^{210}Pb GBq/y	α to water ^{210}Po GBq/y	β to water ^{210}Pb GBq/y
1987	538	50	73	69
1988	843	98	95	40
1989	634	56	99	34
1990	381	34	107	24
1991	687	32	91	21
1992	490	66	166	24
1993	616	52	96	24
Average	598	56	104	34

EMISSION AND BALANCE

Emission and balance

The major emitter of radionuclides is the sintering plant. In 1985 new seawater scrubbers were installed in sintering plants 1 and 2, downstream of the existing fresh-water scrubbers, for the purpose of reducing emissions, including radionuclides, into the environment. Despite the very intensive scrubbing of the sintering waste gases, emissions of radionuclides into the environment occur. Figure 3 shows a summary of the emission balance.



f

igure 3

In general it can be said that the volatile ^{210}Po is emitted almost in its entirety, while the greater part of ^{210}Pb ends up in the calcined precipitator dust. More is measured than is assumed as input to the process.

This was explained in 1994 in terms of:

o measurement accuracy;
o unknown variations in the phosphate ore;
o non-inclusion of the activity in the gravel and coke input;
o the formation of ^{210}Po from the ^{210}Pb in circulation, which can result in more ^{210}Po being emitted than was present in the input to the process.

The activity of all phosphate ores used during 1995 was measured. The measurements give higher concentrations of radionuclides in the ore then assumed in the years before. The result for 1995 is separately shown in figure 3 and is more realistic compared with the period 1990-1994.

DOSE ANALYSIS AT TIBV

Dose study by RIVM

The RIVM (Dutch National Institute for Public Health and Environment) carried out dose studies in the past (RIVM 841217, 1984 and RIVM 248103038, 1988). In order to obtain more insight into the actual dose, in 1991 the monitoring network that, in connection with the Borsele nuclear power station, had been installed in and around the Sloe area, was extended by a number of monitoring points, to enable the dose attributable to TIBV to be determined more accurately.

KEMA study

After consultation with VROM, TIBV commissioned KEMA to carry out a study in 1992 and 1993 to determine the dose caused by TIBV.
The dose to which the surrounding environment was exposed was calculated on the basis of the measured emissions over the period from 1987 to 1991, and the measured immissions in 1991.
A PC was connected to the wind gauge on TIBV's office building for the purpose of recording the wind direction, speed and turbulence at hourly intervals. These data were used to determine the relationship between emission and immission.

The following exposure paths were examined:

o Inhalation of radioactive dust from discharges into the atmosphere.
o Ingestion of radioactive fall-out from discharges into the atmosphere:
  -soil-plant-man
  -soil-grass-cattle-milk-man
  -soil-grass-cattle-meat-man
  -water-shellfish/crustaceans-man
  -water-fish-man
o Ingestion from radioactivity discharged directly into water:
  -water-shellfish/crustacean-man
  -water-fish-man
o External irradiation from cloud
o External irradiation from the soil, attributable to radioactive fall-out.

This study showed that the individual dose caused by TIBV in Nieuwdorp (a nearby village 4 km north/east of the production site) does not, on average, exceed 30 μ Sv/year. The greatest dose is attributable to the inhalation path, which accounts for 96% of the total dose.

POLICY PRINCIPLES OF VROM 1994

Checking against policy principles

The situation at TIBV was checked against the VROM's POLICY PRINCIPLES RELATING TO RADIATION HYGIENE, version 15, December 1993. As well as a "24-hour exposure outside the site" dose, a MID (multifunctional individual dose) and an AID (actual individual dose) were introduced. If, for one practice, either the MID or the AID is below the threshold dose value of MTD of 40 μSv/year, the ALARA considerations apply. This means that optimisation costs have to be weighed against the degree of dose reduction. If the MID and AID both exceed the MTD (40 μSv/year), there is an "urgent remedial action" situation.

24-hour exposure outside the site

The applied policy requires calculation of the dose to which a person would be exposed during 24 hours at places (just) outside the plant (MID without the protection provided by housing: MID*). All possible exposure paths are examined (inhalation, ingestion and external gamma radiation).

Residential reduction factor and MID

The dose attributable to external radiation can be multiplied by 0.25 before it is added to the other doses in order to calculate the total dose. This is because residence is considered as the most common form of long-term sojourn. The protective action (effect) of a residence (building) is set at a factor of 4. This makes the MID a criterion for a "remedial action" situation. The MID must be smaller than the MTD of 40 μSv/year, otherwise there is a "remedial action" situation. Then the AID can be examined to determine the urgency associated with the "remedial action" situation.

Sojourn factor and AID

The AID is determined by taking the MID without residential protection, and multiplying it by an ABC-factor (actual exposure correction factor). The ABC factor is not applied to the ingestion path. If the AID is smaller than the MTD of 40 μSv/year, the "remedial action" situation is not urgent.

Summary

Table 2 shows a summary of the calculations from the evaluation.

Table 2: Summary of evaluation against policy principles.
Note: The figures are based on measurements carried out during the period from 1987 to 1991.

Location site-perimeter and village	Dose conti-nuous inhala-tion μSv/y	Dose conti-nuous exter-nal radia-tion μSv/y	MID* inhala-tion + exter-nal radia-tion μSv/y	ABC-factor	AID inhala-tion + inter-nal radia-tion μSv/y	MID inges-tion μSv/y	AID total μSv/y
van Cittershaven	112	29	141	0.01	1.4	1.16	2.6
SE corner of site	76	1.7	78	0.01	0.78	1.16	2
Aquila	52	7.7	60	0.01	0.6	1.16	1.8
ELF-Atochem	102	5.4	108	0.2	21.6	1.16	22.7
P&H	147	2.6	150	0.2	30	1.16	31.1
Pechiney	141	1	142	0.2	28	1.16	29.6
Nieuwdorp	29	0.04	29	1	29	1.16	30.2

*without the protection provided by housing.

Conclusions 1994

The following conclusions can be drawn from the above:

o A "remedial action" situation does not exist in Nieuwdorp due to the MID* of 29 μSv/y.
o There is not an "urgent remedial action" situation at the other locations (see AID total).
o The ALARA considerations must be applied at both locations, with optimisation costs being weighed against dose reduction.

Legislation and policy principles VROM 1996

In 1996 the council of the European Union adopted a directive on the protection of the health of workers and members of the public against the dangers of ionising radiation. In this directive the cumulative maximum dose for members of the public is set at 1000 μSv/year.
VROM decided in 1996 to affirm the MTD (maximum acceptable dose) for one practice at 100 μSv/year and changed the Nuclear Power Act accordingly. As a result the Dutch legislation is less strict then the former policy principles (1994) and therefore more in agreement with the European Union directive. VROM based its support of the 100 μSv/year threshold limit by arguing that it is possible that members of the public could be exposed to a maximum of 10 different practices. Another benefit of this approach is that one practice will not be dependent on another by filling up the licensed space to the maximum cumulative dose of 1000 μSv/year.
The dose is still the prime unit for legislation instead of the previously used risk in the policy principles.
As a result of this changed legislation the conclusions under 6.6 are still valid in 1997.

The European Directive has an annex with exemption levels. A practice may be exempted from the requirement of reporting and/or licensing if the activity concentration or the quantity does not exceed the values in the annex. However, the exemption levels in the annex are intended to be used only for radionuclides which are processed because of their radioactive properties (the functional activity). Exemption levels for radionuclides in enhanced concentrations which are not processed because of their radioactive properties (the non-functional activity) are excluded from the prime scope of the directive. All the activity in the phosphorus production process must be regarded as non functional. Exemption levels for these non-functional radionuclides are being developed now. It is not clear yet (July 1997) whether the practice "slag's used in the road and dike building" in future will becomes subject to legislation. Similarly the exemption or clearance levels for calcined dust are not yet known. The storage time as a radioactive waste is determined directly by these exemption levels.

ENVIRONMENT-DOSE REDUCTION MEASURES

Trials

Trials have been carried out (including the installation of demister mats) with the aim of improving the existing scrubber systems, but the results were disappointing (in terms of reduction in emissions of radionuclides, etc.).
Moreover, extensive trials have been carried out to determine whether supplementary scrubber systems (venturi scrubbers) can bring about reductions in the emission of radionuclides. These scrubber systems are very expensive, and are undesirable from an energy point of view (additional electrical power). Moreover, the filtration residue, namely dust with radionuclides, can, in view of its large volume and low activity, only be fed back into the precipitator dust cycle. As a consequence the effectiveness of this scrubbing is considerably reduced.
After long and comprehensive research, it was found that only 2 dose-reducing measures are feasible: the construction of a precipitator dust processing plant and a high stack.

Precipitator dust processing plant

In order to ensure the stable operation of the furnace process, some of the precipitator dust must be removed from the precipitator dust cycle.
This Precipitator dust is processed into calcined dust and is stored on site as radioactive waste. At the present time approximately 1000 tons of precipitator dust are taken out of the process each year. This is the necessary amount for the process to proceed stably. Because the storage of the calcined dust is very expensive, only the absolutely necessary amount of precipitator dust is removed.

In the period 1990-1994 a pilot plant trial was carried out to determine whether the stored calcined dust and the precipitator dust could be chemically processed.
On the basis of this pilot plant, TIBV worked out plans for an industrial-scale precipitator dust and calcined dust processing plant (referred to below as a precipitator dust processing plant). In this plant the heavy metals, the radioactive fraction and the other substances are chemically separated from each other. A highly active lead sulphate fraction is formed, which has to be transported to the COVRA (Centrale Organisatie voor Radioactief Afval: The Dutch central organisation that stores radioactive waste).

The advantages of the plant include the following:

o The volume of radioactive waste is reduced considerably (see reservation under: effectiveness below).
o Due to the above reduction, it is possible to remove more precipitator dust from the process. It is possible to reduce the emission of radionuclides by a factor of about 2 if, instead of 1000 ton/year, 3000 ton/year are removed and processed in the precipitator dust processing plant. The level of dose in the surrounding area as a consequence of the emissions will also be reduced by a factor of 2.

The most important arguments against this plant are:

o Costs. The investment cost would be NLG 28,000,000 and the annual operating costs would be NLG 6,000,000.
o Safety. The concentration of radioactivity exposes the operators concerned to additional doses.
o Effectiveness. It cannot be excluded that the activity of the separated zinc fraction (150 ton/year with an expected activity of 30 Bq/g ^{210}Pb) will be above a future limiting value (10 Bq/g appendix EU-directive) and therefore be regarded as a radioactive waste. The most important objective of the project - concentration of activity - will then be only partly realised.
o Another major problem is the coupling with the STPP (phosphate in detergents) production. If this production should be terminated in Vlissingen at some future time, furnace acid (produced out of elemental phosphorus) would have to be used in place of wet-process phosphoric acid. This would involve a downward adjustment of the price of furnace acid to the price of phosphate ore, resulting in a cost item of NLG 14.000.000/year.

Stack
The effect of building a new and higher stack was calculated in the KEMA study. The individual dose in Nieuwdorp would be roughly halved by building a 140 meter high stack.

ALARA CONSIDERATION OF DOSE-REDUCTION MEASURES 1994

General
Because it has been found that the MID caused by TIBV is below the MTD threshold of 40 μSv/year, a "remedial action" situation does not exist in Nieuwdorp. Moreover, because it has been determined that, at the measuring points around the site, the MID exceeds the MTD (40 μSv/year), while the AID is below the MTD, a "non-urgent remedial action" situation exists here. An ALARA analysis has to be carried out. This means that the effects of measures, such as the precipitator dust processing plant, on the reduction of the dose in the surrounding area (in this case by roughly half) must be weighed against the investment costs of NLG 28 million and the operating costs of NLG 6 million/year over 25 years. The Dutch policy statements gives no clear indication of what costs are defensible in relation to the reduction of individual or collective dose. In the absence of nationally or internationally accepted values, TIBV referred to a so-called alpha-value for the purpose of weighing up the reasonableness of an investment. This is a value that indicates what investment can be considered reasonable for the purpose of achieving a reduction in collective dose. The figures published by the National Radiation Protection Board in 1993 specify £20,000 per man-sievert for the general public (Doc. NRPB,4 No.2 75-80 1993). TIBV therefore applied the NRPB alpha-value of £20,000 per saved man-sievert in order to weigh up the reasonableness of an investment.

Precipitator dust processing plant
The collective dose caused by TIBV is 2 man-sieverts/year. Based on an investment for 25 years, the

collective dose reduction is:
2 [man-Sv./year]*25 [years] /2 [reduction]= 25 man-sieverts. Applying the above mentioned alpha values, an investment of 25 [man-Sv]*20.000 [£/man-Sv.]*2.79 [NLG/£] = NLG 1.4 million, can be regarded as defensible.
The investment required to build the precipitator dust processing plant is NLG 28 million. The operating costs would be 25 years * NLG 6 million/year = NLG 150 million, so that the total costs over 25 years would be NLG 178 million. This is many times higher than the sum the NRPB regards as reasonable for reducing the collective dose. The necessity for building a precipitator dust processing plant in order to reduce the dose in the surrounding area is therefore not given. In early 1993, after consultation with VROM, it was decided that the plant would not be built.

Stack
The collective dose reduction that can be achieved by building a 140 meter high stack is 2 man-sieverts/year. Due to the applied calculation specifications in the policy principles, with a cut-off dose for optimising purposes of 4 μSv/year, these 2 man-sieverts/year are an overestimate of the real reduction. On the basis of an investment for 25 years and the overestimated dose reduction of 2 man-sieverts/year, the reasonableness consideration indicates that a sum of NLG 2.8 million is defensible.
(2 [man-Sv./year]*25 [years]*20.000 [£/man-Sv.]*2.79 [NLG/£] = NLG 2.8 million). The cost of a 140 meter high stack would be NLG 5 million. This sum, too, is higher than the sum that is regarded as defensible for a reduction in collective dose. Moreover the erection of a higher stack would not reduce emissions in absolute terms, so that the benefits would be restricted to the immediate vicinity. TIBV therefore decided, in consultation with VROM, not to build the stack.

MAXIMUM DISCHARGE QUANTITIES IN THE LICENCE 1994

Maximum discharge amounts based on 40 μSv/year
The maximum amounts, as a licence constraint, of α- and β-emitting radionuclides that can be discharged into water and the atmosphere were based on the prevailing policy, whereby the ALARA analysis has to take place if the AID and MID are below 40 μSv/year (MTD). If the dose (AID and MID) attributable to the discharges and external radiation remains below the MTD of 40 μSv/year, the ALARA consideration applies as described in section 8. From the measurement values obtained in recent years it is known that the average MID in Nieuwdorp in the period 1987 to 1993 was 30 μSv/year. TIBV works with natural raw materials (ore), which can contain widely fluctuating amounts of naturally occurring elements and their compounds. Partly for this reason, and despite many years of intensive research, some of the phenomena observed during the process are still not wholly understood and are therefore not susceptible to selective manipulation. The marked fluctuation in the emission of radionuclides is one of these phenomena. This is reflected in the standard deviation of 7.6 μSv/year associated with the average dose of 30 μSv/year. In view of the occurrence of large fluctuations, the maximum discharge amounts were based on the discharge amounts that result in a dose of 40 μSv/year.

Exposure paths
In the KEMA report the dose caused in Nieuwdorp was calculated for each exposure path and nuclide type. These calculations were then used to derive conversion factors (emission to dose). The conversion factors differ from path to path and nuclide type to nuclide type. Table 3 shows the discharge amounts. The former 1985 licensed values are also included in the table for purposes of comparison.

Table 3 Licensed discharge value

Discharge per exposure path and nuclide type	former 1985 licensed value in TBq/y. the total of these discharges is 56 μSv/y	Discharge that causes a dose of 40 μSv/y per exposure path. TBq/y
α-emitters to air	0.55	1.243
β-emitters to air	0.22	0.223

α-emitters to water	0.11	9.363
β-emitters to water	0.075	17.049

Verification formula

Because the individual discharge amounts in Table 3 are based, per exposure path, on a dose of 40 μSv/year, compliance with the dose limit is checked with the formula:

$$\frac{emis.\alpha.to.air}{1.243*10^{12}}+\frac{emis.\beta.to.air}{0.223*10^{12}}+\frac{emis.\alpha.to.water}{9.363*10^{12}}+\frac{emis.\beta.to.water}{17.094*10^{12}}<1$$

In this way it can be assured that the sum of the various exposure paths does not exceed the MTD of 40 μSv/year.

Maximum discharge limit, additional limit for water

Because the dose associated with the exposure path "water" is much smaller per discharged unit than that associated with the exposure path "air", the discharge amounts that result in a dose of 40 μSv/year are unreasonably large in comparison with the actual emissions. For this reason it was necessary to determine the maximum discharges into water for α- and β-emitting radionuclides in a different way. These maximum discharge amounts were based on the actually discharged amounts during recent years and have been fixed at $0.35*10^{12}$ Bq/year for α-emitting radionuclides and $0.15*10^{12}$ Bq/year for β-emitters.

Average over several years

As a result of the considerable fluctuations (see 9.1) in the emissions, the MTD may be exceeded in a given year, while the long-term average remains below the MTD-threshold. A statistical analysis of the annual dose figures showed that the average return period associated with such an occurrence is of the order of ten years, and that the long-term average remains below the MTD.
TIBV is, therefore, allowed to take a "rolling" average over 3 years before a check is carried out. The average return period of a violation of the MTD by this "rolling" 3-year average of the annually produced dose values is then, with reasonable certainty, of the order of 100 years. The essential justification of the 3-year averaging method is that the violation did not actually take place, but was a consequence of an unusual coincidence of the time of measurement and the occurrence of increased emissions.

MAXIMUM DISCHARGE UNDER THE LICENCE UPDATE 1997

General

In discussions with the competent authorities, TIBV was asked to apply for new licences updating the present licences. Moreover, all the different licences are put together in one so called "complex licence". With this licence TIBV will have more freedom to change parts of its practices without having to change the licence. For a complex licence it is necessary to have a number of classified radiation protection experts and an internal organisation that guarantees adequate radiation protection for the workplace and environment.

Discharge quantities based on 100 μSv/year

In the new licence-updating request TIBV will base the required maximum discharge quantities on the present MTD of 100 μSv/year. This will be done because of the possible use of alternative ores (see 10.4). Furthermore, the effective particle diameter is smaller then measured (see 10.3). TIBV will request a higher dose because, in the dose range up to 100 μSv/year, the same ALARA and optimisation considerations are valid as used in 7 and 8. It is not certain that the dose to "the environment" will indeed rise to values above the former threshold limit of 40 μSv/year. The use of other ore and the measures taken to lower the cadmium emissions could even lower the dose.

Effective diameter

The AMAD (Activity Median Aerodynamic Diameter) was measured in the past and determined to be 0.5

µm. The dust particles, carrying the radionuclides, leave the stack surrounded by a water layer. The particle size measurements were carried out on particles in the stack. Due to evaporation of the water layer, after leaving the stack, the particle size decreases. The smaller particles are deposited more easily in the human lung during inhalation. For this reason these smaller particles have a higher Dose Conversion Coefficient for inhalation compared to the measured particles size. Table 4 list the DCCs for ^{210}Pb and ^{210}Po for the former ICRP lung model, the new lung model (ICRP 66,1994) and the new lung model with the estimated new AMAD of 0.2 µm.

Tabel 4

Nuclide	old lung model AMAD 0.5 µm DCCinh µSv/Bq	new lung model AMAD 0.5 µm DCCinh µSv/Bq	new lung model AMAD 0.2 µm DCCinh µSv/Bq
^{210}Pb	29	6	10
^{210}Po	5.4	4.7	8

The dose caused in the surrounding area is proportional to the DCC. The reduction of the dose due to the new lung model is countered by the smaller particle size. At this moment more measurements are being carried out with a cascade impactor to determine the particle size more accurately.

The fact that there is a difference between measured and effective diameter was found during the investigations necessary to find a solution for the cadmium problems (see 10.4).

Alternative ore

TIBV used predominantly ore from Florida until 1996. This ore is no longer available. For this reason Jordan ore is used currently. The concentrations of the impurities in this ore differ from those in Florida ore. As a result of the differences in the ore, cadmium emissions to the environment increased to levels above the licensed values given to TIBV. This was remarkable given the fact that the concentration of cadmium in the Jordan ore is lower than that in the Florida ore. In combination with other impurities, notably chloride, cadmium becomes volatile during sintering. In a similar way the ^{210}Pb emissions increased even though the concentrations were lower. The concentration of radionuclides in Jordan ore is about 30% of the concentration in Florida ore. During 1997 TIBV is testing other ores. TIBV cannot exclude an increase in radionuclide emissions after switching to another ore in an effort to reduce the cadmium emissions. Switching is a process that takes at least one year, during which period it is not possible to influence the emissions.

It must be emphasised that it is not the intention of TIBV to emit more radionuclides to the environment. In fact, with another ore, emissions could be lowered. TIBV processes the ore to produce elemental phosphorus and not because of the radioactive properties. Emissions to the environment are controlled by secondary chemical reactions in the production process. These reactions are not fully understood and are not predictable before switching over to another ore. Therefore TIBV is only able to influence the emissions in a limited way and needs time to study the effect a new ore has on the emissions.

In the request to update the licence TIBV will express the required discharge limits in Radio Toxicity Equivalents. Using this concept, described in the policy principles, gives the advantage that the radio-toxic effects of quantities of different radionuclides can be compared immediately.

CALCINED DUST

General

To enable the production process to proceed smoothly, approximately 1000 tons of calcined dust have to be removed each year from the precipitator dust cycle. For a number of years this calcined dust has been kept in intermediate storage on site.

The calcined dust is classified as radioactive waste under current law (800 Bq/g ^{210}Pb+ $t^1/_2$=22 years) and therefore cannot be disposed of in a chemicals landfill.

Immobilisation

KEMA has carried out leaching tests, based on the Dutch government's limiting values memorandum "storten gevaarlijk afval" (dumping hazardous waste) of May 1993. The chemical composition of the waste is such that, after it has been immobilised in cement, it can be disposed of in a C3 landfill without any difficulties. The ^{210}Pb-activity will have fallen below 10 Bq/g (exemption level for ^{210}Pb for functional radionuclides EU-directive) after 150 years. After 150 years, or sooner if the (conditional) clearance levels for non-functional radionuclides will be set at increased levels, the calcined dust can be immobilised and disposed of in a C3 landfill.

Storage at the COVRA

TIBV and the COVRA have signed a contract to store the calcined precipitator dust.
A choice has been made for bulk storage rather than the standard packagings. The material will be stored in 20-foot containers with a plastic lining. These containers will be stacked in a purpose-built storage building. Materials tests were carried out at KEMA. It has been decided that the calcined dust will not yet be immobilised, because immobilisation with cement will increase the volume. This is not desirable because the material will then take up more space in the storage building. Immobilisation can be carried out after the decay period of the radionuclides.

SLAG

General

Slag is a secondary product (see 2.5) that looks like stone and is used in the hydraulic and road engineering sectors. From the very start of its phosphorus production operations, TIBV, in consultation with government bodies, has only released the slag for use in road and hydraulic engineering applications. Even 30 years ago, a system of "conditional clearance" was practised. The use of the slag was supported by governmental bodies responsible for road and hydraulic engineering applications.

Some of the benefits of using slag are:

- Slag is a good substitute for gravel and prevents the formation of gravel pits caused by gravel mining.
- The angular structure of the slag ensures that the road is more resistant to subsidence.

A disadvantage of using slag is that about 1 Bq/g ^{238}U is present in a state of equilibrium with its (gamma-emitting) daughters: ^{238}U+.

The possible consequences of this are:

Distribution of radionuclides

Undesirable distribution of radionuclides in the environment. VROM commissioned the ECN to carry out a study of the leaching behaviour of the radionuclides. The amounts that leach out appear to be so small that a hypothetical calculation - all the dikes of the IJsselmeer were provided with slag as a filler material - yielded a maximum dose of 0.012 μSv/year).

External irradiation

Due to the use of the slag in road and hydraulic engineering applications, members of the public could possibly be exposed to higher levels of background radiation. The top layer of the road surface, which never contains phosphorus slag, shields the external radiation leaving the slag used for road building. Because the thickness of this top layer can vary, it is not possible to specify the exact dose rate associated with the use of slag in road building. In general terms it can be stated that the dose is of the order of magnitude of 40 μSv/year for someone who spends 2 * 0.5 hours/day on a cycle path, and 40 μSv/year for someone who spends 8 hours/day on the road. The difference is attributable to the thickness of the top layer.
The exact dose depends on a number of calculation factors that are not included in the policy principles (see 6.1):

o What sojourn times on roads and cycle paths should be assumed?
o What proportion of roads and cycle paths contain slag as metalling; should the current situation or, for example, the situation in 25 years, be taken as the basis for the calculations?
o What background can be subtracted from the dose rate on the road? The soil at the side of the road or the average road without slag?

Other criteria may also be of importance in this context.

Proposed and/or current legislation
As mentioned before, the European Union has defined exemption levels for radionuclides. $^{238}U+$ (with daughters) stands at 1 Bq/gram for functional radionuclides. The European Union has attached a reporting obligation to the exemption levels. The consequences of this reporting obligation for the use of slag are not clear because the exemption levels for non-functional radionuclides are not known at the moment this article was written (July 1997).

Slag as a building material
At the very start of its phosphorus production in 1968, TIBV decided that it would not allow the slag to be used for house building but only for road and hydraulic engineering applications. The building materials in the house-building sector in the Netherlands are subject to the stand-still principle. Under this principle, it is not allowed for building materials to cause a higher dose then they did in former applications.
Because of the practised conditional clearance, the slag should not become subject to the constraints of the environmental legislation. The environmental legislation is considerably stricter than the stand-still principle applied in the Netherlands to other materials (with comparable activity) used in house-building. The phosphorus slag is still a building material, and should therefore not be subject to stricter standards than those applied to building materials in the house-building sector.

Commentary
TIBV put a number of these facts to the Dutch government after the draft changes in the Nuclear Power Act were published in 1994. (BSK).

Moreover, TIBV wrote to the European Commission concerning the draft European Directive published in 1993.

WORKPLACE PROBLEMS

Introduction
Operators who are involved in the production of phosphorus are exposed to radionuclides (^{210}Pb and ^{210}Po) predominantly from the precipitator dust cycle. These nuclides are alpha- and beta-emitters. To cause a dose there, must be an intake of these radionuclides into the human body. In workplaces an intake occurs predominantly by inhaling the dust that comes from the precipitator dust cycle.

Dust characteristics
The inhaled dust was examined by leaching tests in simulated lung moisture. The result of these tests showed that the relevant radionuclides (^{210}Pb and ^{210}Po) are leached out of the inhaled dust very poorly and as a consequence the lung retention class was set to class Y. This means that the radionuclides are retained in the lungs for periods of up to several years. Consequently the caused dose is received predominantly by the lungs.

Measurements
To obtain the dose received by the operators concerned, Personal Air Sample measurements were carried out.
The measurement device consists of an air pump and a filter in a filter holder, connected to each other by a tube. The measurement device is carried by the operator in such a way that a continuous sample of the air surrounding the operator is passed through the filter in the filter holder. The dust containing the

radionuclides is separated from the air and collected on the filter. The operator carries the pump and filter with filter holder for the working period of 8 hours. The filter is measured for alpha- and beta-counts on a proportional counter tube. The intake of radionuclides can be calculated from the obtained count rate, the flow that passed through the filter and a worker's assumed breathing rate. Given the intake, together with a Dose Conversion Coefficient (Sv/Bq), it is possible to make a dose assessment.

Measurement effort and dose assessment

In the period 1984 until 1993 approximately 30 PAS-measurements per year were taken on the operators in working conditions in which inhalation of dust is most likely to occur. To learn more about specific working circumstances, if the dose assessment for a certain job exceeded a threshold value, more specific measurements were taken. By taking more measurements at the same time at different places in a working area and comparing them with earlier measurements, taking the working and process conditions into account, it was possible to determine the pathways by which the radionuclides from the process reach the operators involved. As a result, a number of measures were taken to prevent the inhalation of radionuclides in order to obtain dose reductions.

In general it can be said that operators concerned with the production of phosphorus at the TIBV-site are exposed to an average dose of 1 mSv/year. This dose is not given in the same dose rate every day. There are days when the dose, extrapolated from one workday (the measuring period) to a year dose, yields an annual dose of 5 mSv/year. On the other hand, there are also days that yield an extrapolated dose of 0 mSv/year depending on the (determined) process and working conditions (pathways).

It is also found that it is possible to obtain dose rates up to 1 mSv per hour if parts of the installation, covered with high concentrations of radionuclides, are polished, jagged or subjected to other operations that remove radionuclides from the contaminated surface with a risk bringing them into the air.

Contamination up to several hundred Bq per cm^2 has been determined on surfaces on the inside of the process equipment. Operators are consequently, under normal circumstances, not exposed to these high levels of contamination. However, during plant stops or repair work, when the installation is opened, preventive measures should be taken to avoid a high inhalation dose.

Legislation

If workers can be exposed to a dose of more then 5 mSv/year, they should be regarded as radiological workers.
It is expected that this value will be decreased to 1 mSv/year by the year 2000. TIBV is in discussion with the competent authorities concerning whether it is necessary and appropriate to give the operators involved the status of radiological worker.

Improving measurements and system

Due to the expected stricter legislation, in combination with the implementation of the new "Human Respiratory Tract Model for Radiological Protection" by the ICRP, TIBV is improving the measurement methods for determining the dose operators are exposed to. In addition TIBV will make dose assessments for all the different functions involved in the production of phosphorus.

POSITION

From the above it is clear that the adopted legislation can bring industrial activities like ours to the limit in terms of the factors that can be influenced. If only small changes are made in the dose calculation system of the ICRP, or emissions increase due to differences in phosphate ore, the dose can rise to just above threshold limits of 40 or 100 μSv/year. (The "natural" background radiation in the Netherlands, one of the lowest in the world, is about 25 times higher). There will then be only the two possible measures to take. These are the building of a precipitator processing plant or a high stack (or the above mentioned filter systems whose efficiency is doubtful (see 7.1). The high cost involved in building a precipitator dust processing plant cannot be justified just below the threshold values. Just above these levels it could be necessary to build this plant.

In the same way the exemption or clearance levels for non-functional radionuclides can be restrictive for products like our slag for the use as building material. Because of the bulk character of many building materials, given the large number of buildings and roads, many people are exposed to the dose caused by these materials. Consequently the collective dose caused by these materials is substantial compared to many functional practices. Exemption levels for non functional radionuclides should take this fact into account.

In future, the use of materials like our slag could be treated as a practice, instead of as a building material. In that case there would be stricter legislation for these materials used in the environment, compared to materials (with comparable radioactive properties) used in the housing sector.

This is a remarkable situation because the policy principles (based on the risk management) concerned with radiation protection were primarily aimed at the members of the public and by protecting them, it was assumed that the "environment" was protected as well. Now a material like phosphorus slag, that causes a small dose to members of the public when applied in the "environment", could be regulated much more strictly than the building materials that cause a much higher dose because sojourn times in houses are longer than on roads. Treating the slag as a practice would be even more remarkable given the fact that there is no legislation, and probable will not be, that prohibits the use of such materials in houses.

Slag should be treated as a building material and should not be punished by becoming a practice due to the self-imposed "conditional clearance".

Abbreviations

^{238}U	Uranium with mass number 238
$^{238}U+$	Uranium with mass number 238 and daughters in equilibrium
ABC-factor	Actual exposure correction factor
AID	Actual Individual Dose
ALARA	As Low As Reasonably Achievable
AMAD	Activity Median Aerodynamic Diameter
Bq	Becquerel (the number of disintegration's per sec. due to RA-decay)
Clearance level (conditional)	Activity levels above which disposal of radioactive matter is not allowed
COVRA	The Dutch central organisation for the storage of radioactive waste
dose	Effective dose: the sum of the equivalent doses, weighted by the appropriate tissue weighting factors, in all tissues and organs of the body
ECN	A Dutch Energy research institute
Exemption level	Activity levels above which a licence is necessary
HHNV	Hoechst Holland NV
ICRP	International Commission on Radiological Protection
KEMA	A Dutch research institute
MID	Multi-functional Individual Dose
MID*	Multi-functional Individual Dose without the protection provided by housing
MTD	Maximum Acceptable Dose 40 or 100 μSv/year
NLG	Dutch Guilder
PAS	Personal Air Sampling
Practice	An activity such as the production of phosphorus that causes a dose.
RIVM	Dutch National Institute for Public Health and Environment
Sv	Sievert. The SI unit of equivalent dose. 1Sv=1 J/kg
TIBV	Thermphos International BV
VROM	the Dutch Ministry of Public Housing, Planning and the Environment