Annex 2

Work Package 2

Case studies with industrial partners

SMOPIE Work Package 2 - NL Case Study 1 (Thermphos)

1. OVERVIEW OF THE PROCESS

Hoechst Holland N.V. began to produce elemental phosphorus from phosphate ore in Vlissingen, The Netherlands in April 1968. Elemental phosphorus is used to produce high-grade phosphoric acid.
Since December 1971 three phosphorus furnaces have been in operation.
In March 1983 the monitoring network of the nearby Borssele Nuclear Power Plant detected radionuclides that appeared to originate from Hoechst. This was discussed with government representatives and resulted in a request for a licence under the Dutch Nuclear Power Act, which was granted in 1985. Since then the licence was amended several times as a result of ongoing supplementary environmental studies.
In July 1997 Hoechst Holland N.V. was divided into four independent companies, after which Thermphos International BV continued the phosphorus production.

2. SCALE OF THE PROCESS

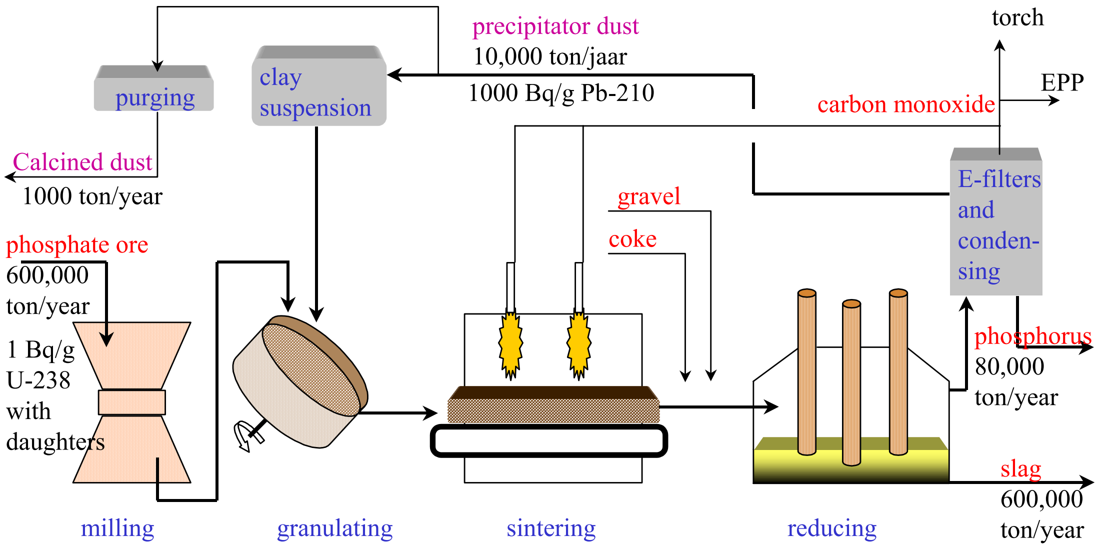
Thermphos produces about 80.000 tons of pure elemental phosphorus per year. They use for this production about 600.000 tons of phosphate ore, which is shipped from the country of origin to the Thermphos site, which is located at the Vlissingen harbour close to the North Sea. As a by-product also about 600.000 tons of phosphorus slag is produced. This slag is mainly used in road construction as a foundation material. For this purpose it is mixed with blast furnace slag from the steel production to form a hydraulic mixture with excellent properties for road construction. Since equal amounts of slag are produced as phosphate ore consumed, the activity of the slag of natural radionuclides other than polonium-210 and lead-210 is the mass weighted average of the input materials.
Besides the products about 1000 ton per year of calcined waste is produced, which contains large amounts of heavy metals as well as lead-210 and polonium-210 in concentrations up to 1000 Bq/g.

3. STEPS IN THE PROCESS

Figure 1 shows the process flow diagram. The different steps in the production process can be distinguished in milling, granulating, sintering and reducing the phosphate ore. In the furnace, precipitator dust is formed, which is recycled into the process, thus yielding an enhancement of certain types of radionuclides in the precipitator dust cycle.

3.1. Raw material store and milling

The phosphate ore, which arrives by boat in shipments of 10.000 to 40.000 tons, is stored on-site at Thermphos. From the warehouse the phosphate ore (a mixture of sedimentary and magmatic ores) is transported on a conveyor belt to the sintering plant, where it is milled to a fine powder. The powder, together with a binder (clay suspension), is fed onto a rotating granulator disk. As the disk rotates, granules (pellets) are formed. Dust concentrations close to the granulator disk are typically 4 mg/m^3.



PHOSPHORUS PRODUCTION AT THERMPHOS INTERNATIONAL

Figure 1: **Phosphorus production by the thermal process**

3.2. Sintering plant

The pellets are transported onto the front end of a 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. There are three sintering lines. The sintered pellets are stored in bunkers before being fed into the electric furnaces.

3.3. Slurry station

In the slurry station clay and other additives are suspended in water to produce the binder suspension used for granulation. One of the additives is precipitator dust, a return flow of the furnace gas dust. There are two slurry lines.

The slurry station also houses the purging unit. This is where a fraction of the precipitator dust that is formed in the production process is discharged. By discharging more or less of the precipitator dust, the concentration of volatile inorganic matter, heavy metals and radionuclides in the precipitator dust cycle can be controlled. The purging unit consists of a high-pressure filter and a rotating calcining kiln where the filtered dust is calcined at temperatures of 500 °C.

3.4. Phosphorus plant

There are three electro-thermal furnaces in the phosphorus plant. The pellets are fed into the furnaces together with gravel and coke. At temperatures higher than 1500 °C a reaction takes place according to:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow 6\ CaSiO_3 + 10\ CO + P_4$$

in which phosphate ore is reduced to elemental phosphorus (P_4).

The elemental phosphorus leaves the furnace as a gas, together with furnace gas (carbon monoxide) formed during the reaction. Entrained dust is separated from the gasses in electrostatic precipitators. This dust is collected in the slurry tanks where it is mixed with water. The resulting slurry is pumped to the slurry station, where it is reused in the granulator binder. The dust-free gasses are cooled, causing the phosphorus to condense to a liquid stream. The furnace gas is used as burner fuel in the sintering plant. Excess carbon monoxide is compressed and transported to a nearby coal-fired power plant, where it is used as an additional fuel. The molten calcium silicate slag, formed in the furnace, is continuously run off and transported to “slag beds” to cool down.

4. WORKPLACE CHARACTERISTICS

The mixture of sedimentary and magmatic phosphate ores contains approximately 1 Bq/g (range 0.25 - 1.5 Bq/g) of uranium-238, with all radioactive daughters in approximate radiological equilibrium. Radionuclides of the thorium chain have a far lower radioactivity of approximately 0.05 Bq/g.

During the sintering process at 800 ^{o}C about 90 % of the polonium and about 10 % of the lead evaporates and is emitted, even after thorough washing of the flue gasses, to the environment. At the even higher temperatures during the electro-thermal production process almost all volatile inorganic substances (metals and radionuclides) evaporate and condense on dust particles in the gas flow.

The dust is trapped in the electrostatic precipitators and is recycled via the clay suspension into the pellets, after which the process of evaporation and condensing can start all over. After a number of cycles this results in an enrichment of the volatile radionuclides up to a factor of 1000 compared to the ore. Since most of the polonium is emitted in the sintering plant the concentration in the precipitator dust cycle is about a factor 10 lower than for ^{210}Pb.

The non-volatile radionuclides, i.e. radium and higher, stay in the smelt and are removed with the phosphorus slag.

Operators involved in the production of phosphorus are exposed to radionuclides from the precipitator dust cycle. The radionuclides involved are predominantly ^{210}Pb and 210Po, which are beta and alpha emitters respectively. To cause a relevant dose, there must be an intake of these radionuclides into the human body. In the workplace this intake occurs mainly by inhalation of dust, which is unavoidable in an industrial environment.

The results of leaching tests of precipitator dust with simulated lung fluid showed that the absorption to blood of the relevant radionuclides is type ‘S’. This means that the radionuclides, once deposited in the deep parts of the lungs, are retained there for several years on average. The resulting effective dose is therefore predominantly received by the lungs. As a result of the deposition characteristics of log-normally distributed particles in the lungs and the low solubility to blood, the dose coefficient (DC) does not significantly change over a range of approximately 0.5 to 5 µm AMAD as is shown in figure 2 for ^{210}Po and ^{210}Pb. Thermphos uses an average DC for the entire particle size spectrum based on the average for the range 0.1 to 5 µm (4.2 µSv/Bq for ^{210}Po and 5.8 µSv/Bq for ^{210}Pb). This will overestimates the dose with a factor of 1.5 compared to the default ICRP value (based on an AMAD of 5 µm for workplaces) which is for type S materials approximately 2.7 µSv/Bq for ^{210}Po and 4.0 µSv/Bq for ^{210}Pb respectively.

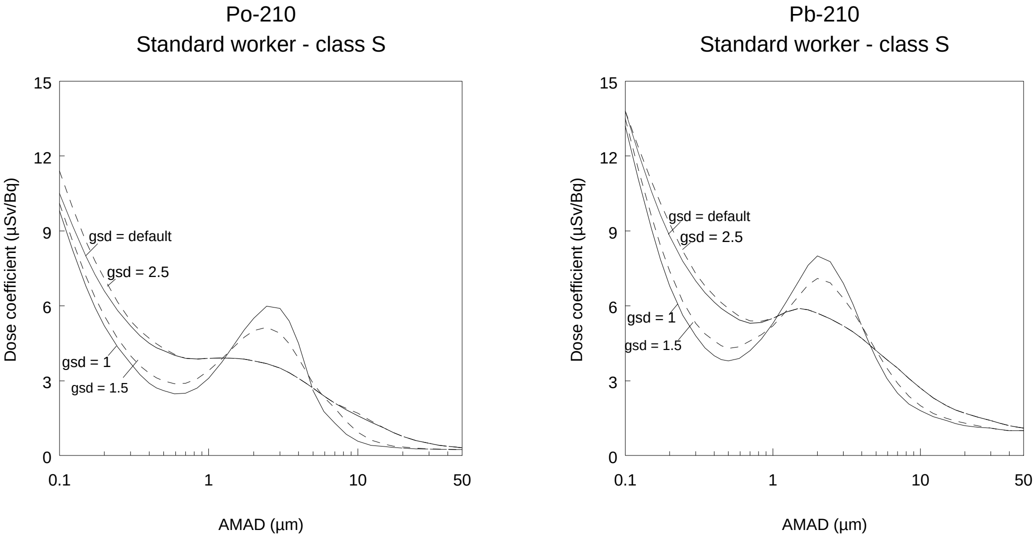


Figure 2. DC as a function of particle size (AMAD) and geometric standard deviation for ^{210}Po and ^{210}Pb

5. ROUTINE SAMPLING

Routine Personal Air Sample (PAS) measurements are carried out to determine the dose to which workers in the phosphorus production plant are exposed. The PAS consists of an air pump (2 litres per minute) and an IOM filter holder with filter on which the dust is collected (See Figure 3).

Figure 3. Air pump and IOM filter holder with filter

The operator carries the PAS for the working period of 8 hours. The filter is measured for alpha and beta activity in a proportional counter tube after a waiting time of three weeks in order to get radiological equilibrium between ^{210}Pb and ^{210}Bi. The ^{210}Pb is then measured by detecting the 1.16 MeV beta particle of ^{210}Bi. The activity of ^{210}Po is measured directly by detecting the 5.3 MeV alpha particles. The measurements are carried out on a proportional counting tube, which can discriminate between alpha and beta particles. Self-absorption of alpha particles is assumed to be negligible since the dust collected on the filter has a typical layer thickness of only 5 μm. The range of alpha particles in solids is of the order of 30 μm. The dust in the workplace is a mixture of phosphate ore and precipitator dust. Since ^{210}Po and ^{210}Pb are the dominant radionuclides in airborne dust in the sintering and phosphorus plant with activities of a few tens of Bq per gram, as an approximation, all alpha particles are counted as ^{210}Po and all beta particles as ^{210}Pb.

In order to be able to measure the lower dose at which employees are designated as exposed workers (1 mSv per year), a 10 channel proportional counter was purchased to replace the 1-channel carrousel. Consequently, it has been possible to increase the measuring time from 3 hours to 5 days in order to obtain the necessary statistical accuracy.

In the period 1984 to 1993 about 30 PAS measurements were carried out each year at workers who were most likely to inhale radionuclides. From 1998 on this number is approximately doubled and amounts nowadays about 70 per year (equivalent to approximately 2% of the 4000 worker shifts per year).

Table 1 gives the results of the PAS measurements for the period 1998 - 2001 differentiated after plant and function. The results of the PAS measurements are extrapolated to a working time of 1600 hours.

Table 1. PAS measurements; average values for the years 1998 to 2001

▪	$\bar{E}$ (mSv/1600 h)	σ	CI	n (1998-2001)
Thermphos total, mean for all functions	1,21	1,23	0,10	245
Phosphorus plant, mean for all functions	0,99	1,10	0,13	122
Function: Control room	0,11	0,06	0,04	5
Filtration operator	0,41	0,25	0,17	5
Condensation operator	0,52	0,22	0,15	5
Electrode welder	0,70	0,31	0,14	9
Daytime operator	1,02	1,28	0,48	13
Furnace feed operator	0,85	0,32	0,22	5
Slag operator	0,60	0,50	0,22	10
Slurry operator	0,58	0,39	0,18	9
Shift supervisor	0,65	0,51	0,26	8
Assistant supervisor / general operator	1,14	1,27	0,37	21
Cleaning operator	2,00	1,70	0,54	18
EMC technician	0,43	0,19	0,16	4
Fitter	1,39	0,83	0,36	10
Sintering plant, mean for all functions	1,42	1,31	0,15	123
Function: Control room	0,21	0,09	0,06	6
Indoor operator	1,56	1,29	0,78	6
Granulator operator	1,06	0,81	0,23	21
Slurry operator	0,73	0,43	0,14	17
Shift supervisor	1,15	0,86	0,26	19
Assistant supervisor	1,60	1,24	0,36	21
Cleaning operator	2,82	1,62	0,53	17
EMC technician	1,93	1,42	1,55	3
Fitter	1,35	1,38	0,64	9
Calcinate dryer operator	2,00	2,80	2,29	4

The results show a variation in individual doses, but it is important to note the statistical uncertainties statistics. These suggest that the variation in result for the same type of workers is typically greater than that between different tasks. This is because different tasks are carried out in the course of a working day and the concentration of radionuclides in the air fluctuates widely. In fact, only the cleaners have doses significantly higher than the average, while the doses in the control room are significantly lower.

6. OTHER MEASUREMENTS

6.1. Cascade impactor measurements

Thermphos has carried out measurements with a cascade impactor to determine the activity distribution as a function of particle size. This cascade impactor, which is specially made for workplace measurements, consists of a number of stacked plates with openings that are displaced 30° from one plate to the next. Filters with the same openings as the plates are inserted between the plates. The holes in the plates decrease gradually from plate to plate, thus increasing the air speed. As a result the size of the particles that can pass through the following plate becomes steadily smaller.

Measurements with a cascade impactor are very labour intensive, but since information on particle sizes is obtained the dose can be calculated more accurately than with total dust samplers.

A simultaneous measurement with an IOM sampler head and a cascade impactor during cleaning work showed that the dose was overestimated with a factor of 2 if no correction was made to compensate for the particle sizes larger than 5 µm.

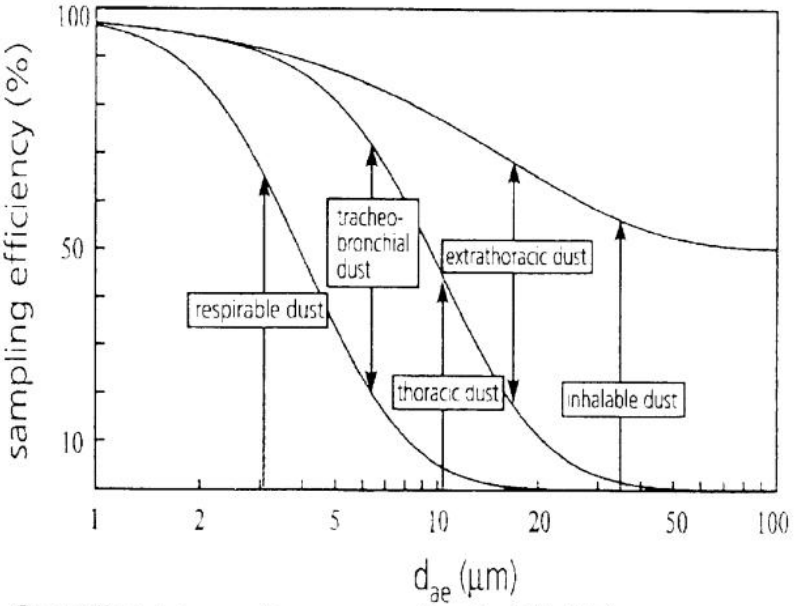
6.2 Measurements during slag operations (Post – Thermphos)

The slag produced by Thermphos is, after it is converted to a hydraulic mixture by addition of blast furnace slag, used for applications in the road and hydraulic engineering sectors. The slag is used as a foundation material for the construction of roads, where it is covered by at least one top layer of asphalt concrete. This provides shielding of external gamma radiation and prevents dust formation.

During the road building work no formation of dust can be visibly observed. This is due to the fact that the mixture is transported in a moist state in order to allow the hydraulic bonding process to take place.

In order to be able to measure dust, a test road surface of phosphorus slag was constructed on the site of Pelt & Hooykaas in Vlissingen. The dust measurements were carried out on a hot summers day, with a maximum input of heat and virtually no wind. During the test, a total of 270 vehicle movements were carried out, resulting in the production of a dust cloud almost every 4 minutes. A number of dust measuring heads were used during the test, including the IOM and the PAS6 filter holders and cyclones with thoracic and respirable separation characteristics in conformity with the EN 481 standard (see figure 4).

- *Figure 4. Sampling conventions*



Sampling conventions according to EN 481

A cascade impactor was used to determine the particle size distribution in the dust clouds.

The results of the measurements are presented in table 2. The test lasted 3 days but only on the first day a cascade measurement was performed. The measurements with the other devices performed on different days agree quite well with each other.

The results of the cascade impactor measurements are shown in figure 5. The results are presented relative to the total amount of dust sampled and normalized to 1 µm of particle size range. From the graph it is evident that the generated dust contains two log-normally distributed fractions, one with an AMAD of 0.3 µm and a gsd of 1.5, and one with an AMAD of 22 µm and a gsd of 2.5.
The graph also shows the mono-disperse dose coefficient for the uranium-238 series in secular equilibrium down to ^{214}Po as a function of the particle size.

Assuming an activity concentration in the slag of 1 Bq/g for the ^{238}U series in secular equilibrium down to ^{214}Po, a dust concentration and particle size distribution as measured with the cascade impactor during extreme conditions, and an inhalation rate of 1.2 m^3/h, a dose is calculated of 0.34 mSv for a working time of 1600 hours.
Considering the worst-case conditions during the tests, the real doses during road construction are most likely to be at least a factor of 10 below this value.

Table 3. Results of the measurements at Pelt & Hooykaas.

Date		**14-8-02**	**15-8-02**	**16-8-02**
Number of vehicle movements		**112**	**92**	**66**
Measuring heads		**Concentration mg/m^3**	**Concentration mg/m^3**	**Concentration mg/m^3**
IOM 1	Inhalable	5.56	3.81	4.39
IOM 2			3.95	
BGI 1	Thoracic	0.99	0.42	0.86
BGI 2			0.47	
Cassella 8	Respirable	0.3	0.28	
Cassella 9			0.3	0.67
BGI 2				0.5
PEM	PM 10	2.14	1.58	1.79
	Range µm	mg/m^3		
Cascade impactor	$d_p > 21.3$	3.21		
	$14.8 < d_p < 21.3$	1.47		
	$9.8 < d_p < 14.8$	0.88		
	$6.0 < d_p < 9.8$	1.07		
	$3.5 < d_p < 6.0$	0.56		
	$1.55 < d_p < 3.5$	0.15		
	$0.93 < d_p < 1.55$	-0.06		
	$0.52 < d_p < 0.93$	-0.09		
	$0 < d_p < 0.52$	0.41		

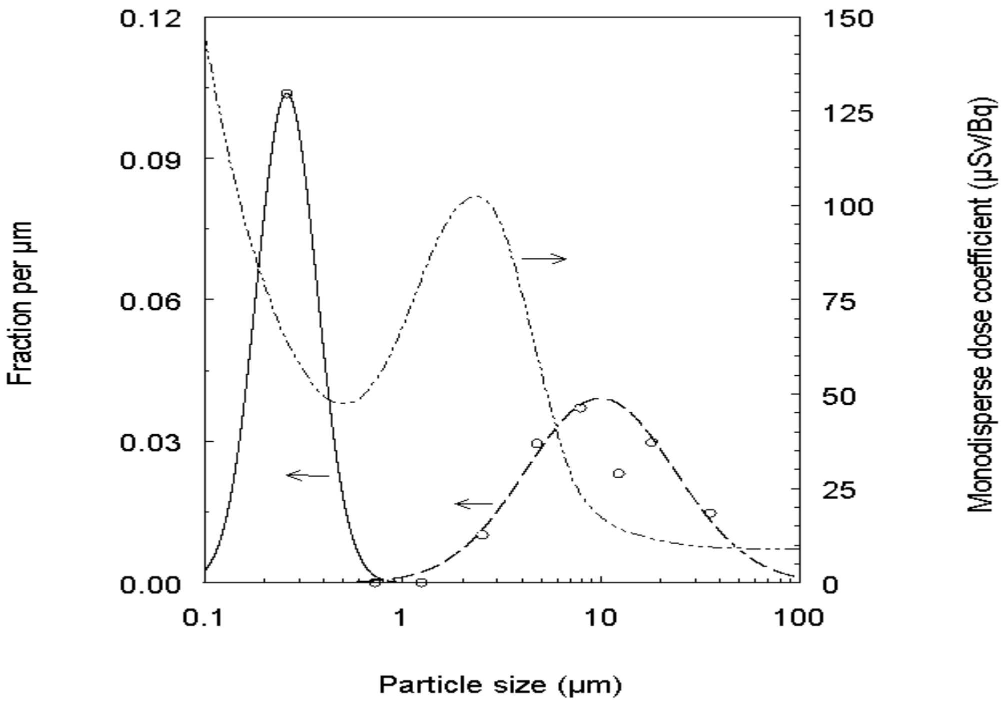


Figure 5. Particle size distribution of generated phosphorus slag dust relative to total dust.

7. SUMMARY OF THE CASE

At Thermphos International B.V. elemental phosphorus is produced by thermal processing of raw phosphate ore. The natural radionuclides of the uranium and thorium series with atomic number above 88 (radium) go mainly to the phosphorus slag, in which they have approximately the same concentration as in the original phosphate ore mixture.

The volatile radionuclides, i.e. lead and polonium, are partially emitted to the atmosphere in the sintering plant or evaporate from the smelt in the phosphorus plant, after which they wind up in the precipitator dust cycle. The activity concentration in the precipitator dust reaches values up till 1000 Bq/g, which means a factor 1000 enrichment compared to the original ore.

Precipitator dust that enters the factories can cause significant exposure to workers. Ongoing surveys of workers wearing Personal Air Samplers show that doses might be as high as 2 - 3 mSv/year for certain functions, while the average dose for both plants and all functions is around 1.2 mSv/year. This will designate them as exposed workers according to the Dutch law and provisions are made to register the dose these workers receive by internal exposure.

From a different point of view also the internal doses that might be received by the application of phosphorus slag with approximately 1 Bq/g of uranium and radium in road construction are investigated. Since in normal circumstances hardly any dust is generated during road construction, a test in the open air was performed under extreme conditions. Measurements were performed with different sampler heads and also with a cascade impactor. From the impactor measurements it was concluded that, even under these extreme circumstances, doses would be far less than 1 mSv per year for road construction workers.

Cascade impactor measurements are complex and difficult to carry out. One of the reasons for this is that the total amount of dust (or activity) is not captured on one filter, but is distributed over 8 filters. Therefore the amount of dust on each filter, especially on those where the very small particles are deposited, is very small and thus difficult to measure. Hygroscopic effects, loss of filter material or dust particles, or deposition of dust from the air while handling the filters may cause weighing errors. These errors are relatively larger than in the case of a total dust filter.

To avoid these problems and yet still be able to work with a correction that takes account of particle size, a filter placed in a thoracic cyclone can be used. This cyclone has a deposition characteristic that agrees quite well with the poly-disperse DC curve (see figure 2). This gives reliable outcomes for particle distributions up to about 10 µm AMAD when an average DC of the particle range 0.1 to 5 µm is applied. In case there is a considerable fraction of particles larger than 20 µm, one can consider applying additionally an inhalable sampler (e.g. an IOM head) and assign the surplus of sampled dust to the fraction above 20 µm. For these larger particles a lower average DC for the region 20 - 100 µm can be used. Applying this method to the ‘road construction’ case yields a dose of 0.38 mSv/year compared to the 0.34 mSv/year estimated from the cascade impactor measurement.

NL Case Study 2 (Kerr-McGee)

1. OVERVIEW OF THE PROCESS

1.1. Type of the process

The present chloride process replaced the sulphuric acid process in the beginning of the nineties of the last century. The plant is operated by Kerr-McGee (KMG) since the year 2000. At KMG titanium oxide pigment is produced from titanium-rich ore. The process involves chlorination of the TiO_2 in the ore with cokes and chlorine at about 900 ^oC in a fluidised bed reactor. Besides $TiCl_4$ (tickle) other metal chlorides will form because of impurities in the ore. The reaction products and part of the raw materials leave the reactor, are cooled down to about 200 ^oC and the solids are then removed in a cyclone. The $TiCl_4$ is separated from the less volatile other chlorides in condensing steps, oxidised to TiO2, purified by sieving and finished to the required end product specifications. The acid liquid containing the chlorides of the metal impurities of the ore is treated with lime to remove the metals to the solid phase as metal hydroxides (MeOH) which are then separated by filtration. The liquid from MeOH filtration is discharged into surface water and the solids are presently wet conditioned by an external company for specific reuse. Titanium ore contains uranium and thorium and their decay products at concentrations that vary considerably between batches from different countries and regions of origin and between ores having been untreated or having received pre-treatment to remove impurities. From 1993 to 2000 the plant was operated by Kemira Pigments B.V. and since then by Kerr-McGee (KMG).

1.2. SCALE OF THE PROCESS

The capacity of the plant is of the order of 80.000 tonnes of pigment produced as well as of ore processed, because of the high titanium oxide content of the ores. Consequently, the impurities in the ore, in particular the metal hydroxides produced in the waste treatment process are concentrated in the MeOH solids relative to the ore by a factor of about 12. This applies generally also to the radionuclides from the decay series of U-238 and Th-232.

2. STEPS IN THE PROCESS

2.1. Raw material store

The ore for the production of TiO_2 pigment arrives by boat and is stored by a warehouse company. There it is loaded into trucks and transported with top cover to KMG and unloaded as local stock for continuous production.

2.2. Raw material feed

The ore from the local stock is fed with a front loader onto a covered transport belt that brings the ore in a rotating barrel dryer. The dried ore is stored for input into the chlorination process together with cokes and chlorine gas.

2.3. Chlorination of TiO_2

Cokes, ore and chlorine are continuously fed into the chlorinator that operates as a fluidised bed reactor at a temperature of about 900 ^oC. TiO_2 is converted into $TiCl_4$ (tickle) but other metal chlorides will also form because of the impurities in the ore. The reaction products and some of the solid raw materials leave the reactor and are separated in a cyclone after cooling down to 190 – 200 ^oC. The tickle is cooled down in a series of condensing columns with decreasing temperature in which the $TiCl_4$ finally condenses to liquid $TiCl_4$ and is further purified by vaporisation and distillation.

2.4. Oxidation and purification

The tickle is vaporised and then oxidised to TIO_2 in a tubular reactor, called burner under continuous sandblasting to prevent TiO_2 to stick to the walls of the burner. Further finishing involves the removal of this sand by sieving the slurried product and again sand-milling, sieving and washing, drying and dry milling the TiO_2 to the required end product specification of purity and particle size.

2.5. Waste treatment

The main waste streams are generated by the treatment of the blow-down solids from the reactor separated by the cyclone and the acid liquid with the condensed metal chlorides. These two streams are collected together and fed to a chamber filter press. The filter cake comprising unreacted ore and coke is sold as an industrial product. The acid liquid from the filter press FL02 is neutralised with lime to precipitate the metals as hydroxides. The precipitate is separated from the liquid in another chamber filter press FL01. The filter liquid is discharged as waste water into surface water and the MeOH filter cake is collected in containers and transferred to another company for immobilisation treatment and final use as back-filling material.

3. WORKPLACE CHARACTERISTICS

3.1. Overview of the history

The change from the sulphuric acid to the chloride process was enforced upon the operator of that time because of the discharges of acid and heavy metals into surface water. When the chloride plant was in the design phase it was decided that the MeOH filter cake had to be dried to reduce the costs of disposal at a dedicated chemical waste repository. The drying system envisaged was a rotating dish dryer. Still in the design phase of the installation it was understood that such drying system would produce a very fine grained easily dispersible product that would be difficult to contain and would require a very reliable and effective off gas cleaning system to prevent aerial discharges. Therefore, drying of the filter cake on a belt dryer with hot air was tested at pilot level, selected as the preferred option and installed.

However in the early years of operation of the chloride process it appeared that the belt dryer exercised significant mechanical force on the cake and produced an uncomfortable fraction of fine-grained dust that was difficult to contain within the dryer and which presented a potentially significant risk of exposure by inhalation and of aerial discharge in cases of sub-optimal functioning of the off gas venturi scrubber. Therefore the room with the belt dryer was monitored with a static air sampler.

The dried product had to be bagged before transport to the disposal facility in order to prevent exposure of the workers at the facility to airborne MeOH.. In this bagging workplace the exposure of the worker could arise from puffs of dust resulting from continues connecting and disconnecting bags. The bagging site had to be fitted with provisions such as local containment and air extraction systems to prevent high levels of dust, and the workplace was monitored by static air sampling to assess the effectiveness of the countermeasures.

Problems with the belt dryer continued to cause difficulties in controlling MeOH dust. Therefore it was decided to refrain from drying the filter cake, to dismantle the belt dryer and to deliver the filter cake wet to the repository packed in big bags. Presently MeOH filter cake is collected in containers, and transferred to another company for immobilisation treatment and final use as back-filling material.

3.2. Potential exposure levels

In order to obtain some measure of the potential significance of the exposure of workers at the plant to MeOH dust derived air dust concentration were calculated in 1992 on the basis of different uranium and thorium concentrations in the ore and a dose limit for workers of 1 mSv/y. On the basis of analytical results it was assumed that part of the Ra-226 and Pb-210 from the ore would not go to the MeOH filter cake but would be discharged with the waste water. The results are shown in Table 1.

The results showed that with uranium end/or thorium at the high end of the concentration ranges for the ores an annual dose limit of 1 mSv could be approached at a dust level of 50 - 70 $\mu g/m^3$ at full time occupational exposure and with conservative dust characteristics. It was clear that significant exposures could result if airborne MeOH dust would not be effectively controlled. Therefore it was concluded that effective measures should be taken to prevent the dispersion of MeOH dust in workplace air and that some monitoring system should be employed to verify the effectiveness of those measures. The measures included local exhaust provisions at the bagging workplace and frequent removal of spilled MeOH with water in the dryer room and the room of FL01.

Table 1. Derived limits for airborne MeOH dust at the workplace for different concentrations of U and Th in rutile. These limits are based on 1700 hrs per year exposure to 0.3 µm AMAD particles of Class Y (the most pessimistic assumptions) on the basis of 1 mSv/a dose limit.

Ore (rutile)	Uranium in ore ppm	Thorium in ore ppm	U-238sec in ore Bq/kg	Th-232sec in ore Bq/kg	Derived dust limit, µg/m^3
1	90	160	1112	649	59
2	80	120	988	487	70
3	7	78	86	317	252
4	59	7	729	28	139
5	22	53	272	215	212
6	20	210	247	852	92
7	50	91	618	369	105
8	53	51	655	207	121
9	12	455	148	1847	50
10	50	5	618	20	165
11	25	123	309	499	127
12	52	59	642	239	118
13	70	119	865	483	77
14	5	36	62	146	490
15	11	176	136	714	119
Average	40	116	494	470	106

NOTE: The dose coefficients used to derive the dust limits in table 1 were taken from J.R. Greenhalgh et. al, NRPB-R162 Report, National Radiological Protection Board, Chilton, Dodcot, April 1985.

4. TEST OF A SIMPLE STATIC MONITORING SYSTEM

At NRG, simple static monitoring systems were used to monitor airborne radioactivity in working areas. They comprised a simple rotary vane vacuum pump drawing air at a rate of 1.5 m^3/h through a gas meter and through a 55 mm circular planar filter in a filter holder. This systems was employed in several test periods at the plant in the beginning of 1993. At that time micro-fine quarts fibre filters were used. Later they were replaced by glass fibre filters. Each sample was taken over a 30 day period. The results are shown in Table 2.

It was decided that spoiled filter cake should be washed from the floor regularly and that a simple static air sampling system would suffice for monitoring the effectiveness of these measures against the build-up of MeOH dust in the areas of the dryer and the filter. Relative long sampling periods at about 1.5 m^3/h allow the determination of the average dust load by gravimetric methods to monitor build-up of dust over time. Long counting times in the analysis of the filters by high resolution gamma spectrometry brings the minimum detectable activity of Th-234 sufficiently down for detection of MeOH dust at levels below those resulting in significant exposures at realistic occupancies but otherwise conservative assumptions. Evidently, the static air sampling does not provide any clew to the real time variation of the dust load in the monitored areas. In addition, the simple sampling system does not provide for a constant air flow over the sampling period. From the results it was also clear that only the nuclide specific analyses by gamma spectrometry could provide the potential link of the dust load with the presence of MeOH dust. The alpha count rate of the filters was apparently related to Po-210 naturally occurring in outdoor air and, during the first few days after sampling, to the short-lived progeny of Pb-212 (half-life 10 h) from the Th-232 decay series.

Table 2. Results of static air sampling test at the TiO2 pigment production plant carried out with about two week sampling periods in the beginning of 1994.

End of sampling	Sampling area	Dust load on filter	Dust concentration	Th-234 concentration *	Max annual dose at full time occupancy **	Max annual dose at realistic occupancy ***
		mg	µg/m^3	mBq/m^3	mSv	mSv
7feb94	Dryer room	25.8	56	0,09	0,6	0,06
21Feb94	Dryer room	62.6	112	0,21	1,2	0,12
15mar94	Dryer room	59.1	89	0,21	0,9	0,09
28Mar94	Dryer room	33.9	46	0,007	0,5	0,05
19Apr94	Dryer room	39.1	46	0,09	0,5	0,05
13May94	Dryer room	47.0	80	0,06	0,8	0,08
7Feb94	FL01 (MeOH)	38.4	60	0,13	0,6	0,16
21Feb94	FL01 (MeOH)	47.6	91	0,08	1,0	0,24
15Mar94	FL01 (MeOH)	49.5	79	0,16	0,8	0,21
28Mar94	FL01 (MeOH)	36.3	54	0,003	0,6	0,14
19Apr94	FL01 (MeOH)	32.9	42	0,06	0,4	0,11
13May94	FL01 (MeOH)	52.5	57	0,05	0,6	0,15

* All results with relative large counting error; in bold: based on minimum detectable activity

** Based on conservative dust characteristics and average rutile from Table 1

*** Based on 10% occupancy in dryer room and 25% occupancy in filter room and otherwise conservative assumptions

5. ROUTINE SAMPLING

Routine sampling with two simple static air samplers in the FL01 room and the dryer room has been continued since 1994 to the present, the belt dryer having been out of operation since mid 1994. In some periods the sampler from the dryer room was used to monitor other working areas but the sampling in the filter room has been nearly continuous over the whole period. During the last two years the samplers were only used in the dryer room and in the filter room.

The results of dust load measurements in recent years are shown in Figure 1 for the MeOH chamber filter room (FL01) and in Figure 2 for the former dryer area where wet MeOH filter cake is loaded from a transport belt into containers. Neither of these work areas showed build up of dust over time. Highest average dust loads over about one month sampling period were limited to about 130 µg/m^3 in the filter area and 140 µg/m^3 in the dryer area. Average dust loads over all sampling periods amounted to 54 µg/m^3 for the filter area and 63 µg/m^3 for the dryer area (these values are very close to outdoor background levels). They show that the present waste treatment process does not give rise to dusty conditions. An important potential source of dust had been the belt dryer and the filling of gabs with dried cake. As these two operations have been abandoned already some years ago the only potential source of airborne dust has been spilled filter cake drying on the floors and equipment. Apparently the countermeasures against accumulation of dust have been effective. As has been illustrated in Table 2 the resulting maximum annual doses calculated with rather conservative assumptions with respect to dust characteristics are well below 1 mSv/a.

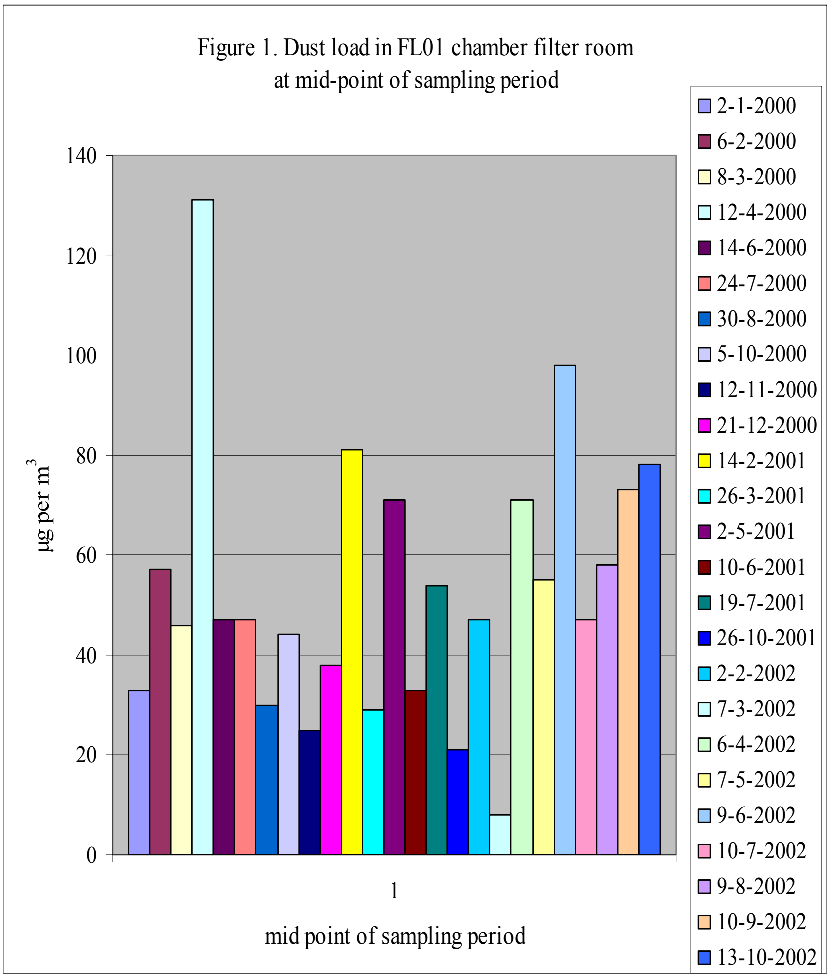
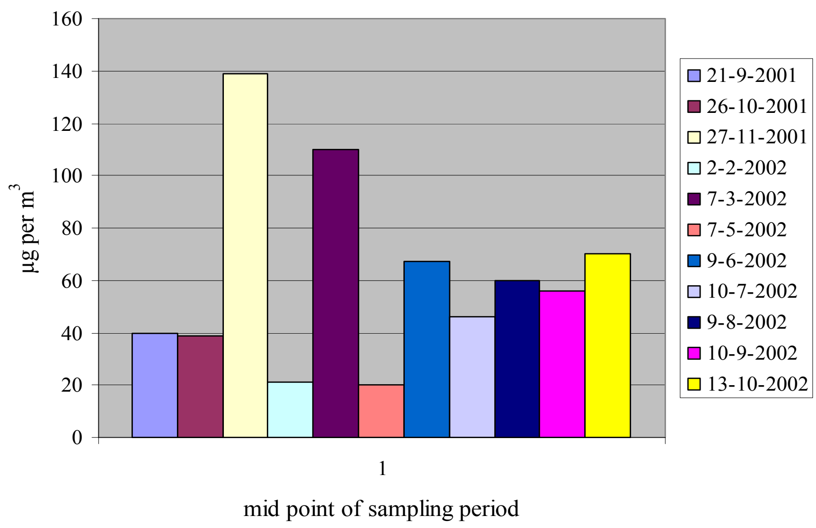


Figure 1. Dust load in FL01 chamber filter room at mid-point of sampling period

Figure 2. Dust load in former belt dryer working area at mid point of sampling period



6. SUMMARY OF THE CASE

The potential for significant exposure of workers in the TiO_2 chloride production process arises from the treatment of the acid chloride waste in which the natural radionuclides from the ore are concentrated. From the start of the production of TiO_2 pigment with the chloride process the potential for significant exposure of workers by inhalation of the MeOH dust had been recognised. Consequently, the dish drying system envisaged for drying of the filter cake was not installed. A belt dryer system, expected to produce a large grained dry residue on the basis of pilot tests, did not perform as expected. Therefore local exhaust provisions were installed at the bagging station. However dust production from the dryer still involved risks of significant discharges to the environment in case of malfunctioning of the venturi scrubber on the dryer exhaust. Instead of putting continued extensive efforts in containment of the dust the operator decided to significantly reduce risks from exposure to dust by avoiding drying at all at significant extra costs for disposal of the MeOH as chemical waste. Presently, potential exposure to dust arises only from the drying of spilled MeOH. A simple static air sampling system for monitoring build up of dust in working places has been in operation for many years and is regarded as effective for the purpose envisaged. Potential exposures at the front loading place for ore and at the warehouse were the trucks are loaded have not been assessed. It should be noted that although the activity concentrations in ores are about a factor of ten lower than in the solid MeOH, the dust concentrations are expected to be much higher. These were not however assessed at the time of this case study.

UK Case Study 1

1. OVERVIEW OF THE PROCESS

1.1 Type of Process

The case study concerns a UK factory that processes zircon to produce milled zirconium silicates. The basis of the process is the milling of zircon sand to reduce the particle size. Several steps may be required to progressively mill the material (depending on the final product) using both wet and dry techniques. This followed by careful grading to obtain a series of products with well-defined particle size distributions, which are then bagged and sold commercially.

There are many different uses for the products. Typical examples include:

precision steel castings and other foundry coatings (the product is used to form the moulds);

refractories (the material is resistant to very high temperatures and is used as a furnace lining);

ceramics (the finest grade products are used to produce opacity in glazes); and

glass in cathode ray tubes (the material is used as an additive to improve the properties of the glass, and to provide shielding against adventitious x-rays).

It is understood that similar processing is carried out at many factories in Europe and elsewhere.

1.2. Scale of the Process

The factory in this case study, processes large quantities of zircon sand per year, nearly all of which is converted into the final products (waste material is negligible). The factory is based around a single large processing facility, within which are housed the various (interconnected) pieces of industrial plant, such as milling and bagging machines. Separate buildings are provided for the bulk storage of the raw material and bagged products.

Much of the process is automated and a relatively small number of employees are required to operate the plant over the three working shifts per day (the plant operates continuously, except for planned shutdowns).

2. STEPS IN THE PROCESS

The raw material is imported into the UK by sea, and is transferred to the factory by lorries where it is transferred (via a closed system) into the raw material store. This case study is concerned only with the subsequent process at the factory, i.e:

Raw materials store

2.1 Transfer from raw materials store

- The zircon sand is moved using a large mechanical shovel. Batches to be processed are transferred onto the back of an open tractor trailer, which is then driven into the processing factory.
- This operation produces a lot of airborne dust, clearly visible to the naked eye. Although the sand is mostly composed of coarse particles, finer particles are present due to self-milling (the material is very hard and abrasive).
- The store is not fitted with forced ventilation or any other dust control system. Natural ventilation, via the (open) vehicle access door is, however, provided.
- This step requires only one worker, i.e. the operator of the mechanical shovel, who remains inside an enclosed cab.

Processing plant

NOTE: Although each of the following process steps is typically undertaken in a specific area or piece of plant, they all occur within the same overall area, often at the same time. Consequently, in terms of exposures from dust inhalation, each step may be contributing to the overall exposure levels.

- The general ventilation of the processing plant is based on roof-mounted fans and good natural ventilation (via large open doors). However, for most operations, the emphasis is on installed local containment and local exhaust ventilation (LEV) systems to control airborne dust.

- Transfer of process materials between the various pieces of plant is, with very few exceptions by mechanical means, such as automated conveyors. The systems used for mechanical transfer of dry materials are all enclosed, i.e. to restrict the resuspension of dust into the workplace air.

2.2 Receipt of raw materials into processing plant

- The sand is tipped out of the trailer into storage bays in the processing factory. This operation briefly produces large amounts of airborne dust. The sand is introduced into the milling plant by an enclosed conveyor.
- This step requires only one worker, i.e. the operator of the tractor/trailer who is present throughout. Other workers in the process plant may also be nearby.

2.3. Calcining

- This operation is not considered in any detail in this case study.

2.4. Dry milling

- A series of enclosed rotating ball mills are used to progressively grind the material (using a grinding media) into smaller particles. Transfer of material to/from mills is via enclosed mechanical systems.
- Material in the mill is effectively contained, and LEV systems are installed at the feed and discharge points to control dust. However, total containment is not usually practicable, and some escape of dust does occur at these positions.
- This is essentially an automated operation that takes place unattended, although process workers may be in the vicinity at some time.

2.5 Wet milling

- As with dry milling, the material being processed is well contained, and the operation is mostly automated.
- Enclosed transfer systems are normally used to feed the mills. However, occasionally it is necessary to manually feed some dry materials into the mills. This has been identified as a source of airborne dust (see later).
- The material is milled with water, thereafter substantially reducing the potential for airborne dust. Because of this, however, there are less rigorous dust containment systems for material transfer, either as slurry or a wet “cake”. Consequently, splashes and spills can lead to the accumulation of material on nearby surfaces. Such material dries to form a solid layer; airborne dust can subsequently be generated through the abrasion or vibration of the dry material.

2.6. Product bagging

- The finished product is held in hoppers awaiting final packaging. Usually products are packed in 25 kg paper sacks, although 1 tonne woven plastic bulk bags are also used.
- Product bagging is done at dedicated bagging stations. Some of these are entirely automated, but semi-automated bagging was the norm during this case study. This involves a single worker operating the bagging machine. The machine consists of a product delivery mechanism inside a partial enclosure fitted with a LEV system.
- The operator places the neck of an empty bag over the material delivery tube. The bag is then filled automatically with the appropriate product. The operator detaches the bag neck and folds it to seal in the product. He then lifts the bag out of the enclosure, verifies the weight on an adjacent balance, and then stacks the bag on a pallet. Full pallets are shrink-wrapped in polythene before being transferred to the product store.

2.7. Other activities – area cleaning

- There is a continuous cleaning programme that include the use of a mechanical “roadsweeper” machine, as well as brushes and shovels to clean the floors and other workplace surfaces. All the plant operators undertake this at various times, as required.

- In addition, more rigorous cleaning of all accessible surfaces in the processing plant is undertaken at periodic intervals.

2.8. Other activities – plant maintenance

- As stated earlier, the process materials are abrasive and aggressively wear away the plant. Consequently, a rolling programme of plant inspection, repair, refurbishment and replacement is in place. At any one time, at least one part of the plant machinery is expected to be undergoing some type of maintenance activities.
- Routine maintenance involves small groups of workers (including, as necessary, sub-contractors) for periods extending between a few hours to a few days. Major plant refurbishment or replacement may take several weeks to complete. Entry into containment systems is often necessary and the work typically involves significant amounts of airborne dust.

3. RADIOACTIVITY IN THE PROCESS

The zircon sand contains both the uranium-238 and thorium-232 decay series in secular equilibrium[1]. The activity concentrations of individual radionuclides are as follows:

Uranium-238 decay series:	3 Bq g^{-1}
Thorium-232 decay series:	0.7 Bq^{-1}

The raw material and products all contain essentially the same radionuclide activity concentrations. The enhancement of activity concentrations in certain parts of the process (e.g. in plant scales or waste materials) is not an issue in this case.

4. WORKPLACE PROBLEMS/CHARACTERISTICS

It is worth noting that when the plant was originally designed, the process materials were essentially regarded as non-hazardous. Consequently, the control of airborne dust was not given the priority that it has today. As the plant has evolved, increasingly sophisticated engineering controls to minimise airborne dust have been installed. The situation now is that, where practicable, materials are transferred and processed within closed mechanical systems.

With regard to this study, the main issues are as follows:

- The process involves the handling of finely divided material on an industrial scale using moving and vibrating machinery. As such it is an inherently dusty process.
- The total containment of process materials (i.e. to prevent escape into the working atmosphere) is not practicable in an operation of this scale. Certain parts of the process do provide effective containment, although this is not always guaranteed (e.g. because of plant failure and/or wear). However, in some parts of the process, containment is either partial or non-existent.
- There are several steps in the process, most of which take place within a single large structure (the processing plant). Consequently, it can be difficult to identify and quantify discreet sources of dust.
- Except during planned shutdowns, production is continuous, although different parts of the plant will be operating at any one time. Several direct sources of dust are expected to present at any one time. Consequently, elevated levels of airborne dust are expected whenever the plant is operating. However, the contributions from the different individual dust sources will vary over time.
- Deposits of dust accumulate on horizontal surfaces in the workplace, in some cases in substantial amounts. Resuspension of this material due to mechanical (e.g. vibrating plant) or

---

[1] Uranium-235 is also present in accordance with the isotopic composition of natural uranium. Daughter radionuclides in the U-235 decay series are also present in secular equilibrium.

human actions (e.g. walking across dusty floors, and from cleaning/maintenance activities) is also a source of airborne dust.

- Occupancy by individual workers in areas where airborne dust is present is high; in most cases 100% occupancy (2000 hours per year) is not unrealistic. Individual workers normally undertake a range of tasks in any one shift, and only occupy specific locations during certain tasks (e.g. product bagging).

From the above, it is concluded that there are many sources (both direct and indirect) of airborne dust in the processing plant. The various dust sources overlap and their relative contributions to the total dust level are constantly changing. Airborne dust is present in process plant throughout the working year, although the levels will vary from location to location, and over time.

Other factors that may also be relevant are:

- Zircon is a high-density material, and this will encourage the settlement of airborne dust under gravity. However, it is also a very hard, abrasive material, and this increases the likelihood of dust leaks due to wear and tear on process machinery.
- There is very limited information on the particle size distribution of airborne dust in the workplace. The raw material zircon sand, mostly has a relatively coarse particle size (mostly well above 100 μm diameter) although some much finer particles are present due to self-milling, as stated earlier. The process is dedicated to producing much smaller particle sizes (a few μm diameter or less). Consequently, a wide range of particle sizes might be present in any airborne dust. Analysis of two air sample filters taken specifically for this project indicated a particle AMAD close to 10 μm.

5. EXPOSURE MONITORING TECHNIQUES

Two monitoring programmes have been used in this workplace. The first is a well-established programme of periodic personal air sampling to assess dust levels in the factory. The second consists of a series of real-time dust measurements undertaken specifically for this project. Both types of programme are explained in more detail below.

5.1 Routine air sampling programme with Personal Air Samplers (PAS)

5.1.1 Monitoring strategy and method

This monitoring programme has been in operation for at least 13 years (archive results are available from 1989 onwards). The monitoring was introduced in response to concerns about the (non-radiological) hazards to persons in dusty workplaces. The monitoring method for such hazards is specified in guidance issued by the UK regulatory authorities (ref), and the monitoring programme adopted by the factory closely follows this guidance. Because of this, alternative types of monitoring for internal exposures (e.g. biological monitoring) have never been considered.

The basic characteristics of the monitoring programme are listed below.

- The (gravimetric) airborne dust level is measured, in terms of mg m^{-3}.
- Measurements are made using personal air samplers (PAS) to assess “total” dust levels (in practice, samplers assess “inhalable” dust and, by using a size-selective “cylcone” sampling head, “respirable” dust levels may also be determined). Sampling is typically performed over an 8 hour working shift. For specific operations, shorter sampling times may be used (typically 1 hour).
- To obtain additional information, PASs are sometimes placed in specific locations (i.e. operating as static air samplers (SAS)). Sampling is typically over a 4 hour period.
- Air sampling is carried out approximately 4 days each month. A higher frequency is used for specific investigations, for example after changes to the plant or during certain maintenance operations.
- The filters used in the PAS are carefully weighed before and after sampling to accurately determine the weight of dust collected. This is combined with the sampler air flow and sampling time to determine the airborne dust loading. Annual calibrations are performed to verify the airflow of each PAS.

5.1.2 Monitoring results and ALARA

It worth repeating that the monitoring programme was not originally introduced for the purposes of radiological protection. Instead, the driving force was industrial hygiene in which compliance with a recommended “nuisance dust” limit, rather than optimising exposures, was the main goal. Monitoring using PASs was effectively pre-chosen by the UK regulatory guidance. Only recently has radiological protection (and thus ALARA) been a consideration.

The basic measurement results are in terms of the gravimetric airborne dust levels (in mg m^{-3}) averaged over the sampling period (between 1 and 8 hours). Typically, up to 100 measurement results are obtained each year.

Since 1999, the results of the routine PAS monitoring have also been used to estimate radiation doses to workers from inhalation of dust. An example of this is shown in Appendix 1. The results indicate that annual committed effective dose received by workers from inhalation of airborne dust are of the order of 0.5 mSv per year. This value is based on assumptions about “average” working conditions and exposure patterns. Dust levels measured during certain procedures are approximately 5 times the average value. Consequently, certain workers may receive higher exposures.

Although very important, estimated doses are only the starting point for implementing the ALARA principle. Ideally, monitoring programmes should also provide more detailed information, i.e. to identify the sources and characterise the pattern of exposures. For example, in this case an analysis of the monitoring data indicates that:

- *all activities* in the processing plant involve some exposure to airborne dust. However, certain areas/tasks show consistently higher results;
- there is some variation in the measured dust levels when different workers undertake similar tasks; and
- the dust levels measured in the processing plant over several years show no obvious trends upwards or downwards (although the levels in certain areas may have changed).

In practice, only limited ALARA-type analysis of the monitoring results has been undertaken. One reason for this is that estimated annual doses to workers are relatively low. However, another reason is that although the results can suggest certain problems exist (e.g. higher dust levels at a certain step in the process), they cannot pinpoint the source of the problem (e.g. the specific source of airborne dust).

This case study has identified a number of advantages and limitations of the monitoring arrangements. For example:

- The use of an existing monitoring programme is a benefit in itself. Employees are already familiar with the programme and this helps make the best use of the available monitoring resources (i.e. by addressing both industrial hygiene and radiation protection issues).
- Employee work patterns are varied and local resuspension of dust due to the actions of workers is expected to be an issue. PASs are considered much more suitable than SASs for estimating individual exposures.
- The sensitivity of the dust measurement technique is very good. All the results obtained have been above the limit of detection, which is broadly equivalent to a committed effective dose of 0.1 microsievert for an 8-hour sampling period. The relatively low flow-rate of PASs (typically 2 litres per minute) is not, therefore a problem in this case. Also, the extended counting times required for radiometric measurements (i.e. to increase the sensitivity of the measurement) are not an issue with gravimetric assessment techniques.
- The monitoring strategy relies on representative sampling, and this always imposes some limitations on the interpretation of the results. In this case, PASs results obtained over several years indicate that dust levels during routine processing steps have not varied greatly (e.g. less than a factor of 2 or 3). In these cases, it may be reasonable to assume that the sample results are representative. In other cases, especially non-routine work, individual dust sample results can

vary by up to a factor of 10. This raises questions about whether the frequency of personal air sampling is sufficient to properly assess exposures.

- Air sampling determines the *average* dust level during the sample period and does not provide details such as when and where dust levels peak during the work. This has been partially addressed by short-duration sampling (1 hour is the practical minimum) during specific tasks.
- The measurements provide only a broad indication of the variation in dust levels between different workplace locations. More specific information has been obtained by placing PASs in static locations; even then it has still not been possible to pinpoint specific dust sources.
- Measurements do not provide instantaneous results. The air filter needs to be "conditioned" at a set temperature and humidity to ensure accurate weighing. Typically, results are only available 1-2 days after the sample was taken.
- The number of measurements is limited by the number of PASs available; in practice, only a few measurements can be made per day. To analyse results for trends, etc., results obtained over a period of several months or even years are required.
- Only very limited information about the particle size distribution is provided (basically an indication of the inhalable: respirable dust ratio).

5.2 Real-time air sampling

5.2.1 Monitoring strategy and method

This monitoring was specifically arranged for this project for comparison with the existing PAS monitoring programme described above. Brief details of the monitoring equipment and method are given below.

- A commercially available portable real-time dust sampler was used. The equipment sucks workplace air into a sample chamber where the dust loading (in mg m^{-3}) is determined using a light-scattering technique. Size-specific dust fractions (total, inhalable, thoracic and respirable) can be measured, according to the user-selected sampler settings.
- Various types of dust measurements were made over the course of 2 consecutive working 2 days. These included:
  - spot measurements at key locations throughout the plant to assess the space-variation in total dust levels. The same measurements were taken on both days;
  - repeated measurements at specific locations, and during certain operations, to assess the time-variation in total dust levels; and
  - measurements of the inhalable, thoracic and respirable dust levels at key locations within the processing plant to investigate the possible variations in dust particle size distribution.

5.2.2 Monitoring results and ALARA

Examples of the results obtained are shown in Appendix 2. The results obtained indicated that the range of measured dust levels in the workplace (in mg m^{-3}) was consistent with the results obtained from PASs. However, the real-time monitoring results provided a significant amount of new information and a number of issues were immediately raised, for example:

- The dust levels on Day 2 were generally lower than on Day 1. One possible reason for this was a dust leak observed from material transfer pipes at a height of about 10 metres.
- On both days there were substantial levels of airborne dust at the end one of the dry ball mills. From the measurements, it was clear that the source of dust was the exhaust air from the mill motor housing.
- The mechanical "roadsweeper" used to clean the floors was clearly resuspending significant amounts of dust into the air.
- A number of especially dusty tasks were identified over the two days, for example sweeping up, plant maintenance, etc.

As a result of the above findings, the following preventative measures were taken within the next few days:

- The dust leak from the material transfer pipe was repaired before the measurements on Day 2. Although there may be other reasons for the difference in dust levels, this particular source was rapidly controlled at practically no extra cost.

- An action plan for controlling the dust in the exhaust air from the mill motor was drawn up, and the installation of an air filtration system has been selected as the most suitable protection option.
- The vacuum system on the sweeper was inspected, found to be faulty and promptly repaired.
- The dusty tasks identified were reviewed and in most cases, it was considered impractical to control the dust at source during these activities. Consequently, greater emphasis has since been placed on wearing respiratory protective equipment (disposable dust masks) during such tasks.

It is considered that the above clearly indicates the significant potential of real-time dust monitoring in implementing ALARA. The general benefits found in this case are summarised below.

- A striking difference compared with the PAS monitoring programme was the number of measurement results obtained. Over 200 measurements were made in 2 days; the PAS programme would require about 2 years to produce the same number of results.
- An instant indication of the pattern in airborne dust levels was provided. In radiation protection terms, this was considered more similar to using a survey meter, whereas PAS is more similar to the use of a passive personal dosemeter. This provides invaluable feedback to the person undertaking the monitoring.
- It was possible to pinpoint individual dust sources. Although some of these sources could perhaps have been inferred from an analysis of the PAS monitoring results, this would have taken a long time. In addition, certain dust sources (e.g. due to leaks from the plant) were found that were hitherto unknown.
- The effectiveness of plant modifications could be assessed immediately, and adjustments made on the spot.

In this study, little use was made of the ability to measure different particle size fractions. Some results are given in Appendix 2 and, while there would appear to be some differences in the particle size distributions at different locations, these differences are not obviously associated with the various processing steps.

5.3 DISCUSSION AND CONCLUSIONS

Strengths and weaknesses of the two monitoring strategies have been described above. In terms of the implementation of the ALARA principle, the main issues in this case are:

- Airborne dust arises from a number of sources both direct (from the plant) and indirect (from resuspension) and is ever-present in the workplace in varying amounts. Although occupancy is almost continuous, individual work patterns are very varied and for most routine activities, personal air sampling (PAS) is considered the best means of determining individual exposures from dust inhalation.
- The existing PAS monitoring programme, originally introduced for industrial hygiene reasons (i.e. measuring dust levels in mg m^{-3}) is also suitable for estimating occupational radiation exposures from dust inhalation during routine work. During certain (non-routine) activities there is a greater variation in airborne dust levels and it is is suggested that a higher frequency of monitoring may be necessary to properly characterise the exposures arising.
- Real-time sampling was not used in this case study to estimate worker doses, although it is considered that this would be appropriate in certain circumstances. For example, it would be a useful means of rapidly determining that doses are low. Also, it could be used to provide additional information (i.e. to the PAS monitoring results) in the case of non-routine activities where dust levels are rapidly changing. In other cases, it is more generally better to sample over several hours to assess doses; PAS is still the most practical way of achieving this.
- Air sampling can also provide other information, such as the variation in dust levels between different locations and tasks, and trends over long timescales. However, in practice it cannot pinpoint specific dust sources.

- Detailed information on the variation in dust levels (with location/time) is required to identify problems. It is also very useful when options to reduce exposures are being considered. This information cannot be provided by PAS, but is available from real-time dust monitoring.
- Real-time monitoring provides an instant indication of the dust levels. This provides valuable feedback that enables dust sources and patterns to be rapidly identified. An unexpected benefit of obtaining results quickly was that the focus on ALARA was maintained, and remedial actions were quickly explored and implemented. Even though air sampling can provide results within a few days, it was felt that this was sufficient delay to allow the focus to shift to other issues.
- Real-time sampling allows a much larger number of measurements than the PAS sampling programme. Although not all the results are of equal value, it is concluded that the scope for analysing monitoring results for trends and patterns is vastly increased.
- Particle size distributions have not been actively considered in this case study. Particle size can significantly affect the estimated doses, and should be determined, if only approximately, in workplace dust. In terms of implementing ALARA (i.e. reducing doses) in practice, however, there is little evidence that particle size is an important measurement parameter.
- Finally, in this case study, the airborne contaminant consists of a low specific activity material with a consistent activity concentration. As such, it is recognised that gravimetric air sampling techniques are ideally suited. This may not be the case in other workplaces where the use of real-time samplers, as described in this study, may not be appropriate.

FOOTNOTE

Since completing the case study, personal air sampling campaigns have shown an all-round reduction in the dust levels in the workplace, this is considered to be the result of the protection measures described in section 5.2.2. Results are only preliminary, but reductions of the order of 25 to 50% have been observed.

APPENDIX 1 – Estimation of annual radiation doses from PAS monitoring results.

An example of how the PAS monitoring programme in case study UK1 is used to estimate committed effective doses to workers from inhalation of dust is given below.

Intakes due to inhalation are estimated from personal air sampling data supplied by the Company. This data is from samples taken in various parts of the plant during different operations. The samples were typically taken over a full 8 hour working shift.

All the results from samples taken during normal "average" work activities are in the range 0.4 to 1.5 mg m^{-3} total dust. Results from a number of other activities also fall within this range, such that the results for all **routine activities** may be summarised as follows:

- Range of results: 0.4 to 1.5 mg m^{-3}
- Average result: 1.0 mg m^{-3}
- Standard deviation: 0.3 mg m^{-3}

Higher results have been obtained for certain **dusty operations**, as follows:

Location/comments	Total dust (mg^{-3})
Bag packing station (unusually high dust levels)	1.9 and 2.7
Dust observed cascading from gantries	3.6
Dust observed leaking from bags	1.9
Manual loading of wet mill	5.8 and 9.0
Maintenance inside mill	2.0 and 2.8
Mechanical Shovel (loading hoppers with sand)	1.9

The manual loading of the wet mill appears to be a particularly dust operation and will be given separate consideration in this assessment (assuming an average value of 8 mg m^{-3}). For **all other dusty operations**, the data may be summarised as follows:

- Range of results: 1.9 to 3.6 mg m^{-3}
- Average result: 2.5 mg m^{-3}
- Standard deviation: 0.6 mg m^{-3}

A breathing rate of 1.2 m^3 h^{-1} (ICRP reference man, "light activity") and no respiratory protective equipment (RPE) are assumed. For the purposes of this assessment, the following work and exposure patterns have been assumed:

Work activity	Annual exposure time (hours)	Average dust level (mg m^{-3})	Dust inhaled (g y^{-1})
Normal operations	1500	1.0	1.8
Dusty operations	400	2.5	1.2
Slow Mills loading	100	8	1.0
TOTAL	**2000**	1.65	**4.0**

It is assumed that all the airborne dust is zircon sand. The following activity concentrations, based on the results of samples analysed at NRPB, have been used to estimate the activity inhaled:

- Uranium-238 plus daughters in equilibrium: 3 Bq g^{-1}
- Thorium-232 plus daughters in equilibrium: 0.7 Bq g^{-1}

To estimate the internal radiation exposure of persons, dose coefficients for the most significant radionuclides have been taken from ICRP Publication 68. Only whole body radiation exposure has been considered (individual organ doses have not been calculated but are not expected to be limiting). Zircon sand is an insoluble material and the dose coefficients are, therefore, based on lung classification S (or M where values for S are not available) and the lowest gut transfer factor (f_1). The relevant data are given below.

Radionuclide	**Committed effective dose equivalent Per unit intake (Sv Bq^{-1})**	
	Ingestion[2]	**Inhalation**
Thorium-232	$9.2\ 10^{-8}$	$1.2\ 10^{-5}$
Radium-228	$6.7\ 10^{-7}$	$1.7\ 10^{-6}$
Thorium-228	$3.5\ 10^{-8}$	$2.5\ 10^{-5}$
Radium-224	$6.5\ 10^{-8}$	$2.4\ 10^{-6}$
Uranium-238	$7.6\ 10^{-9}$	$5.7\ 10^{-6}$
Uranium-234	$8.3\ 10^{-9}$	$6.8\ 10^{-6}$
Thorium-230	$8.7\ 10^{-8}$	$7.2\ 10^{-6}$
Radium-226	$2.8\ 10^{-7}$	$2.2\ 10^{-6}$
Lead-210	$6.8\ 10^{-7}$	$1.1\ 10^{-6}$
Polonium-210	$2.4\ 10^{-7}$	$2.2\ 10^{-6}$
Uranium-235	$8.3\ 10^{-9}$	$6.1\ 10^{-6}$
Protactinium-231	$7.1\ 10^{-7}$	$1.7\ 10^{-5}$
Actinium-227	$1.1\ 10^{-6}$	$4.7\ 10^{-5}$
Thorium-227	$8.4\ 10^{-9}$	$7.6\ 10^{-6}$

Using the above methodology, the estimated annual dose received by employees from inhalation of dust is **0.5 mSv**.

---

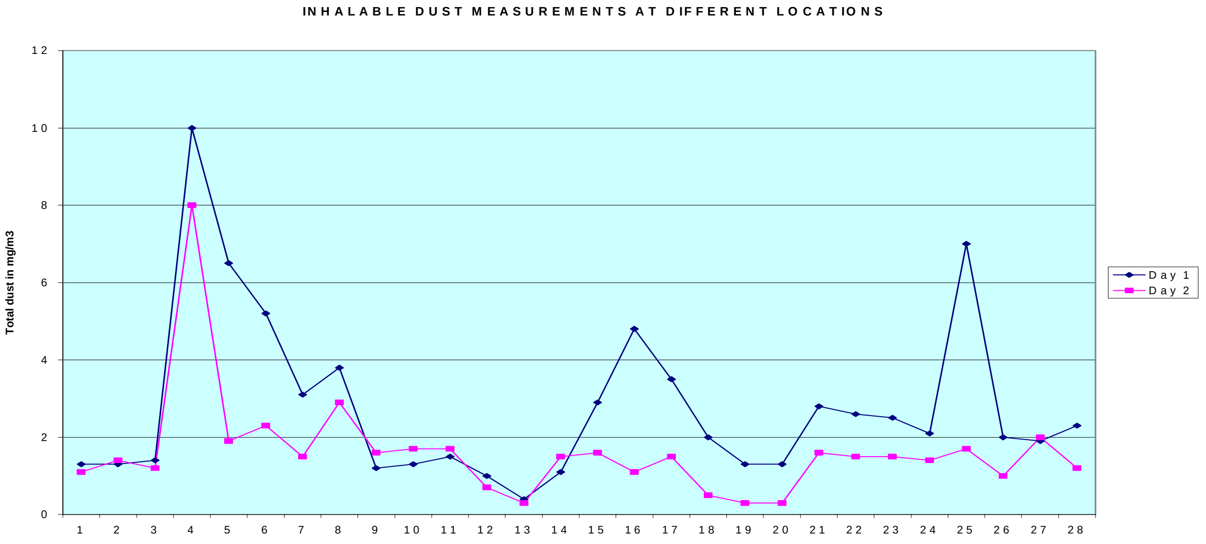
[2] Intakes due to ingestion cannot be assessed by air sampling and are, in any case, considered impossible to accurately quantify. To estimate the significance of this exposure pathway it is assumed (in line with previous generic assessments undertaken by NRPB) that 10 mg of material is inadvertently ingested each working day. Combining this with the measured activity concentrations, and the dose coefficients above gives an estimated annual committed effective dose of **0.01 mSv**.

Appendix 2 – Example of results obtained from real-time dust monitoring

SUMMARY OF RESULTS OBTAINED AT VARIOUS LOCATIONS

The following results are all from short-duration sampling, typically of the order of 10 minutes at each location.

LOCATION	DESCRIPTION	INHALABLE DUST (mg/m3)	
	Area descriptions removed prior to publication	Day 1	Day 2
1		1.3	1.1
2		1.3	1.4
3		1.4	1.2
4		10	8
5		6.5	1.9
6		5.2	2.3
7		3.1	1.5
8		3.8	2.9
9		1.2	1.6
10		1.3	1.7
11		1.5	1.7
12		1	0.7
13		0.4	0.3
14		1.1	1.5
15		2.9	1.6
16		4.8	1.1
17		3.5	1.5
18		2	0.5
19		1.3	0.3
20		1.3	0.3
21		2.8	1.6
22		2.6	1.5
23		2.5	1.5
24		2.1	1.4
29		7	1.7
30		2	1
31		1.9	2
32		2.3	1.2



UK1 Inhalable dust measurement results for DAY 1 displayed by workplace location

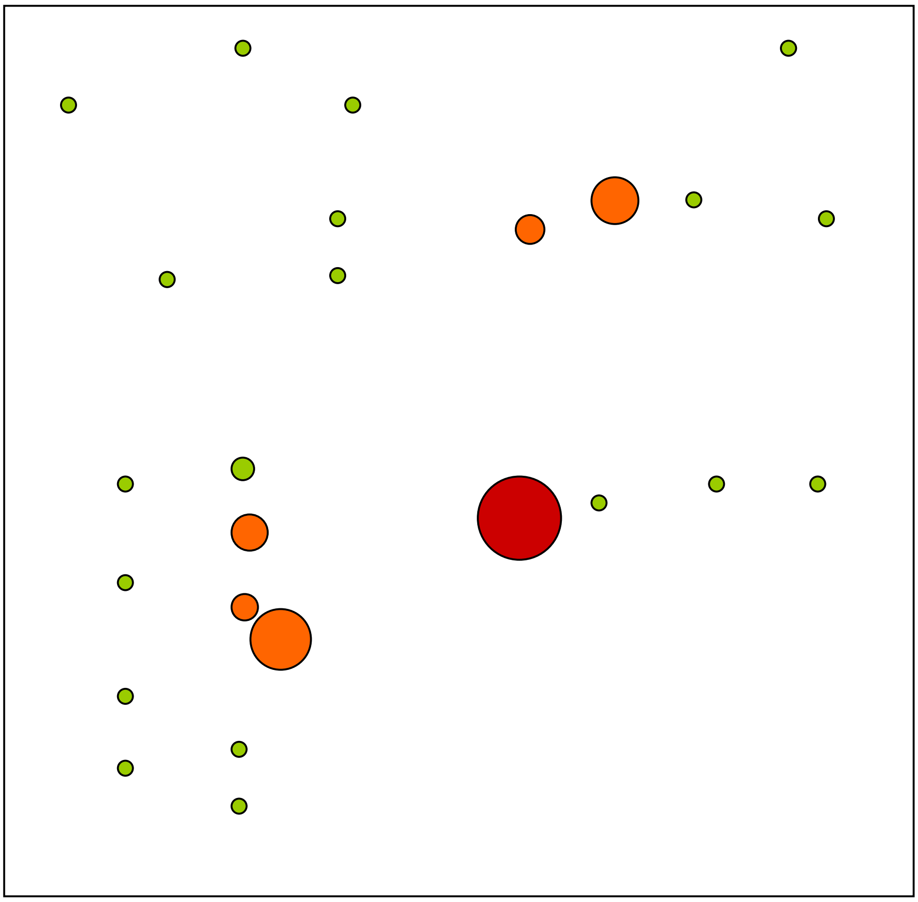
Note: The results were originally superimposed on a detailed plan of the works. This plan has been removed prior to publication.

Key:

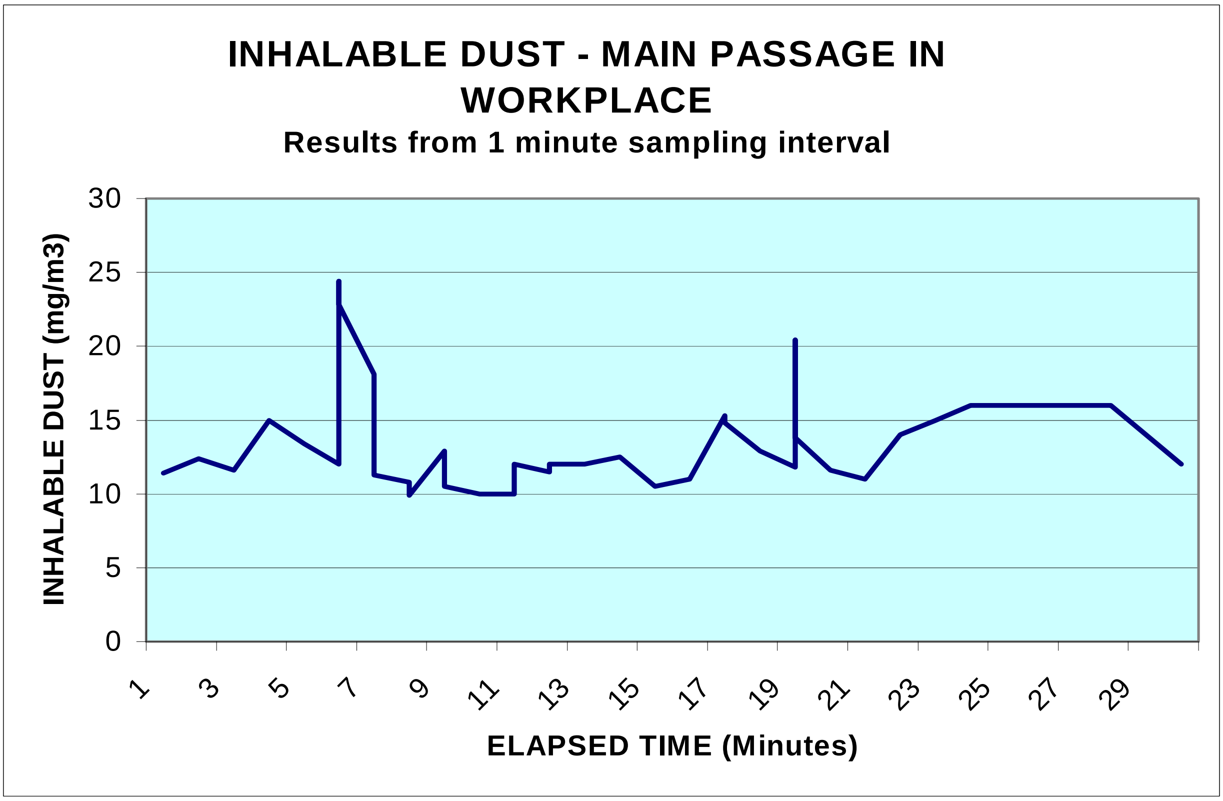
🟢 Up to 3 mg m^{-3}

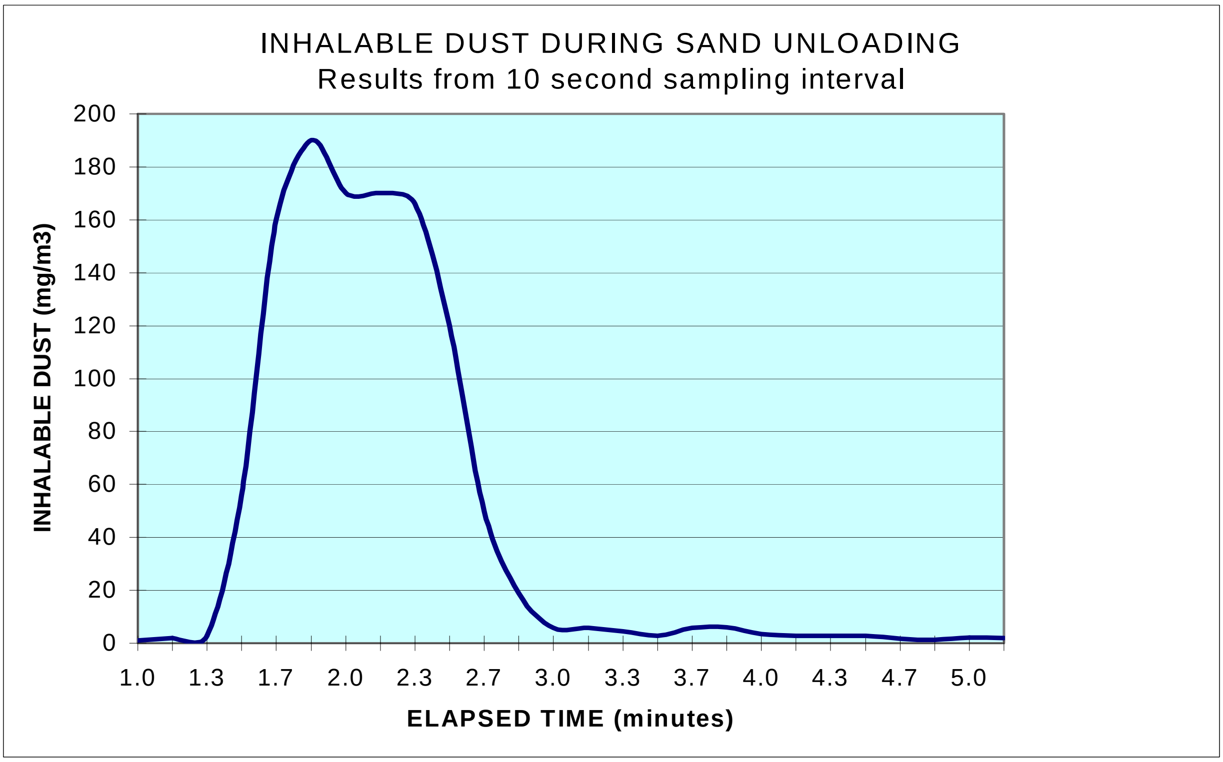
🟠 3 – 10 mg m^{-3} (diameter proportional to dust level)

🔴 Above 10 mg m^{-3} (diameter proportional to dust level)



TIME-PROFILE MEASUREMENTS



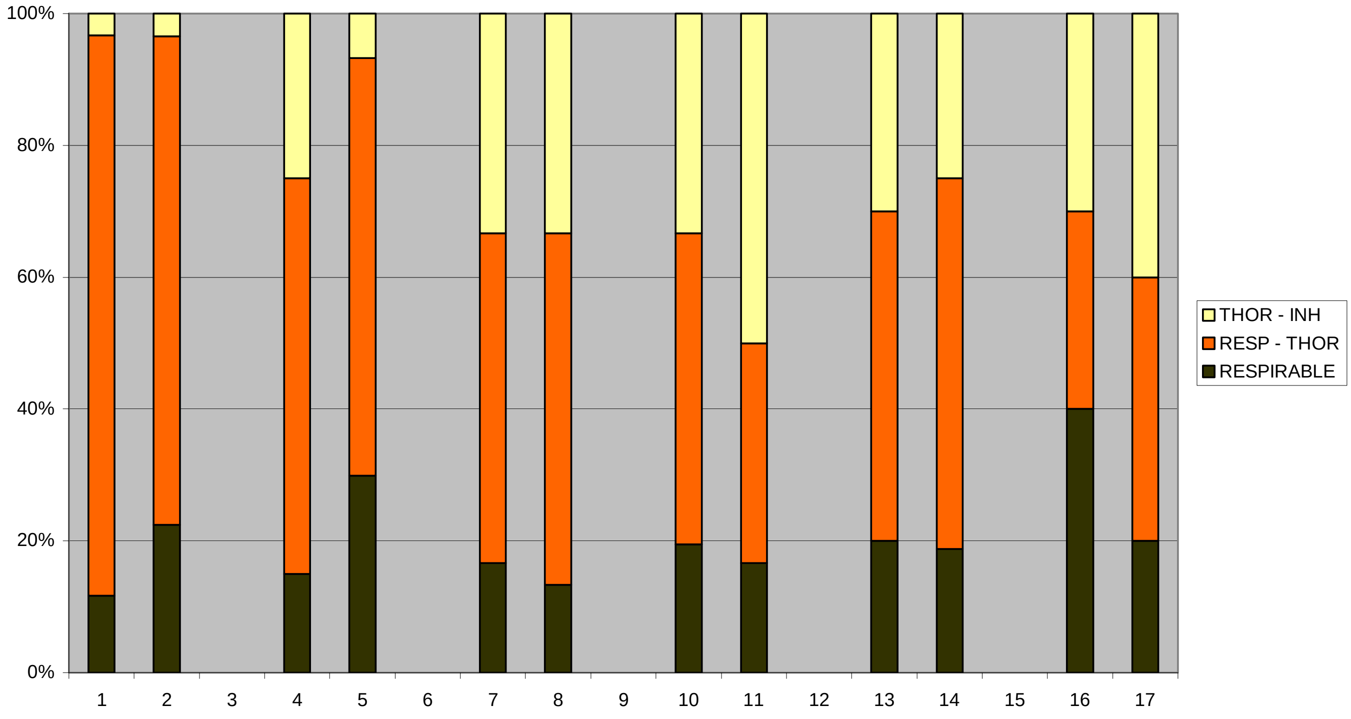


MEASUREMENTS OF DIFFERENT PARTICLE SIZE FRACTIONS

The following results were based on typically a 10 minute sampling period.

LOCATION	**INHALABLE**	**THORACIC**	**RESPIRABLE**
In main processing plant. Details removed prior to publication.	6	5.8	0.7
	5.8	5.6	1.3
	4	3	0.6
	3.55	3.31	1.06
	3	2	0.5
	1.5	1	0.2
	1.8	1.2	0.35
	1.2	0.6	0.2
	1	0.7	0.2
	0.8	0.6	0.15
Outdoors 1	0.1	0.07	0.04
	0.1	0.06	0.02

RELATIVE CONTRIBUTION OF DIFFERENT SIZE FRACTIONS



UK CASE STUDY 2

1. OVERVIEW OF THE PROCESS

1.1. Type of process

This case study has been carried out in conjunction with a UK chemical plant that processes natural ores to produce high purity titanium dioxide (TiO_2), which is used primarily in the production of pigments. Titanium dioxide pigments are most effective in imparting whiteness to paints, plastics and paper. This is due to their exceedingly high reflectance. Another important property of titanium dioxide is its high refractive index, which gives the potential for producing opacity or hiding power far greater than that of other commonly produced white pigments. Titanium dioxide is also the most stable white pigmentary compound known and for all practical purposes is chemically inert. This chemical stability contributes to colour stability, a very important property in many applications. Many plastics are degraded by ultraviolet light when they are exposed outdoors. Titanium dioxide absorbs this radiation, which enables the production of paints and plastics that have exceptional weather resistance. As a consequence of the above properties titanium dioxide it utilised in the production of paints, plastics, paper, food colouring, cosmetics as well as pharmaceutical products.

The ore feedstocks for the process comprise mainly rutile and beneficiate. Rutile is naturally occurring titanium dioxide. It can vary in colour from brown to reddish black and its major impurities are compounds of iron. It normally has a TiO_2 content in the order of 95%. The second feedstock is beneficiate (or beneficiated ilmenite) in which natural ilmenite ore, which contains 45-60% TiO_2, is treated by physical or chemical means to increase its TiO_2 content. The above products are mined and produced around the world and transported to the UK by bulk cargo ship.

In the plant the feedstock ores are processed by the well established “Chloride Process”, which is described below. The process depends on the following chemical reactions:

$$TiO_2\text{ (impure)} + 2\,Cl_2 + C \rightarrow TiCl_4 + CO_2 \quad (1)$$

$$TiCl_4 + O_2 \rightarrow TiO_2\text{ (pure)} + 2Cl_2 \quad (2)$$

The dry ore is fed into a large chlorinator reactor vessel in which it forms a bed, fluidised by an air stream. Heat is applied and the temperature is increased to approximately 650 ^{o}C. Crushed coke is fed in on top of the ore, where it ignites, increasing the temperature to 960 ^{o}C and enabling the initial heat source to be removed. When the required temperature is attained the air stream is replaced by chlorine gas and reaction (1) above occurs to form titanium tetrachloride vapour. As the reaction proceeds the bed is continuously charged with ore and coke to keep its height constant. The reaction is highly exothermic and it is necessary to maintain constant temperature by cooling the reacting mass.

On leaving the chlorinator the gas stream is cooled and any solid matter is precipitated out. This precipitated material is then passed to a filter press facility where it is neutralised by the addition of calcium hydroxide and then de-watered prior to disposal. The titanium tetrachloride is then further cooled and distilled to produce a pure product, suitable for oxidation to titanium dioxide. To produce this oxidation successfully it is then necessary to bring the reagent gases together at a suitable temperature and to provide suitable nuclei on which the pigment particles may form. The heat evolved when $TiCl_4$ is burned in oxygen (reaction (2) above) is not sufficient to raise the temperature of the reactants to reaction temperature and to maintain that temperature. The oxygen is, therefore, heated by an electrical discharge and introduced into the reaction system by a plasma flame. Nucleation of the reacting gases is necessary to promote the formation of pigmentary particles. This is achieved by the combustion of hydrocarbons as part of the reaction process.

The gases carrying the fine TiO_2 pigment from the reactor must be cooled rapidly to prevent excessive growth of pigment particles. The pigment is collected by cyclone filters and may be calcined to remove any traces of chlorine and to control crystal size. The final product is then milled to break down oversize particles. Depending on the intended final use of the pigment it may then be coated by a variety of processes prior to drying and bagging ready for despatch.

1.2. Scale of the process

The process utilises approximately 20 000 tonnes per annum of rutile and 70 000 tonnes per annum of beneficiate, the majority of which is converted into titanium dioxide with relatively small quantities of waste material. The plant is based around two new modern ICON (Integrated Chlorination Oxidation) systems with supporting plants for coating and bagging operations. Operation of the plant is on the whole automatic requiring only a few operatives for maintenance duties and supervising the unloading of the ores.

2. STEPS IN THE PROCESS

The ores are imported into the UK by sea being landed at Hartlepool docks. The ores are then transferred from the ship by lorry to a dockside warehouse for storage. When the ore is required at the chemical plant it is transferred by lorry and tipped into the ore storage silos at the plant before being transferred by conveyor into the production process. These various stages are discussed in more detail below. Note that some photographs of the processing plant have been included in Appendix 2.

2.1. Transfer from ship to storage warehouse

The ores are removed from the ship by mechanical grab and loaded into a lorry located on the dockside. This lifting operation does, due to its nature, produce a lot of visible airborne dust, the amount of which will depend on the prevailing weather conditions at the time. An attempt is made, however, to control the generation of some dust by use of a containment system around the lorry to prevent a cloud of dust escaping when the dry ore is loaded in. The unloading area is not an area populated by any other workers other than the crane driver and lorry drivers. In addition the material is observed to quickly settle onto the ground as a result of its relatively high specific gravity (3.5–4.0). The lorry drivers remain in their cabs at all times during the ship unloading operations and are also required to wear dust masks at all times. Once the lorry is full it is driven the short distance to the storage warehouse where it is tipped. The tipped material is then moved around the warehouse by use of two mobile items of plant, an excavator and a loading shovel. The warehouse consists of a large open building with no dust extraction fitted. The tipping and subsequent movement of the ores around the warehouse generates visible amounts of airborne dust. The mobile plant operators sit inside sealed cabs but also wear disposable dust masks at all time when they are inside the warehouse. The lorry drivers remain in their cabs at all times except to release the tailgate on the lorries to facilitate tipping of the ores. The lorry drivers wear dust masks at all times when inside the warehouse (ARCO disposable NPF 50, APF 20).

2.2. Transfer to bulk storage silos at Huntsman Tioxide plant

The ore is transported from the warehouse to the main Huntsman Tioxide site by road on a regular basis. On arrival at the site the ore is tipped into a bunker with a loading conveyor installed underneath. The bunker is enclosed with lorries passing through a rubber “sectioned” curtain to allow access. The lorry is tipped slowly to eliminate as much airborne dust as possible. The tipped ore is fed from the bottom of the bunker by conveyor to the adjacent bulk storage silos. The tipping operation needs to manned at all times and employees working in this area wear air stream helmets (TORNADO T5 powered respirator (NPF 50, APF 20).

2.3. Transfer to ICON plant

Transfer to the chlorinator reactor vessel is by covered conveyor. This is an automatic process with ore leaving the bottom of the storage bunker being fed onto a transport conveyor. Transfer to the process is then carried out by a covered conveyor system.

2.4 ICON plant

Once the ore has entered the reaction process this is a sealed system, which is out in the open air. None of the naturally occurring radioactive material present in the ore feedstock appears in the final titanium dioxide product but is retained in the reactor bed or is removed with the precipitator solids during the clean up of the gases leaving the chlorinator. The precipitator solids, which are wet, are first neutralised by the addition of calcium hydroxide before being sent to a filter press facility for de-watering after which they are transferred to metal skips for subsequent disposal to landfill. This process is automatic and as the material remains wet at all times the generation of dust is minimal.

It is anticipated that the chlorinator reactor beds will need to be purged on an annual basis, which will generate some airborne dust albeit for a short period of time and in the open air.

3. RADIOACTIVITY IN THE PROCESS

The feedstock ores to the process contain both the uranium-238 and thorium-232 decay series in secular equilibrium. The typical activity concentrations of the individual radionuclides present are as follows:

Rutile

Uranium-238 series: 0.2 Bq/g
Thorium-232 series: 0.2 Bq/g

Beneficiate

Uranium-238 series: 0.2 Bq/g
Thorium-232 series: 0.7 Bq/g

The radionuclides present in the ores tend to concentrate in the material sent to the filter press and in the chlorinator reactor bed material. These waste products contain both the uranium-238 and thorium-232 decay series in secular equilibrium. The typical activity concentrations of the individual radionuclides present are as follows:

Filter press material:

Uranium-238 series: 0.2 Bq/g
Thorium-232 series: 1.0 Bq/g

Purged reactor bed material:

Uranium-238 series: 1.5 Bq/g
Thorium-232 series: 3.0 Bq/g

Radionuclide analysis of the final titanium dioxide product indicate that it contains only trace levels of radioactive material as indicated below:

Titanium dioxide product:

Uranium-238 series: 0.02 Bq/g
Thorium-232 series: 0.03 Bq/g

4. WORKPLACE PROBLEMS

Although the production process is large scale, there is limited potential for the generation of airborne dust as the majority of the process is based upon wet chemistry within closed vessels. The volatile or corrosive nature of the chemicals used in the process also means that the whole system is well sealed and maintained to prevent their release and therefore the release of any solid products. It is also noted that, by the nature of the chemistry of the process, the naturally occurring radioactive material is not carried with the final product but is contained in either the chlorinator reactor bed or the filter press waste material. This means that potentially dusty operations involving the final titanium dioxide product such as drying, crushing or packing do not pose a radiological hazard.

The main potential for the generation of airborne dust is at the front end of the process involving the unloading and subsequent transfer of the loose bulk ores. These operations can generate significant levels of airborne dust both directly and by re-suspension of previously deposited material. The specific density of the material is such, however, that it quickly settles out of the air.

In the warehouse it is not possible to fit any sort of dust extraction due to the scale of the operation and consequently any persons working inside the warehouse during ore unloading operations are obliged to wear respiratory protective equipment in the form of disposable dust masks. The work inside the warehouse is, however, intermittent and the time individual employees work in the area is logged with the maximum number of hours worked on ore movement operations being 750 per annum.

The ore discharge point at the main Greatham plant also generates significant quantities of airborne dust despite the engineering control measures in place. These controls take the form of an enclosure around the tipping process with a sectioned curtain to allow the lorry to discharge its load. In addition there is a dust extraction system fitted to remove dust generated within this enclosure. It was noted, however, that the enclosure was poorly sealed allowing visible clouds of airborne dust to escape. It was also reported that the dust extraction system is not subject to regular maintenance or testing. The discharge operation needs to be manned and such employees wear air stream helmets. Employees not directly supervising the unloading operation are kept away from the area. The work is intermittent in nature and is also rotated between a number of employees such that a typical employee spends on average 350 hours per year carrying out the work.

The waste stream from the dust cyclones to the filter press plant does contain radioactive material at a slightly elevated level compared to the feedstock material. The transfer of the material from the process to the filter press plant is however via enclosed pipe work and the material is wet. The purpose of this filter press plant is to de-water the material prior to disposal to landfill, although the final product is still wet and is, therefore, unlikely to generate airborne dust. The process itself is clean with no evidence of spilled product on the floor so that the possibility of the re-suspension of dust by human activities such as walking or maintenance work is minimal.

The operation by which the main reactor beds are purged will generate considerable quantities of airborne dust as the material is emptied out of the bottom of the reactor and dropped onto the ground. Subsequent handling operations to remove the material from site may also generate dust. The design of the new plant is such, however, that this operation is only planned to be carried out once per annum and it has not been possible to carry out dust monitoring as this has not yet been carried out. It is considered, however, that since the bed purge operation only takes a short period of time and the area where the material is dropped is in the open air then it should not pose a considerable radiological hazard to employees due to the inhalation of dust.

5. EXPOSURE MONITORING TECHNIQUES

Two monitoring programmes have been used to monitor the levels of airborne dust at the various workplaces. The first is a well-established programme of periodic air monitoring using personal sampling pumps. The second consists of a series of real time dust measurements undertaken specifically for this project. Both of these programmes are described in more detail below.

5.1. Routine air sampling with personal air sampling equipment

5.1.1. Monitoring strategy and method

The company has 10 off Gilair-3RC personal sampling pumps, which are used with either cyclone sampling heads to sample for respirable dust or with 7 hole total inhalable dust sampling heads. An ongoing programme of dust monitoring is currently carried out, primarily to comply with the requirement of UK legislation in respect of nuisance dust in the workplace (Control of Substances Hazardous to Health Regulations (COSHH)). These regulations specify the types of dust measurements to be carried out and the type of sampling equipment to be used. As a consequence the majority of measurements are carried out to determine total inhalable dust concentrations. The appropriate sampling flow rates for the personal sampling pumps are set before each sample and remeasured after the sampling period to ensure that the flow rate has not deviated by more than 5% of the original value. In addition the sampling pumps are sent away for calibration on an annual basis.

The airborne dust concentrations are determined gravimetrically, with the filters being weighed "in house" using a balance capable of weighing to 5 decimal places (0.01 mg). The filters are conditioned prior to use and following sampling by placing them in a humidity controlled cabinet for a period of 24 hours before being weighed. The volume of air sampled is calculated from the flow rate of the pump and the time of sampling, which is displayed by the pump.

5.1.2. Sampling results

As indicated above the dust sampling programme was initiated to comply with the requirements of COSHH. Since 1999, however, the results have been used to estimate radiation doses to employees exposed to airborne dust. An example calculation demonstrating how this is carried out is given in Appendix 1.

A significant number of dust monitoring results are carried out each year and a summary of the results is given below. The results reflect the monitoring that has been carried out since 1999.

RESULTS OF DUST SAMPLING WITH PERSONAL AIR SAMPLERS

Sampling Location and Work Activity	Average Annual Total Inhalable Dust (mg/m^3)[1]	Maximum Total Inhalable Dust (mg/m^3)[2]
Workers on ICON plant – maintenance and technicians	0.6	1.4
Workers on "Black End"[3] plant – maintenance and technicians	0.8	2.8
Ore offload area at storage warehouse – lorry and plant drivers	6.5	34.6

Notes:

1. Average values are based on a set of twelve (monthly) samples. Individual samples were typically taken over a period of 6 hours. The results, however, are reported in terms of an 8 hour time weighted average, in accordance with industrial hygiene monitoring conventions.
2. Represent the highest reported monthly sampling result, as described above.
3. Area of plant between storage silos and ICON plant.

5.2. Real time dust monitoring

5.2.1 Monitoring strategy and method

The monitoring was carried out using a portable hand held real time dust monitor which uses a laser beam scattering effect to determine the concentration of airborne dust particles in particular size ranges. For the measurements carried out the instrument was set to sample in accordance with the total inhalable dust particle size convention. The instrument gives an indication of the real time airborne dust concentration in mg/m^3 and also displays the average result over the period sampled.

The instrument has a good response to changes in dust levels and was used, therefore, as a tool to identify particularly dusty operations or sources of dust. The instrument was also used to carry out spot measurements of the levels of dust at various locations to assess the general levels of dust in the workplace. The instrument can also be used to determine the levels of dust during relatively short operations, which would not normally produce a mass of dust that could easily be collected and determined by gravimetric type samplers.

5.2.2. Monitoring results

Airborne dust measurements were made in the following locations:

i. Around the ore storage warehouse during periods when the ore was being loaded into the warehouse and as a comparison during periods when no such work was being carried out.
ii. Around the ore discharge point at the main Greatham works during ore unloading operations and during a period when ore was being removed from the storage bunker and loading into the process.
iii. Around the filter press facility.
iv. Around the bottom of the reactor vessels.
v. Bottom of reactor vessels (open air).

The results of the monitoring carried out are given below. The results indicate that the ore unloading operations generate significant amounts of airborne dust. Workplaces away from these areas such as the filter press and around the bottom of the reactor vessels were, by comparison, found to have very low levels of dust.

Measurements were made over a **10 minute** period except during lorry tipping, when measurements were made over the duration of the activity (**2 minutes**).

RESULTS OBTAINED FROM REAL TIME DUST MONITORING

i. Ore storage warehouse during ore unloading operations

Sample Description	Total Inhalable Dust (mg/m^3)
Excavator driver – average in cab during ore moving operations	6.0
Loading shovel driver – average in cab during ore moving operations	13.0
10 m from active tipping face – general levels in warehouse during ore moving operations	13.1
1 m inside warehouse from door – general levels in warehouse during ore moving operations	11.3
1 m outside door of warehouse – during ore moving operations	3.0
2 m from lorry tipping ore into warehouse – average level over tipping operations (machines not working)	6.2
Inside warehouse - no ore moving operations taking place	0.2
Outside warehouse – open air, no ore moving operations taking place	0.15

ii. Ore discharge point at main works during ore discharge by lorry

Sample Description	Total Inhalable Dust (mg/m^3)[1]
Operator's position – during lorry unloading operation (next to hopper)	2.2 13.0 (max)
Boundary of ore unloading area – during lorry unloading	1.0
Hopper observation hatch (side of hopper) – during lorry unloading	10.0 24.0 (max)
Rear of hopper – during unloading operations	
next to hopper	50.0
10 m from hopper	10.0
next to hopper one min after tipping finished	2.0
next to hopper two mins after tipping finished	1.0
Front of hopper during unloading operations	4.0 19.0 (max)
First floor landing walkway directly above hopper – during lorry unloading	14.0 35.0 (max)

Notes:

1. Values are based on a 2 minute sampling period. "Max" indicates the maximum reading obtained at the specified location from a 10 second sampling interval.

iii. Ore discharge from storage bunker to ICON plant ("Black End")

Sample Description	Total Inhalable Dust (mg/m^3)[1]
In front of hopper	2.9
Behind hopper	1.9
First floor landing walkway directly above hopper	6.5
First floor landing away from hopper	1.0
Below ore discharge conveyor	56.0
Next to ore discharge conveyor	9.0
Next to leaking access panel in ore feed to conveyor	
- next to leak	50.0
- 1 m away	20.0
- 2 m away	5.0
- 3 m away	2.5

Notes:

1. Values are based on a 10 minute sampling period.

iv. Filter press facility

Sample Description	Total Inhalable Dust (mg/m^3)[1]
Inside filter press facility – next to filter press	0.3
Outside filter press facility – next to disposal skip (open air)	0.2

Notes:

1. Values are based on a 10 minute sampling period.

v. Bottom of reactor vessels (open air)

The average total inhalable dust concentration measured around the bottom of the two reactor vessels was 0.05 mg/m^3 (10 minute sampling period).

5.3. Discussion

Airborne dust is produced by a number of the processes on site, some of which are intermittent in nature. In addition, individual work patterns are varied so it is considered that the results of personal air sampling are the best means by which radiation doses as a consequence of dust inhalation can be assessed. Based on the 8 hour time weighted average total inhalable dust measurements made in the various locations and times of occupancy, estimates of the radiation doses have been made and are given in the table below.

It was noted, however, that the range of the results was quite wide with some individual dust results significantly higher than the average.

ESTIMATED RADIATION DOSES DUE TO DUST INHALATION

Sampling Location and Work Activity	Estimated Time of	Estimated Effective

	Occupancy (hours/annum)	Radiation Dose (mSv/annum)
Workers on ICON plant – maintenance men and technicians	2000	< 0.1
Workers on “Black End” plant – maintenance men and technicians	2000	< 0.1
Ore offload area at storage warehouse – lorry and plant drivers	750	0.2
Ore discharge point at Greatham plant – ore offload supervisor	350	0.3

The results of the real time dust monitoring were in broad agreement with those obtained from the personal air sampling programme. These results have not, however, been used for estimating doses, as the analyser used was not calibrated specifically for the type of dust being sampled.

However the following points relating to the use of the analyser were noted:

i. The ease of use of the instrument allows a lot of spot measurements to be taken in a short period of time.
ii. The instrument can identify individual sources of dust, most noticeably the leaking access cover below the feed from the storage bunker.
iii. The instrument was useful in determining average dust concentrations over relatively short operations such as during a lorry tipping ore at the plant discharge point.
iv. An indication could be obtained on how the levels of dust varied with distance from a source of dust.
v. Information could be gained on how quickly the airborne dust settled out of the air with time.

In addition the analyser could be used to quickly identify the relative effectiveness of any dust reduction schemes introduced. The instrument could also be used to investigate the causes for the wide range of dust sampling results for each of the particular workplaces.

In conclusion it is considered that the most appropriate sampling programme would be based on the use of personal sampling pumps to determine 8 hour time weighted dust exposures, which could be used to assess the resultant radiation doses. In conjunction with this a real time dust analyser could be used to investigate unusual occurrences, identify individual sources of dust and measure the effectiveness of any improvements introduced to reduce the levels of dust.

APPENDIX 1 – Estimation of annual radiation doses from PAS monitoring results – example calculation for ore discharge at warehouse.

Intakes due to inhalation are estimated from personal air sampling data supplied by the Company. This data is derived from 23 total inhalable dust samples taken during ore discharge operations in the storage warehouse.

Average total inhalable dust measurement = 6.5 mg/m^3
Average time of occupancy = 750 hours/annum

A breathing rate of 1.2 m^3 h^{-1} (ICRP reference man, "light activity") and no respiratory protective equipment (RPE) are assumed. It is assumed that all the airborne dust is beneficiate. The following activity concentrations, based on the results of samples analysed at NRPB, have been used to estimate the activity inhaled:

Uranium-238 plus daughters in equilibrium	0.2 Bq/g
Thorium-232 plus daughters in equilibrium	0.7 Bq/g

To estimate the internal radiation exposure of persons, dose coefficients for the most significant radionuclides have been taken from ICRP Publication 68. Only whole body radiation exposure has been considered (individual organ doses have not been calculated but are not expected to be limiting). Beneficiate is an insoluble material and the dose coefficients are, therefore, based on lung classification S (or M where values for S are not available) and the lowest gut transfer factor (f_1). The relevant data are given below.

Radionuclide	Committed effective dose equivalent Per unit intake (Sv Bq^{-1})	
	Ingestion[3]	Inhalation
Thorium-232	9.2 10^{-8}	1.2 10^{-5}
Radium-228	6.7 10^{-7}	1.7 10^{-6}
Thorium-228	3.5 10^{-8}	2.5 10^{-5}
Radium-224	6.5 10^{-8}	2.4 10^{-6}
Uranium-238	7.6 10^{-9}	5.7 10^{-6}
Uranium-234	8.3 10^{-9}	6.8 10^{-6}
Thorium-230	8.7 10^{-8}	7.2 10^{-6}
Radium-226	2.8 10^{-7}	2.2 10^{-6}
Lead-210	6.8 10^{-7}	1.1 10^{-6}
Polonium-210	2.4 10^{-7}	2.2 10^{-6}
Uranium-235	8.3 10^{-9}	6.1 10^{-6}
Protactinium-231	7.1 10^{-7}	1.7 10^{-5}
Actinium-227	1.1 10^{-6}	4.7 10^{-5}
Thorium-227	8.4 10^{-9}	7.6 10^{-6}

---

[3] Intakes due to ingestion cannot be assessed by air sampling and are, in any case, considered impossible to accurately quantify. To estimate the significance of this exposure pathway it is assumed (in line with previous generic assessments undertaken by NRPB) that 10 mg of material is inadvertently ingested each working day. Combining this with the measured activity concentrations, and the dose coefficients above gives an estimated annual committed effective dose of **0.01 mSv**.

Using the above methodology, the estimated annual dose received by employees from inhalation of dust for this work situation is **0.2 mSv**.

APPENDIX 2 – PHOTOGRAPHS OF PROCESS

ORE DISCHARGE POINT AT GREATHAM WORKS

INSIDE OF FILTER PRESS ROOM

DISCHARGE OF FILTER PRESS WASTE MATERIAL

COMURHEX MALVESI CASE STUDY

1 SITE HISTORY

The COMURHEX Malvési site is located in the south of France near Narbonne. The plant originated in 1959 as the Uranium Refinement Society (SRU) to produce metallic uranium ingots for the graphite-gas reactor system. In 1971, the society for COnversion of URanium into Metal and HEXafluoride (COMURHEX) resulted from the merging between SRU and the Pierrelatte Chemical Plants Society (SUCP) that produces since 1962 on the site of Pierrelatte uranium hexafluoride (UF_6) for gaseous enrichment from the uranium tetrafluoride (UF_4) produced on the Malvési site. The development of the enriched fuel reactors has required a large increase in the UF_4 production while the abandonment of the natural uranium reactor system has led to the cessation of the uranium metal production in 1992. COMURHEX is a COGEMA subsidiary company since 1992.

2 PROCESS DESCRIPTION

Uranium mining concentrates from all over the world (France, South Africa, Namibia, Australia, China, Canada, Spain, Gabon, Nigeria, Portugal and states from former USSR) are received in 225 l drums. The concentrates, that contain from 70% to 75% of uranium, have different chemical forms: magnesium, sodium and ammonium uranates (MgU_2O_7, $Na_2U_2O_7$, $(NH_4)_2U_2O_7$), oxide (UO_3 - U_3O_8) resulting from ammonium uranate calcination, and uranium peroxyde (UO_4).

The refining/conversion process has a double function: first, to refine the uranium concentrates in order to achieve a nuclear grade final product (to remove neutron poisons such as cadmium and boron as well as other impurities that would impair the physical and chemical processes needed to produce the final product); second, to carry out the chemical conversion towards the desired chemical form (UF_4).

Following receipt, the mining concentrates are dissolved into nitric acid (HNO_3) to obtain uranyl nitrate (UO_2 $(NO_3)_2$). This solution is then purified in columns where liquid-liquid exchange takes place between the uranyl nitrate solution and the tributyl-phosphate (TBT) solvent. The resulting solution is then concentrated. By injection of gaseous ammonia (NH_3), ammonium diuranate $(NH_4)_2U_2O_7$) is obtained, that is calcined at 500°C to obtain uranium trioxide. This is then passed through a series of vertical furnaces, where it is first reduced into uranium dioxide (UO_2) and then transformed into uranium tetrafluoride (UF_4) by hydrofluorination on a gaseous hydrofluoric acid (HF) current.

The process is summarised in Figure 1

2.1 Sampling

The sampling step is fundamental for economical and political reasons: the plant is required to achieve a minimum conversion yield of 99.5%, by customers and by the international authorities that control the non-proliferation of radioactive materials.

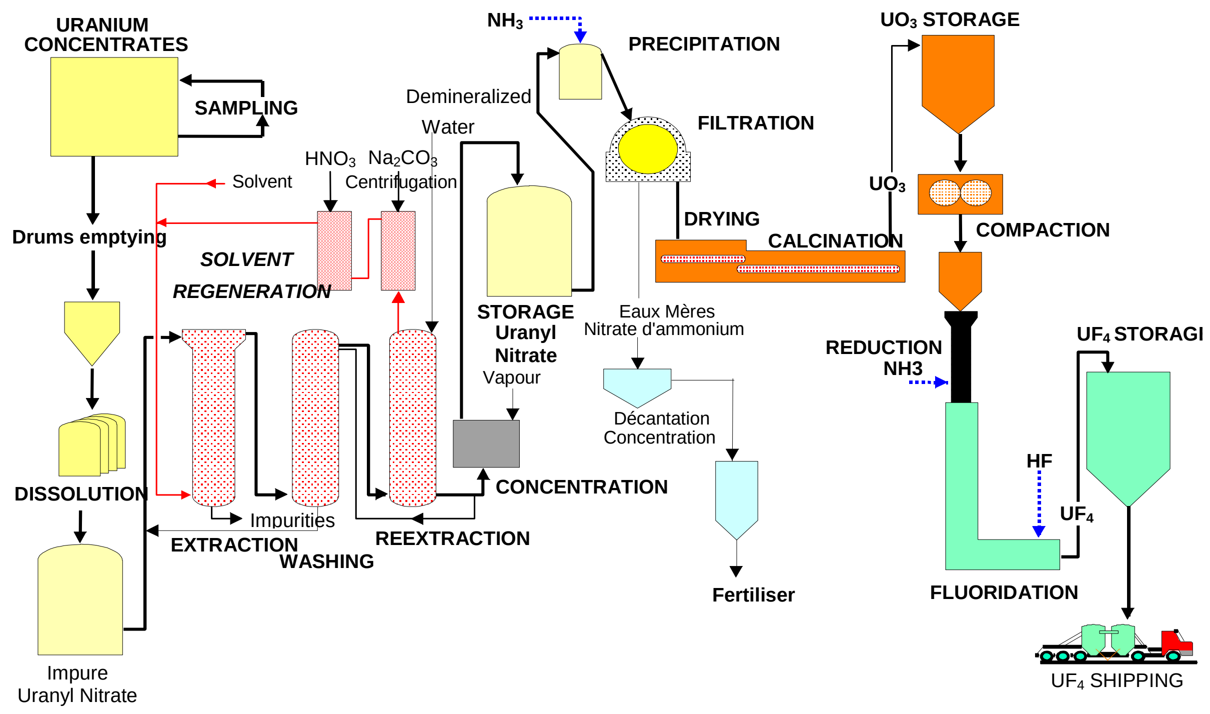


Figure 1 : Wet Process for refining/conversion of uranium mining concentrates

2.2 Dissolution

The drums of sampled concentrates are emptied into a silo. The concentrates are then dissolved with concentrated nitric acid (HNO_3) in a series of stainless steel tanks to produce an impure solution of Uranyl Nitrate ($UO_2 (NO_3)_2$).

2.3 Purification

The purification workplace uses a liquid-liquid exchange technique between the aqueous uranyl nitrate solution and the tri n-butyl phosphate (TBT) solution in dodecane that takes place in the largest purification column in the world, with a capacity of 14 000 t/year.

$2\ NO_3^- + UO_2^{\ 2+} <-> [UO_2\ (NO_2)_2],\ H_2O <-> [UO_2\ (NO_3)_2]\ (TBP)_2$

This workplace comprises an extraction column, a washing column and a re-extraction column: The extraction column, where uranium is moved from the aqueous phase to the organic phase, receives at the top the impure uranyl nitrate solution and at the bottom the TBT solvent. The organic phase carries the uranyl nitrate/TBP complex and is collected at the top. The aqueous phase, depleted in uranyl nitrate but containing almost all the impurities present in the concentrate is collected at the bottom. In the washing column,the residual impurities are removed from the organic phase. In the re-extraction column uranium is removed from the organic phase to the aqueous phase. The organic phase, now depleted in uranyl nitrate, is collected at the top for further regeneration of the solvent while the aqueous phase with the purified uranyl nitrate, containing only some few ppm of impurities, is collected at the bottom of the column.

2.4 Precipitation/calcination

Gaseous ammonia (NH_3) is injected in the uranyl nitrate solution in order to produce an ammonium diuranate ($(NH_4)_2U_2O_7$) precipitate.

$2\ [UO_2\ (NO_3)_2] + 6\ NH_4OH -> (NH_4)_2\ U_2O_7 + 4\ NH_4NO_3 + 3\ H_2O$

The solid precipitate is separated from the water in a rotating filter operated under vacuum. The water constitutes a very pure solution of ammonium nitrate (NH_4NO_3) which is concentrated and used as liquid fertiliser. The ammonium diuranate falls directly from the filter on the moving conveyor belt of a drying and calcinating continuous furnace, where the filtration cake is passed through by a 500°C air flow.

$(NH_4)_2 U_2O_7$ -> 2 UO_3 + 2NH_3 + + H_2O

The resulting uranium oxide (UO_3) powder is stored and compacted before its introduction in the reduction/fluoridation furnaces.

2.5 Reduction/hydrofluorination

A parallel battery of several fluidised bed vertical furnaces is used to perform the reduction from uranium trioxide (UO_3) to uranium dioxide (UO_2), followed by the fluoridation of the uranium dioxide into uranium tetrafluoride (UF_4). The hydrogen required by the reduction of UO_3 into UO_2 is obtained *in situ* by the thermal cracking of gaseous ammonia (NH_3) on the uranium oxide bed heated up to 700°C.

UO_3 + H_2 -> UO_2 + H_2O

The UO_2 produced meets then the gaseous fluorhydric acid (HF) and produces UF_4 at a reaction temperature of 500°C.

UO_2 + 4HF -> UF_4 + 2 H_2O

The uranium tetrafluoride produced is finally stored in a silo from which it is loaded on special trucks for transport to the Pierrelatte COMURHEX plant.

2.6 Recycling

The recycling workplace receives all the uranium-bearing flows from the different workplaces and recycles them in the main production flow. This workplace processes also the uranium-bearing materials whose uranium grade is too low to enter directly the main flow. These materials come from the Pierrelatte plant as well as different installations (from France or foreign countries) that process natural uranium. The fluids that contain traces of non-reusable uranium are sent to decanting and evaporation ponds after having been neutralised with lime.

3 PROCESSING CAPACITY

With a yearly processing capacity of 14 000 t of uranium, COMURHEX supplies one third of the world UF_6 market and exports 40% of its production.

In 2001, the Malvési plant processed 12 000 t of uranium in the concentrates and produced the same quantity of uranium as UF_4. It used 16 000 t of nitric acid, 3 500 t of ammonia and 4 000 t of hydrofluoric acid, 3 500 t of gas oil and 29 000 million kWh.

4 IDENTIFICATION OF THE SAMPLING STATION

A study has been conducted in 1995 to estimate the annual external and internal exposure of the 170 exposed workers. Internal exposure by inhalation has been derived, from the data of daily averaged activity concentration measured by 26 Fixed Air Sampling (FAS) devices distributed among the several production units, and also, from an annual estimate of the time spent by each operator at the different workstations, together with the use of the ICRP 68 [1] dose coefficients appropriate to the solubility (moderate for uranates and slow for oxides) and the particle size distribution (Activity Median Aerodynamic Diameter (AMAD)=5µm) of the considered compounds. The results of this study showed that the annual collective effective dose (external+internal) of these 170 workers was 350 man.mSv, corresponding to an average annual individual effective dose of 2 mSv with an average contribution of the external exposure of 70%.

A more thorough study of these results showed that, 60% of the exposed workers were exposed to an annual individual dose below 2 mSv and most annual doses were below 5 mSv. However 6 workers from the sampling workplace (representing only 3% of the 170 exposed workers) received 12% of the plant collective dose, with corresponding annual individual doses between 6 and 12 mSv. In terms of internal exposure, those 6 workers were exposed to seven times more than the average and received about 25% of the plant annual internal collective dose, with corresponding annual individual doses between 1.5 and 6 mSv.

Finally, interpretation of the monthly urinary excreta as well as the yearly lung counting results of the sampling station workers for 1993 (with use of the ICRP 66 [2], 54 [3] et 68 [1] models as well as the LUDEP 2.0 code [4] for slow, 5µm AMAD compounds) showed that the annual dose estimates based on workplace air sampling could possibly underestimate the annual effective internal dose. Annual individual doses derived from urinary excreta ranged from 10 to 40 mSv, while doses derived from the yearly lung counting results - all below the detection limit – could nevertheless be compatible with annual doses as high as 50 mSv.

The results of this first study initiated efforts to better assess the dose of the workers of the sampling station as well as to study the principal characteristics of their exposure, in order to identify possible corrective actions and optimise the radiological protection of these workers. A comparison of the adequacy of various dose assessment methods for the optimisation of radiological protection in the case of exposure by inhalation to natural uranium compounds was then conducted in 1997. The best-adapted dose assessment methods were then used to conduct several measurement campaigns in 1997 and 1998 at the sampling workplace.

5 EXPOSURE ANALYSIS AND MEASUREMENT METHODS COMPARISON IN THE SAMPLING WORKPLACE

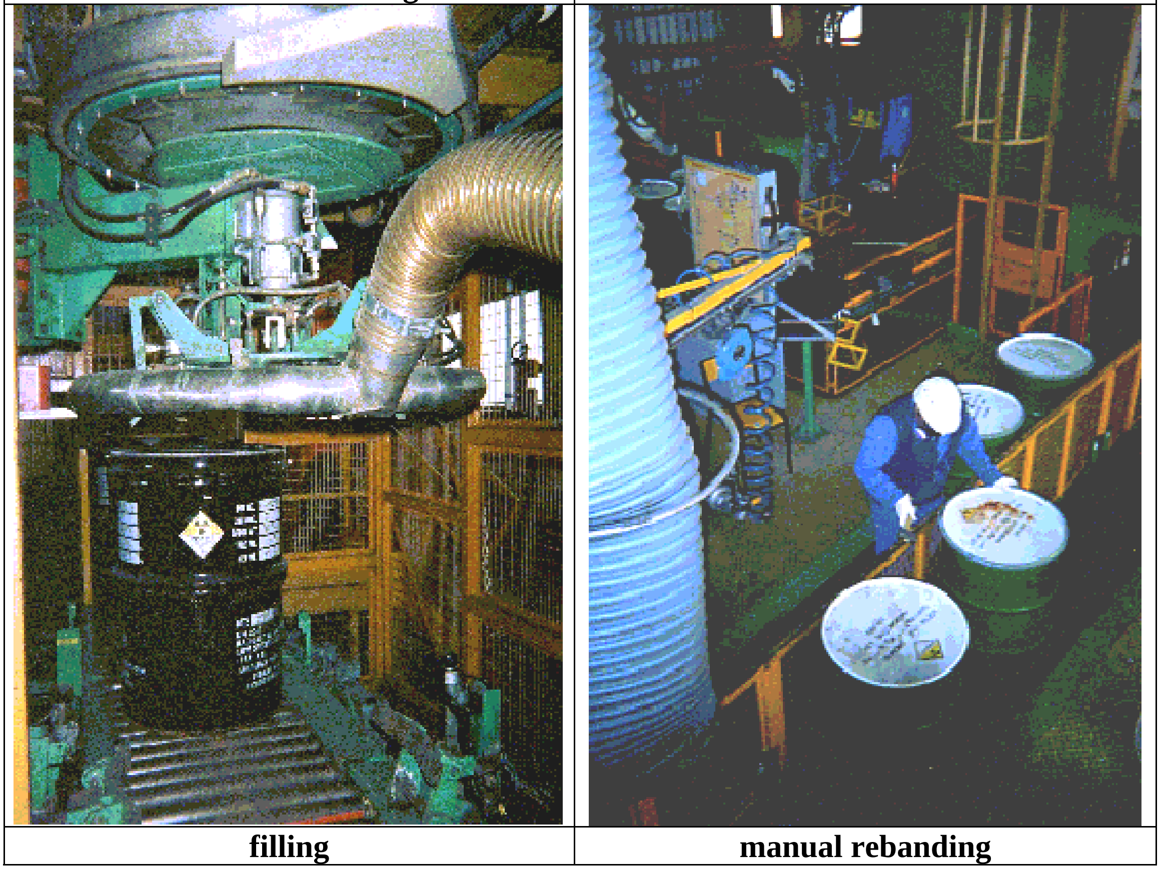
The workers of the sampling workplace take systematic samples of every drums of mining concentrate in order to analyse and record their uranium and impurities content. The successive steps of the process (see Figure 2) are the manual unbanding of the drum (unbanding stations), the - fully automated and confined - lid removal, drum emptying, primary (1%) and secondary sampling (1%) of the drum content, the automated filling and lid replacement of the drum (filling station), the manual removing of the secondary samples (secondary sampling station), the drum rebanding (rebanding stations 1 and 2), and finally the preparation of samples in a laboratory.

The study attempted to identify, through a number of measurement campaigns using personal and fixed air sampling apparatus, the operations that contributed the most to the exposure of operators at the sampling workplace. The study also included a comparison and analysis of the results of the different air sampling measurement methods, so as to determine which were, in this particular situation, the most suitable for analytical (task by task) estimation of individual doses with a view to optimisation of exposures.

This study relied on three types of sampling devices (see Figure 3) :

- Fixed Air Samplers (FAS) ; 1 200 $l.h^{-1}$ pump and 110 mm filter open sampling head ; Appareil de Prélèvement d'Air (APA), Merlin-Gerin. Most of those FAS were already present at the workstations for routine monitoring. Additional FAS were installed for this study at the sampling workplace.
- Low sampling rate Personal Air Samplers (PAS) ; 2 $l.h^{-1}$ centrifugal pump and 25 mm filter sampling head ; Integrated System for Individual Dosimetry (ISID), ALGADE. These light PAS (200 g) were originally designed for the monitoring of underground miners. The (integrated) pump and sampling head were worn on belt.

manual unbanding **lid removal**



filling **manual rebanding**

Figure 2: Sampling workplace process successive steps (floor 0)

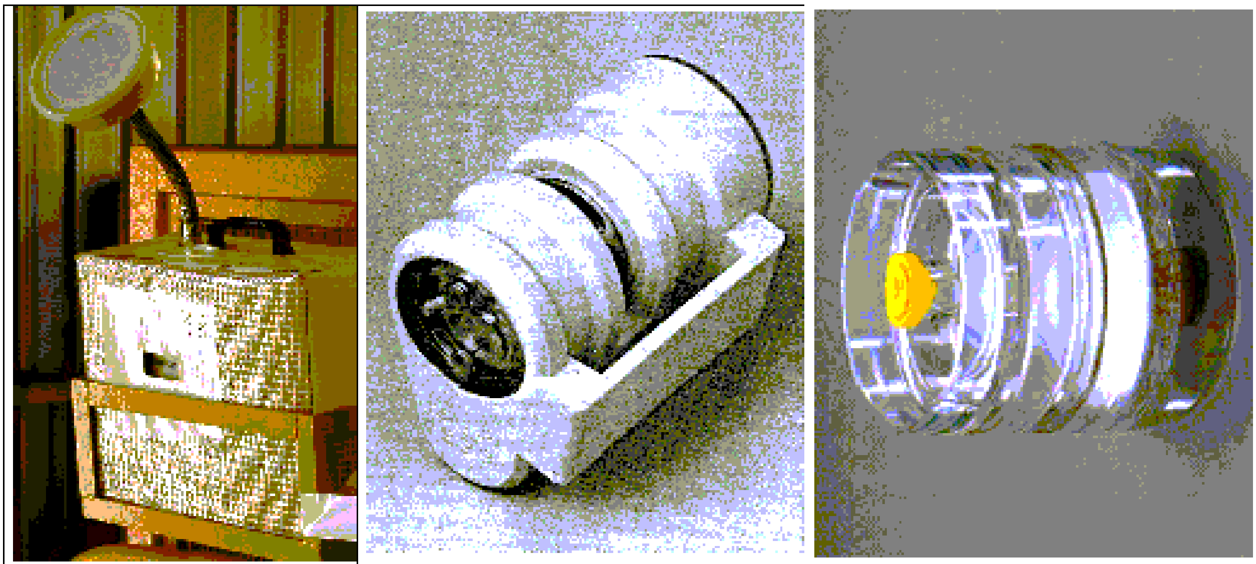
- High sampling rate Personal Air Samplers (HSR-PAS) ; 120 $l.h^{-1}$ SKC pump and 37 mm filter plastic cassette SKC sampling head. This is the standard 37 mm cassette PAS. The pump was worn on belt and the sampling head in the operator's breathing zone.

The alpha activity on the filters from the FAS is measured with a large-area alpha counter with a detector diameter of 140 mm and an alpha background count rate of 1.5 cpm. The sample changer of the counting system allows 50 samples to be counted automatically. Routine counting times are 5 minutes. Filters from PAS were alpha counted on a low-background multi-detector alpha-beta counting system (IN20) with a background alpha count rate of 0.1 cpm. Usually eight filters were counted per day and counting times were extended to up to 20 hours.

The counting of filters on both counting systems was delayed to 20 hours after sampling to allow the decay of the short lived radon daughters.

5.1 Estimation of exposures per task with collective air sampling

Determination of per-task exposures by the combined use of fixed air sampling apparatus (FAS) (for the evaluation of daily average activity concentrations) and personal air sampling systems (PAS) assigned to each task (for evaluation of the daily work times at each station of a reference operator) has shown (see Table 2) that the workstations with the highest exposure in the months of May and June 1997 (excluding cleaning operations) were the rebanding stations (54%) and the unbanding stations (18%) (platform function) as well as the laboratory (14%) and the secondary sampling stations (8%) (laboratory function). It is interesting to note that the platform function which represents only 51% of the time spent, makes a 77% contribution to total exposure, which shows the more than average activity concentrations encountered at the corresponding workstations. Conversely, the laboratory function, which represents 49% of the time spent, represents only 23% of the total exposure excluding cleaning, which shows the less than average activity concentrations encountered there.



FAS
(APA, Merlin Gerin)

PAS
(ISDS, ALGADE)

HSR-PAS
(37 mm cassette, SKC)

Figure 3 : Fixed and personal samplers used in the COMURHEX case study

5.2 Estimation of exposures per task with individual air sampling

Comparison of the results of these exposure calculations with those of evaluations based on the one-month accumulated exposure readings of the PAS assigned to each of the tasks has shown (see last column of Table 2 and Table 3) that the latter indicated a similar ranking of the stations in terms of relative contribution to exposure with 86% of exposure for the unbanding and rebanding stations, and 14% for the secondary sampling station, which were the only two working stations for which the one-month integrated activity was greater than the detection limit.

However, it was found that the exposure estimates for May and June 1997 based on the PAS results for those two tasks were greater by a factor of 30 to 100 (45 to 70 for both months combined) than the corresponding estimates made using the FAS. Thus, the annual individual doses corresponding to exposure during these two months of the reference operator (calculated using a 1.2 m^3/h inhalation rate and a dose factor derived from ICRP Publication 68 [1] with the help of the LUDEP 2.0 software [4] for a compound of low solubility and an AMAD of 10 µm[4]) were 0.43 mSv/year and 16 mSv/year respectively, depending on whether they were determined using FAS or PAS.

The study then tried to determine the reasons for the significant difference between the measurements made by FAS and PAS, seeking to establish whether these differences result from the existence of air contamination peaks during operations (whose contribution is correctly integrated by the PAS but underestimated in the daily average of the FAS), the presence of systematic bias in the activity concentration measurement of either method, or the different sampling positions (distance and height) of both apparatus in relation to the sources of contamination.

Table 2: Contributions of tasks to total operation time and exposure

	• Contribution to total operation time	• Contribution to total exposure	
		• (FAS)	• (PAS)
Platform function			
Unbanding	**26%**	**18%**	**86%**
Rebanding	**17%**	**54%**	
Lid unsticking	3%	2%	BDL
Empty drums	1%	2%	BDL
Computer room	4%	1%	BDL
Laboratory function			
Computer room	3%	1%	BDL
Laboratory grinding	**5%**	**3%**	BDL
Laboratory heating	**36%**	**11%**	
Secondary sampling	**5%**	**8%**	**14%**
Total	100%	100%	100%
Platform function	**51%**	**77%**	**86%**
Laboratory function	**49%**	**23%**	**14%**

(BDL) One month integrated activity below detection limit

---

[4] Standard value close to the activity median aerodynamic diameter of 9 µm measured at the workstations.

Table 3: Dose estimates per task (2 months) by FAS and PAS

	• Effective dose (Sv)		• • PAS / FAS
	• FAS	• PAS	
Platform function			
Unbanding **Rebanding**	**$6.1\ 10^{-5}$**	**$2.7\ 10^{-3}$**	**44**
Lid unsticking	$2.1\ 10^{-6}$	BDL	-
Empty drums	$1.5\ 10^{-6}$	BDL	-
Computer room	$1.1\ 10^{-6}$	BDL	-
Laboratory function			
Computer room	$5.8\ 10^{-7}$	BDL	-
Laboratory grinding **Laboratory heating**	**$1.2\ 10^{-5}$**	BDL	-
Secondary sampling	**$6.6\ 10^{-6}$**	**$4.6\ 10^{-4}$**	**69**
Total	**$8.6\ 10^{-5}$**	**$3.2\ 10^{-3}$**	
Total annual dose	**$4.3\ 10^{-4}$**	**$1.6\ 10^{-2}$**	

(BDL) One month integrated activity below detection limit

5.3 Testing for the existence of contamination peaks during operations

To determine whether any concentration peaks generated by the operations themselves could explain the disparity between the exposure evaluations made with FAS and PAS, the best approach appeared to be to study the correlation between the daily averaged activity concentrations measured with the FAS at the different workstations and the amount of time spent there by the operators.

This study showed a significant positive correlation between the daily average concentration at the unbanding station and the time spent by the reference operator at this place, as well as a significant negative correlation between the daily average concentration at the secondary sampling station and the time spent by the reference operator at this place. No significant correlation between the average concentration and the time spent by the operator were found for the other stations.

In order to interpret the observed correlations, we may try to formulate as follows the relation existing, at a given workstation, between average activity concentration measured by a FAS and activity concentrations existing at this station during and outside the operations conducted at this station:

$$C_{FAS} = (T_{work}\, C_{work} + (T - T_{work}) \,.\, C_{T - T_{work}}) / T$$

with:

C_{FAS}	Daily averaged activity concentration measured by the Fixed Air Sampler (FAS)
C_{work}	Daily averaged activity concentration during operations
$C_{T-T_{work}}$	Daily averaged activity concentration outside operations
T	Daily measurement duration of the FAS
T_{work}	Daily operation duration

Similarly, activity inhaled during operations at a given workstation may be expressed as follows:

$A = V_R \, . \, T_{work} \, . \, C_{work}$

with:

A	Daily activity inhaled during operations
V_R	Ventilation rate

We may then test the impact on these formulations of three simple categories of activity concentration time profile during operations:

1 - Operations at a given workstation have no impact on the contamination of this workstation ($C_{FAS} = C_{work}$)
The average activity concentration and the operation duration are then independent and activity inhaled during operations at a given workstation may then be expressed as:
$A = V_R \, . \, T_{work} \, . \, C_{FAS}$

2 - Operations at the workstation are the only source of contamination of this workstation ($C_{T-T_{work}} = 0$)
The average activity concentration and the operation duration are then positively correlated and activity inhaled during operations at a given workstation may then be expressed as:
$A = V_R \, . \, T. \, C_{FAS}$

3 - The contamination of the workstation is null during operations ($C_{work} = 0$)
The average activity concentration and the operation duration are then negatively correlated for
$C_{FAS} = (1 - T_{work} / T) \, C_{T-T_{work}}$ and activity inhaled during operations at a given workstation may then be expressed as:
$A = V_R \, . \, T_{work} \, . \, C_{work} = 0$

This formulation, together with the observed correlations between activity concentrations measured by the FAS and total duration of operations, allowed us to divide the workstations into three types:

1 - The rebanding workstation is characterised by the fact that the operations carried out there appear to be the main source of contamination of the station. The estimation of the exposure there using FAS could be thus carried out by simply multiplying the daily average activity concentrations measured by the sampling time per day. However, an exposure estimate of this type still remains lower by a factor of 10 than one using PAS.

2 - The secondary sampling station exhibits contamination which appears to diminish while operations are carried out there. The use of FAS measurements would appear to be ill suited for estimating the exposure received in such a station.

3 - Finally, it would appear that the operations carried out in all the other workstations have little impact on the contamination prevailing there and that the method consisting of multiplying the average daily activity concentration measured using FAS by the daily work duration appears to be the best suited for determining exposure on the basis of FAS measurements.

5.4 Testing for the existence of systematic bias in the activity concentration measurement methods

To detect systematic bias in FAS and PAS exposure estimates, two measurement campaigns were carried out (December 1997 and March 1998) to compare the monthly activity accumulated over eight hours per day by PAS and FAS placed at a distance of less than 30 cm and operated simultaneously. The results of these measurements have made it possible to observe differences of up to a factor of three (on one side or another) in exposure estimates made using FAS and PAS. In the light of these results, there is assumed to be no systematic overestimation of the measurement of activity concentration by PAS compared to FAS but an important variability which may be possibly due to high activity concentration gradients.

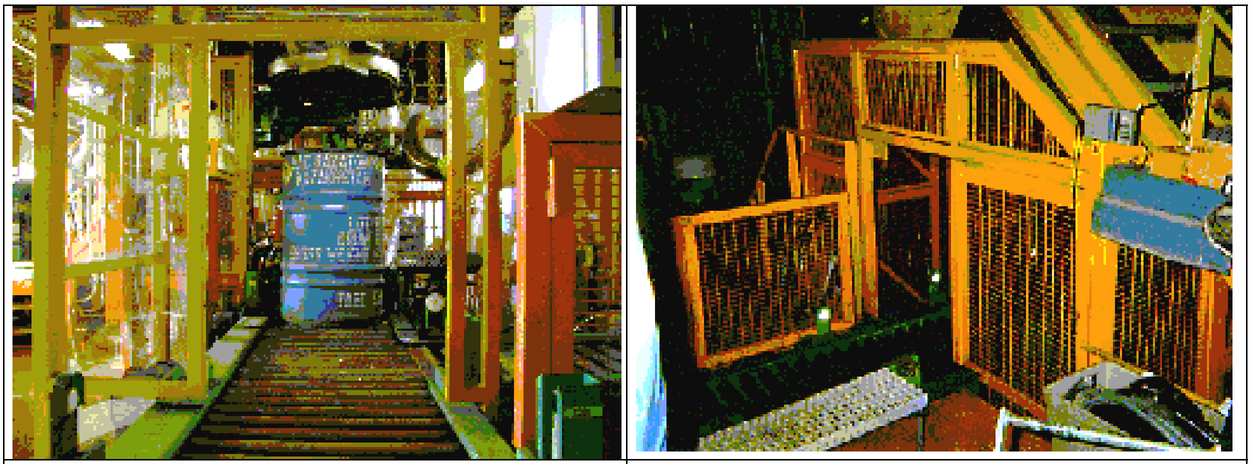
5.5 Testing for the importance of sampling position

Finally, the importance of the sampling point position relative to the sources of contamination and the operator's respiratory tract entrance was evaluated during a March 1998 measurement campaign to compare simultaneous estimations of exposure carried out using a PAS worn at the waist and a HSR-PAS, offering greater exposure estimation reliability, due to its higher sampling rate and its sampling point as close as possible to the entrance of the operator's respiratory tract. The results of this campaign have shown that for both platform and laboratory tasks, monthly exposure estimates made using PAS exceeded those made using monthly totals of the daily HSR-PAS measurements by a factor of two. That difference can be possibly explained by the greater proximity to the sources of contamination of the PAS, which is worn at the waist. These results confirmed thus the acceptable accuracy of the PAS measurements under these conditions and suggested the existence of important contamination gradients which may partly explain the still lower activity concentration measurements of FAS, which are further away from the sources of contamination and higher, compared to HSR-PAS.

6 EXPOSURE ANALYSIS IN THE SAMPLING WORKPLACE AFTER CONFINEMENT OF THE FILLING STATION

Following this first PAS measurement campaign, it was decided to implement two corrective actions at the filling station:

- the filling hopper was modified in order to eliminate frequent drum overfilling incidents that were the source of significant contamination.
- The filling station was confined, however with some unprotected openings (see Figure 4) allowing for the entrance of the empty drums and the exit of the filled drums to the rebanding workstations.



Empty drums entrance **Filled drums exit**

Figure 4: Openings in the filling station confinement

6.1 First measurement campaign

A first measurement campaign was conducted during one month in October 2001 in order to estimate the impact on exposures (especially those received at the rebanding stations) of the filling station modification and to identify additional protection actions that would allow, if necessary, to decrease further the exposures.

For this purpose, three types of air sampling devices were used in combination (see Figure 5):

- Twelve FAS were allocated to the various workstations in the sampling-taking workplace. They were switched on during the whole work shift duration and measured thus the time-averaged concentration during the shift at the given location.
- HSR-PAS were used in the following way:
    - The two workers belonging to the platform function (and thus involved in the drums unbanding and rebanding operations) carried HSR-PAS that were switched on during their whole work shift duration and allowed thus to estimate during a shift the collective exposure and work duration associated with the operations of the platform function.
    - Three HSR-PAS were allocated to the most potentially exposed workstations (unbanding, rebanding 1, rebanding 2) and used as FAS. They were switched on[5] by the workers only when they carried out a task at the given workstation. These HSR-PAS allowed thus to estimate, for each of these three workstations, the collective working time spent during a shift at the given workstation, as well as the averaged activity concentration during the operations.
- A Continuous Air Monitor (CAM)[6] was used at various locations (inside the filling station and at the rebanding workstation) to record the time-profile of the airborne activity concentration.

Three sets of uranium oxide drums were sampled during the campaign:

- set 1: RANGER drums (524 drums, 16 days).
- set 2: PRIARGUNSKY drums (190 drums, 4 days) ; easily dispersible product
- set 3: MAC ARTHUR drums, (150 drums, 4 days) ; damaged drums

---

[5] using the Pause button in order not to reset the pump volumeter

[6] CAM with α, β real-time detection by silicium detectors on a paper filter, and dynamic compensation for α, β radon daughters ; ABPM 302 CAM, MGP Instruments (see Figure 5)

Figure 5: Detailed measurements with FAS, PAS, switched PAS, CAM and RTMD

The statistical comparison (comparison of means before and after protection of the filling station) of the daily average concentrations measured by switched HSR-PAS at the rebanding 1 station have shown that while the average daily concentrations measured by the FAS were not statistically different, the average daily concentrations measured by the switched PAS after protection were both much lower (by a factor of 10) and less dispersed than those measured before the protection measures were implemented.
In addition, one could observe that the daily averaged concentrations measured by APA at the rebanding 1 workstation were always lower (by a factor of 4 on average) than those measured inside the confinement of the filling station. Moreover, the ratio of the average activity concentration measured by switched HSR-PAS and APA has been found to be much lower (ratio of 1.5) for the rebanding 1 station than for the rebanding 2 and unbanding stations (ratios of 7 and 3).
The results of this analysis are coherent with the hypothesis that the confinement of the filling station has significantly reduced the contamination peaks from the filling station reaching the rebanding 1 station.

The daily averaged activity concentration at the rebanding station 1, measured either by a FAS or a switched HSR-PAS (see Figure 6) has been found to be highly variable from one day to another and a detailed statistical treatment (multiple mean comparison) of the measurements analysing the impact of the drums set processed showed that:

- the FAS activity concentration at the rebanding workstation was significantly different for the three sets of drum processed, with set 3 > set 2 > set 1
- the switched PAS activity concentration at the rebanding workstation was significantly different for the third set of drum, with set 3 > set 2 = set1

Further analyses have been thus conducted separately for each set of drums, in order to take into account the potential importance of the product dispersability characteristics and the condition of the on the workers exposure.

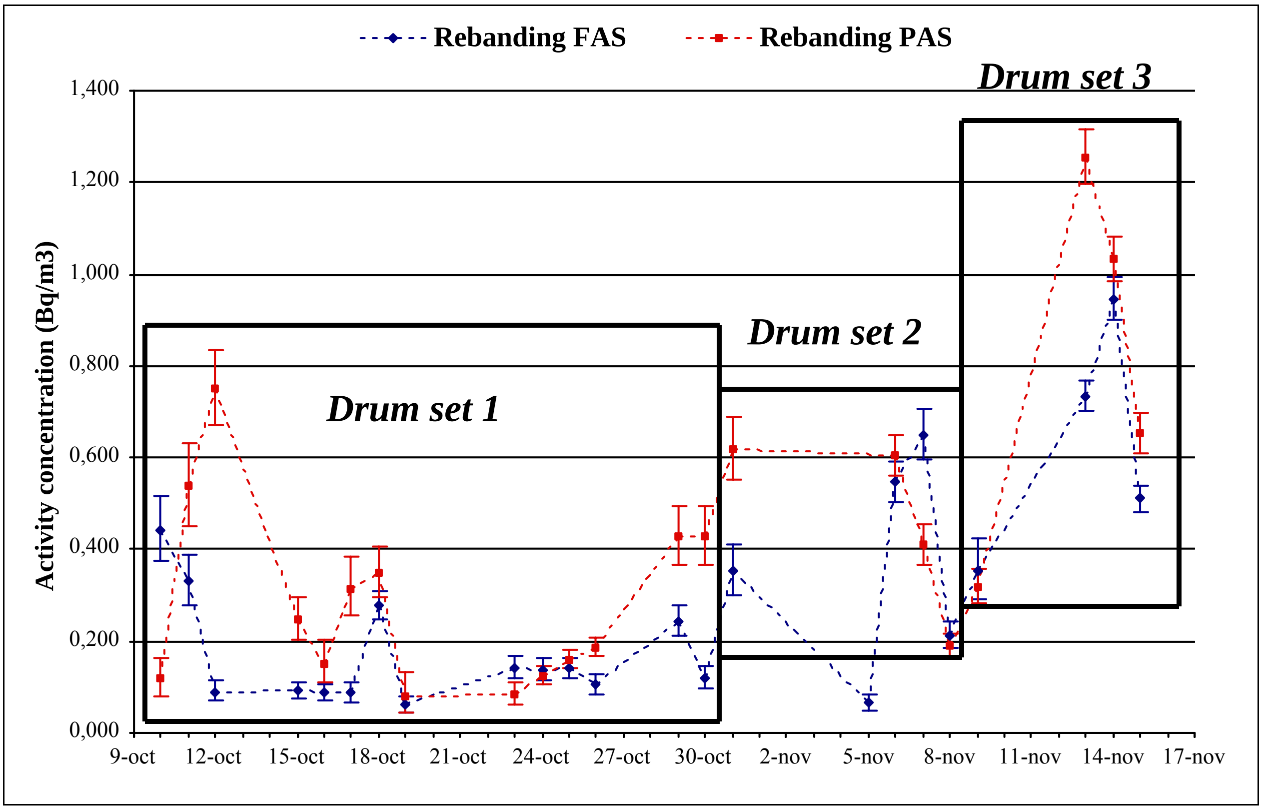


Figure 6: Comparison of the averaged activity concentration measured by FAS and switched PAS at the rebanding station

As shown in Table 4 the annual individual exposure estimated on the basis of the PAS worn by the workers PAS has been significantly reduced (by a factor of 6) by the modification and confinement of the filling station.

Table 4: Comparison of annual individual dose estimates before/after protection of the filling station

	Effective dose (Sv/year)	
	LSR-PAS	HSR-PAS
Before protection		
Platform function	16 10^{-3}	8 10^{-3}
After protection		
Platform function		
Drum set 1		1.1 10^{-3}
Drum set 2		1.7 10^{-3}
Drum set 3		1.3 10^{-3}
All sets average		1.2 10^{-3}

The expected annual collective exposure associated with the three sets of drums has not been found to be statistically different. However the comparison (for each set of drums) of the contribution of operations held at the unbanding and rebanding workstations to the collective work duration and exposure (measured by the switched HSR-PAS)has shown that these contributions did depend on the type of drums:

- After the implementation of protection measures, for drum sets 1 and 2 combined, the unbanding and rebanding workstations were no longer major contributors to exposure (they represent 29% of the exposure for 41% of the working time)
- in contrast,, for drum set 3, those workstations were still major contributors to exposure (they represent 61% of the exposure for 33% of the working time).

The results of this analysis, indicating that the rebanding operations (and to a less extent unbanding operations) could give rise to significant contamination releases when damaged drums were processed were found to be in good accordance with the observation of visible contamination releases from the damaged drums of set 3 during their rebanding.

6.2 Second measurement campaign

Finally, a three days measurement campaign was conducted in March 2002, in collaboration with the SERAC IRSN laboratory (see [5]), in order to:

- compare in a real working environment the performances of the air sampling devices used at COMURHEX with those of reference samplers (see Figure 7)
    - The APA FAS was compared with a CATHIA FAS
    - The 37 mm cassette HSR-PAS (closed and open) were compared with a button and IOM PAS, with the help of the CALTOOL device
- study the capabilities of a Real Time Monitoring Device (RTMD) (GRIMM G 1.108 eight channels optical particles counting device, GRIMM) to provide information on the air concentration time profile in order to better distinguish, at the rebanding station, the respective contributions to the airborne contamination of the contamination escaping from the filling station and from the rebanded drums (see Figure 5)

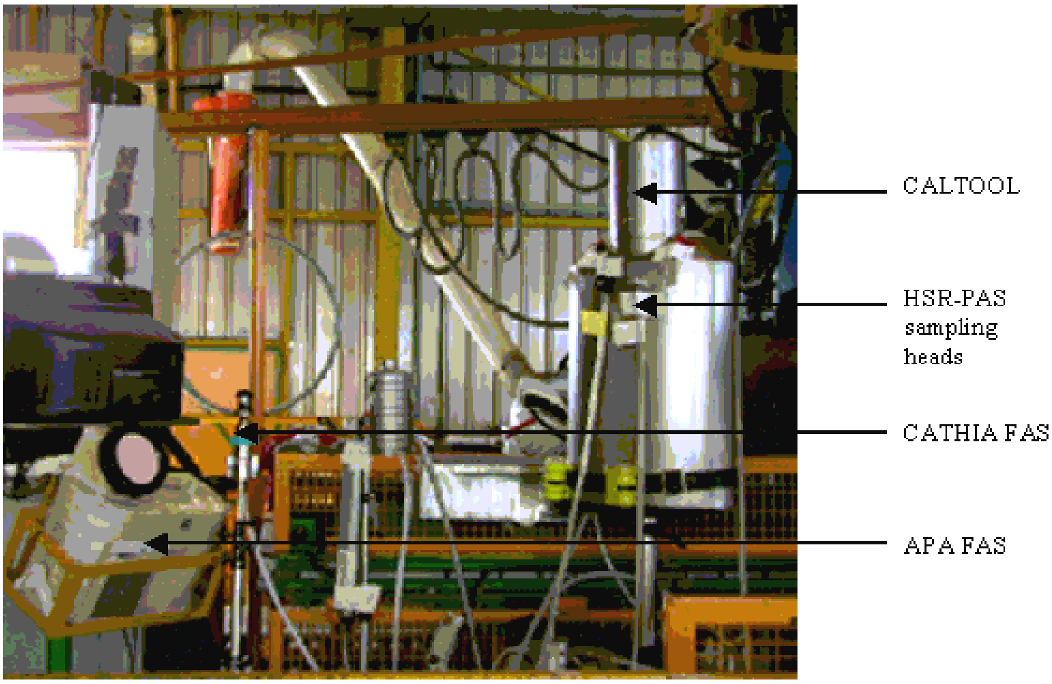


Figure 7: On-site comparison of air samplers with reference air sampling devices

Concerning the performance of the air sampling devices used at COMURHEX, the main results of this measurement campaign are as follows:

- activity concentrations measured by the APA FAS have been found to be very close to those measured by the reference CATIA FAS.

LSR-PAS

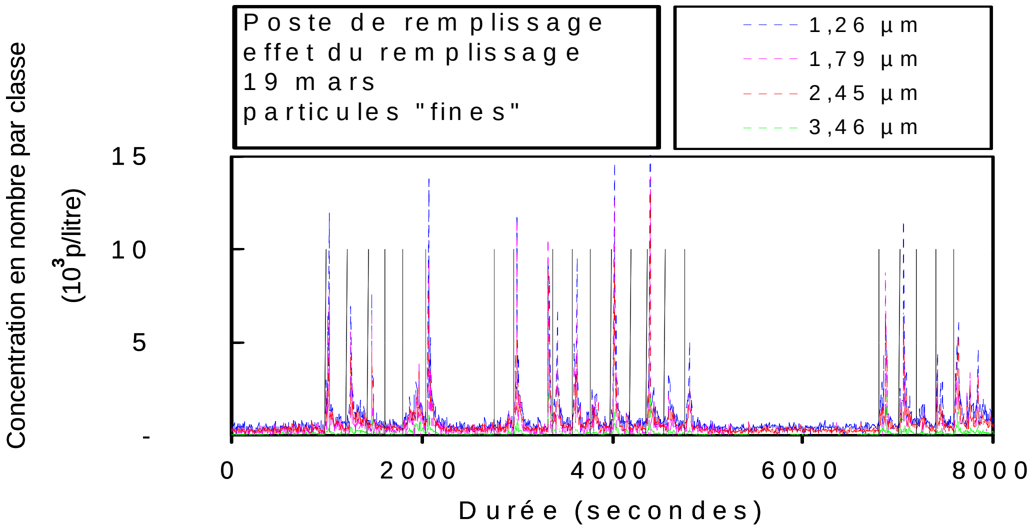
- activity concentrations measured by the HSR-PAS have also been found to be close to those measured by the reference CATIA FAS, but more dispersed than those measured with the APA. This comparison showed thus no systematic overestimation by the HSR-PAS of the activity concentration.
- activity concentrations measured by the IOM and Button PAS have been found to be very close to those measured by the reference CALTOOL PAS.
- Activity concentrations measured by the 37mm cassette (closed or open) have been found to be more dispersed, with activity concentrations measured with open face always higher than those measured with closed face. This comparison showed however no systematic overestimation by the HSR-PAS of the activity concentration.

The GRIMM real-time multi-channel optical particle counter was used for two days, in two locations (inside the filling station and at the rebanding workstation). The first day corresponded to a normal operation of the sampling station while the second one corresponded to separate filling and rebanding operations, in order to try to separate their contributions to the particle counts.

Inside the filling station (see Figure 8 and Figure 9), the measurements have shown a visible correlation of the particle counts with the filling operations (presented as vertical bars) that was more marked for fine particles (right side of Figures 8 and Figure 9) and bigger particles than for all sizes together (left side of Figure 8 and Figure 9), due to the important background of ultra fine particles. One can also note the visible impact on particle counts (see middle peak on Figure 9 for fine particles) of the resuspension of deposited contamination due to the entrance of an operator inside the confinement for maintenance purpose.

At the rebanding workstation (see Figure 10 and Figure 11), while particle concentrations peaks were still visible, these peaks were less pronounced and while the effect on particle counts due to dust resuspension by operators movements could be noticed, it was not possible to discriminate the contribution to these peaks of the filling and rebanding operations. Actually, for measurements held on March 20, the filling and rebanding operations were too close in time to allow any discrimination (see left part of Figure 10) and for measurements held on March 21, the background of ultra fine and fine particles (see left part of Figure 11) was so high compared to the process-related particles, that particle counts peaks could hardly be noticed, even for medium and bigger particles (see right part of Figure 11).

These measurements showed that contamination was released inside the filling station during the filling operations and that some contamination peaks (although much less important) were also present at the rebanding 1 workstation. They indicated not only the effectiveness of the filling station confinement on the contamination levels at this workstation, but also the existence of residual contamination peaks at the rebanding workstation, that could come both from the filling and rebanding operations. Lastly, these measurements highlighted the need for a multi-channel RTMD (that could differentiate particle sizes), in order to discriminate the process-related particles from the background particles.



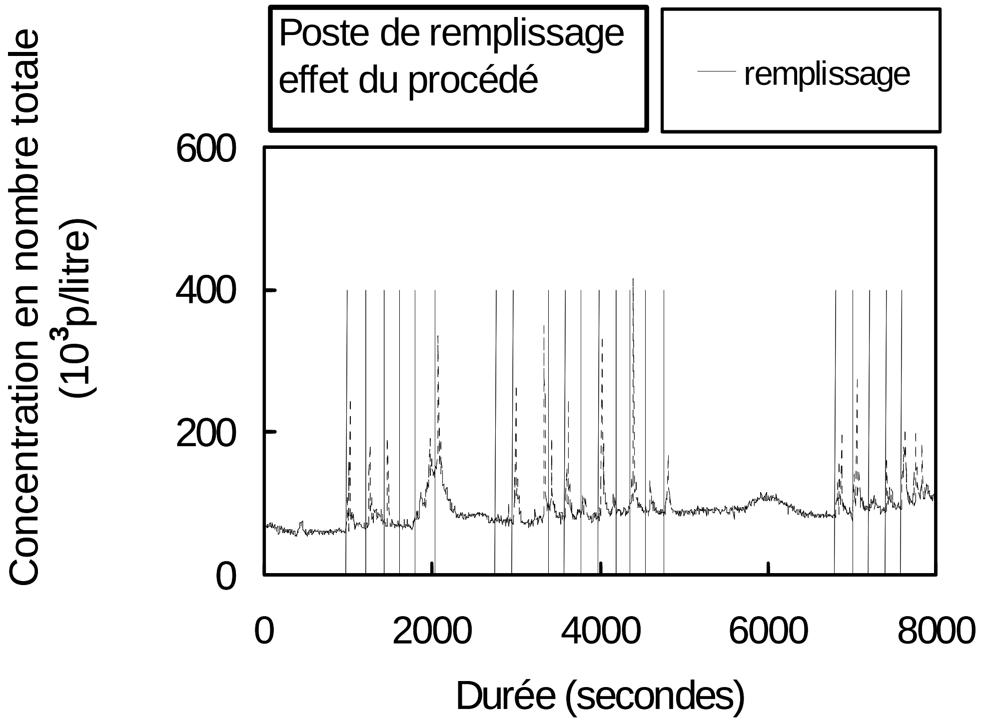


Figure 8: Particles concentration at the filling station (GRIMM, March 19). Fine particles above, all particles below.

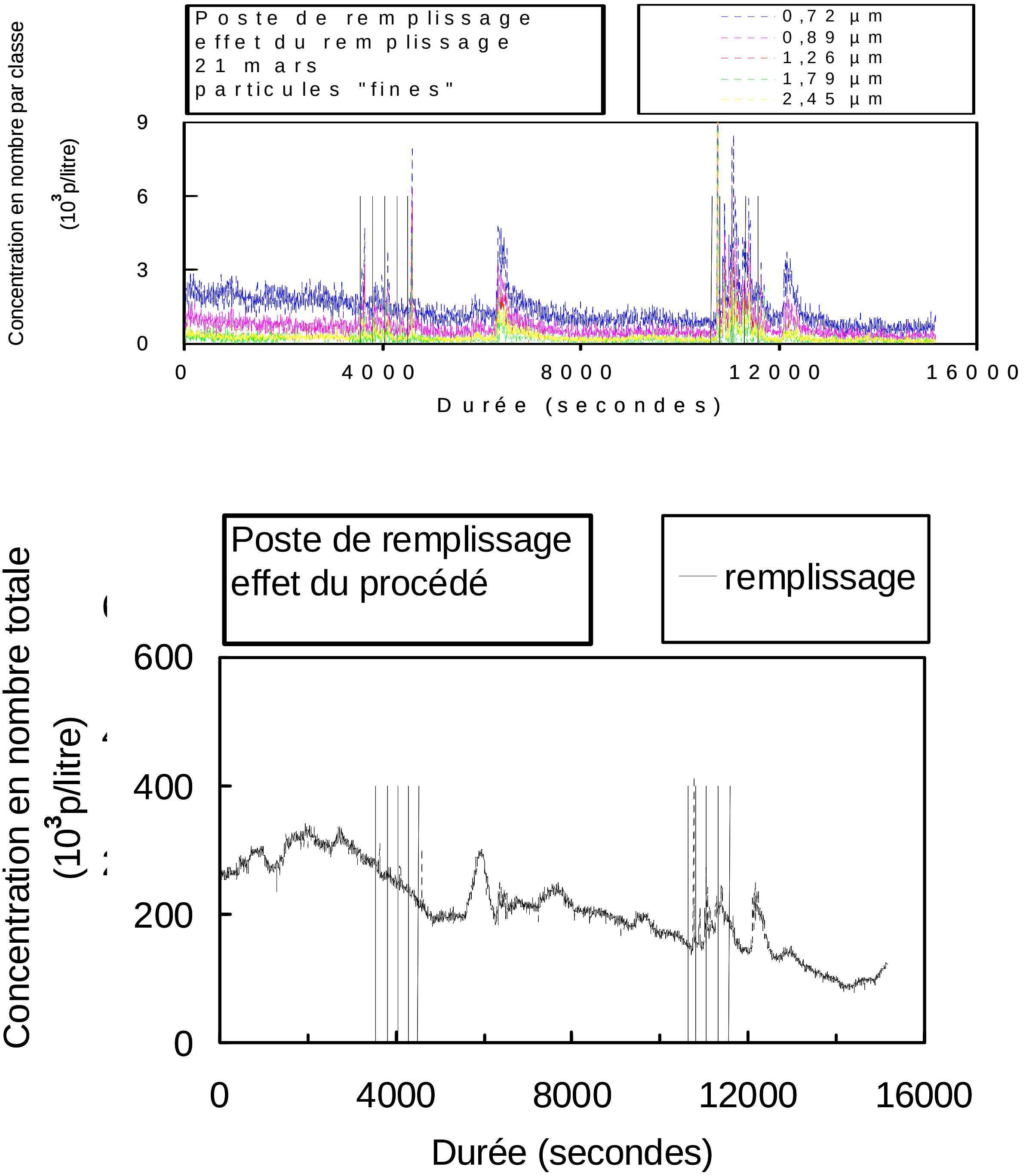


Figure 9: Particles concentration at the filling station (GRIMM, March 21). Fine particles above, all particles below.

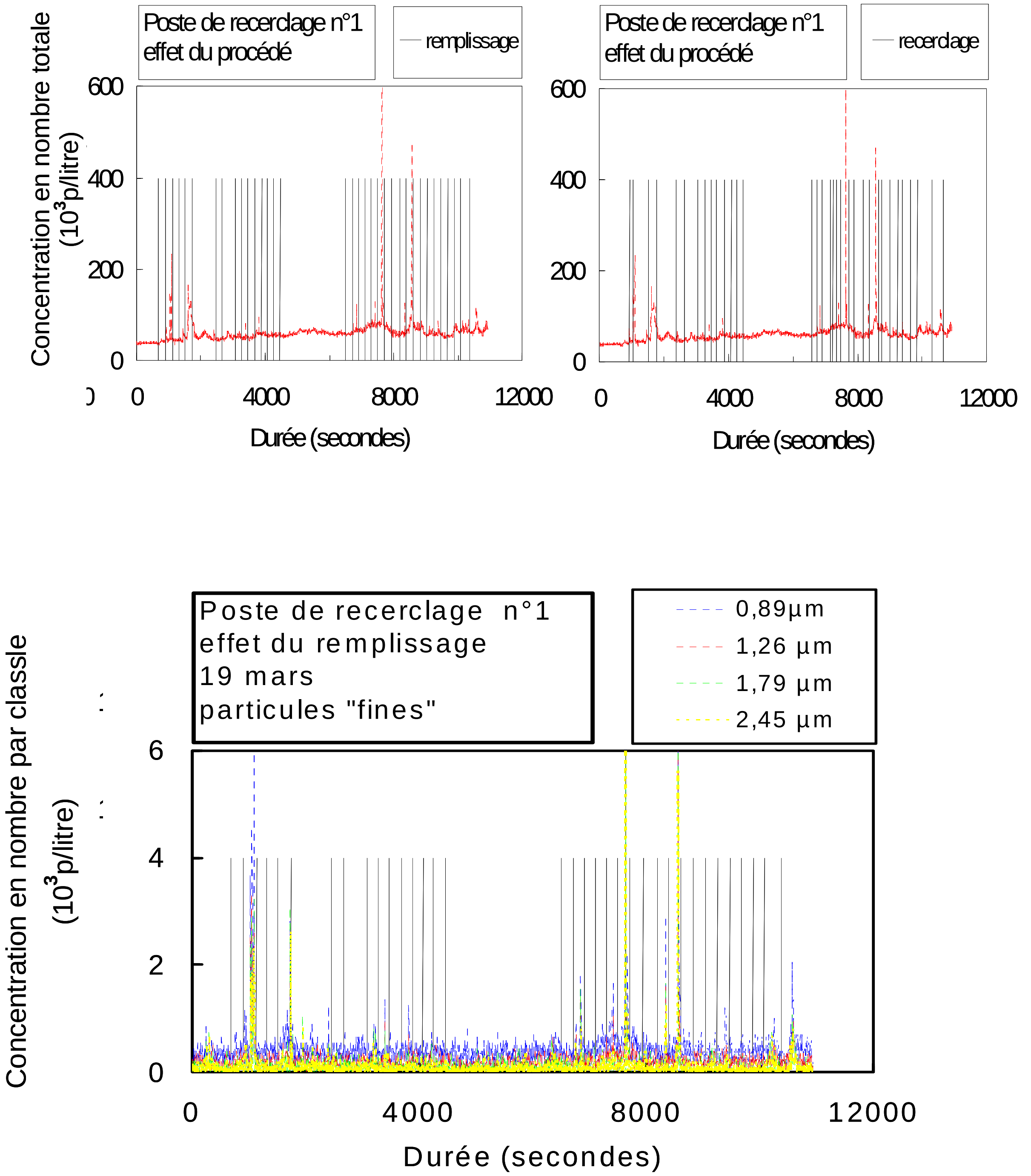


Figure 10: Particles concentration at the rebanding station (GRIMM, March 19). All particles above, fine particles below

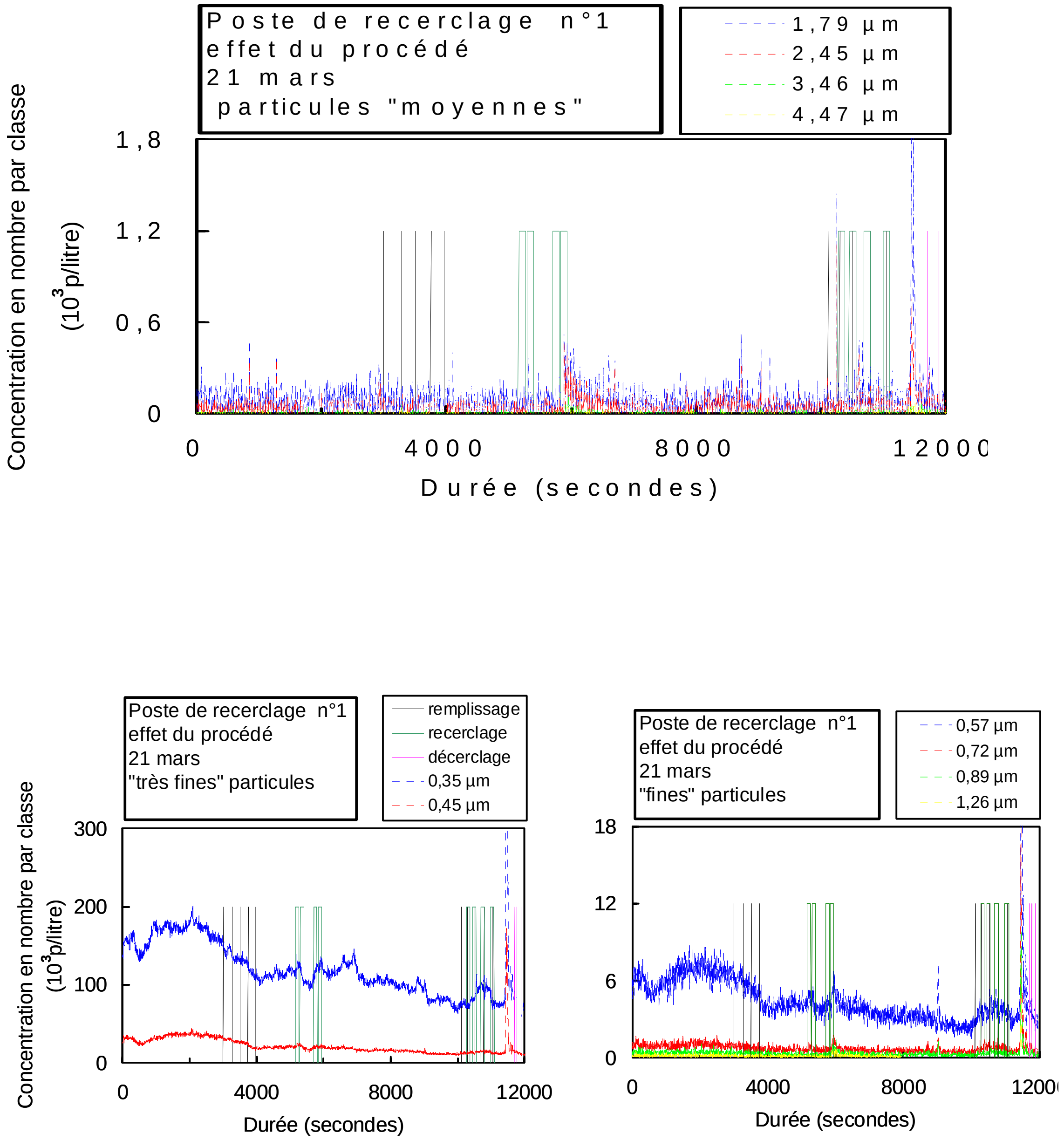


Figure 11: Particles concentration at the rebanding station (GRIMM, March 21). Medium particles above, fine and ultra-fine particles below.

7 ADDITIONAL PROTECTION ACTIONS

The two measurement campaigns following the introduction of protection measures at the filling station prompted two further protection actions that had been envisaged:

- the important contribution to exposure of rebanding operations with damaged drums led to a modification of the drums handling equipment.
- This latter fact, together with the identification of residual contamination peaks at the rebanding station, led to the removal of the rebanding workstation from the filling station, to the automated shutting of the lid during the rebanding operation, in order to avoid contamination releases, together with a dynamic confinement for this workstation (see Figure 12).

Figure 12 : New dynamically confined rebanding workstation, equipped with a lid shutting device

8 CONCLUSION

The different results of this case study have shown that although FAS may produce representative measurements of average daily activity concentrations at sampling points close to workstations, their use for the estimation of exposure (including the case where there is precise information on exposure times), is more uncertain and may result in substantial underestimation of exposure. This is because FAS measurements fail to properly reflect the dynamics of exposure, due to variation in contamination over time and space in the workstations and to operator movement.

As PAS are worn by operators, a more representative estimation of exposure is obtained, but their low sampling rate can provide, for reason of sensitivity, only monthly exposure estimates. Moreover, when this type of device is worn at the waist, a representative sample of the air inhaled cannot be obtained in the presence of high activity concentration gradients.

Due to their high sampling rate and their sampling point which is representative of the air inhaled, HSR-PAS make it possible to make sensitive estimates that are highly representative of daily exposure and appear to be the most suitable for analysis of exposures. The possibility of making daily measurements means that this device not only constitutes an operational dosimetry system but also a tool for analysing the causes and implementing corrective action in the event of abnormally high individual exposure. Its daily measurements could also be used to determine a realistic incorporation time-profile for the dosimetric interpretation of bioassays. Finally, the measuring campaigns carried out have demonstrated the feasibility of on-site daily measurement of the activity of the filters of the HSR-PAS. The main drawback of this system remains the fact that it is relatively heavy, weighing approximately one kilogram. However, the possibility of placing the sampling head at a distance from the main part of the equipment makes it possible to envisage a suitable carrying system.

The different measurements made with FAS and PAS have made it possible to establish the substantial contribution (more than half) of the rebanding station to the sampling workplace operators exposure. The study of correlation between activity concentration and operation duration permitted to postulate that most of the exposure at the rebanding station result from contamination peaks generated by the operations carried out there· And confirmed the decision to modify and confine the filling station.

Additional PAS (and switched PAS) measurements allowed an assessment of the efficiency of the filling station protection measures, and confirmed the need for additional protection actions (modification of drums handling equipment and modification, removal and dynamic confinement of the rebanding station). The use of a multi channels RTMD showed the usefulness of such devices in identifying contamination peaks and relating them to specific process steps, although such devices are more suited to situations with low specific activity materials.

Finally, this case study showed the significant day to day variability of the results, and the real importance of gathering numerous measurements and applying to them standard statistical analysis methods to obtain useful results. Furthermore, it put in evidence the practical interest of such measurement campaigns that have allowed to reduce significantly the exposure of the operators at the sampling station.

9 REFERENCES

[1] ICRP 68 International Commission on Radiological Protection: Dose coefficients for intakes of radionuclides by workers. ICRP publication 68. Annals of the ICRP 24 (4). Pergamon Press, Oxford,1994.

[2] ICRP 66 International Commission on Radiological Protection: Supporting guidance 3: Guide for the practical application of the ICRP Human Respiratory Tact Model, ICRP publication 66. Annals of the ICRP 32 (1-2). Pergamon Press, Oxford, 2002.

[3] ICRP 54 International Commission on Radiological Protection: Individual Monitoring for Intakes of Radionuclides by Workers: Design and Interpretation, ICRP Publication 54, Annals of the ICRP18, (1-4). Pergamon Press, Oxford, 1988.

[4] LUDEP 2.0, Jarvis, N.S., A. Birchall, A.C. James, M.R. Bailey, and M.-D. Dorrian. LUDEP 2.0: "Personal Computer Program for Calculating Internal Doses Using the ICRP Publication 66 Respiratory Tract Model.", National Radiological Protection Board, NRPB-SR287, Chilton, UK, 1996.

[5] S.Fauvel, G.Basso Et O.Witschger, Comparaison de techniques de prélèvement d'aérosols.atelier d'échantillonnage des fûts d'uranium de l'usine COMURHEX, Rapport DSU / SERAC / 03- 06, IRSN, 2003.

COMURHEX MALVESI CASE STUDY

1 SITE HISTORY

The COMURHEX Malvési site is located in the south of France near Narbonne. The plant originated in 1959 as the Uranium Refinement Society (SRU) to produce metallic uranium ingots for the graphite-gas reactor system. In 1971, the society for COnversion of URanium into Metal and HEXafluoride (COMURHEX) resulted from the merging between SRU and the Pierrelatte Chemical Plants Society (SUCP) that produces since 1962 on the site of Pierrelatte uranium hexafluoride (UF_6) for gaseous enrichment from the uranium tetrafluoride (UF_4) produced on the Malvési site. The development of the enriched fuel reactors has required a large increase in the UF_4 production while the abandonment of the natural uranium reactor system has led to the cessation of the uranium metal production in 1992. COMURHEX is a COGEMA subsidiary company since 1992.

2 PROCESS DESCRIPTION

Uranium mining concentrates from all over the world (France, South Africa, Namibia, Australia, China, Canada, Spain, Gabon, Nigeria, Portugal and states from former USSR) are received in 225 l drums. The concentrates, that contain from 70% to 75% of uranium, have different chemical forms: magnesium, sodium and ammonium uranates (MgU_2O_7, $Na_2U_2O_7$, $(NH_4)_2U_2O_7$), oxide (UO_3 - U_3O_8) resulting from ammonium uranate calcination, and uranium peroxyde (UO_4).

The refining/conversion process has a double function: first, to refine the uranium concentrates in order to achieve a nuclear grade final product (to remove neutron poisons such as cadmium and boron as well as other impurities that would impair the physical and chemical processes needed to produce the final product); second, to carry out the chemical conversion towards the desired chemical form (UF_4).

Following receipt, the mining concentrates are dissolved into nitric acid (HNO_3) to obtain uranyl nitrate (UO_2 $(NO_3)_2$). This solution is then purified in columns where liquid-liquid exchange takes place between the uranyl nitrate solution and the tributyl-phosphate (TBT) solvent. The resulting solution is then concentrated. By injection of gaseous ammonia (NH_3), ammonium diuranate $(NH_4)_2U_2O_7$) is obtained, that is calcined at 500°C to obtain uranium trioxide. This is then passed through a series of vertical furnaces, where it is first reduced into uranium dioxide (UO_2) and then transformed into uranium tetrafluoride (UF_4) by hydrofluorination on a gaseous hydrofluoric acid (HF) current.

The process is summarised in Figure 1

2.1 Sampling

The sampling step is fundamental for economical and political reasons: the plant is required to achieve a minimum conversion yield of 99.5%, by customers and by the international authorities that control the non-proliferation of radioactive materials.

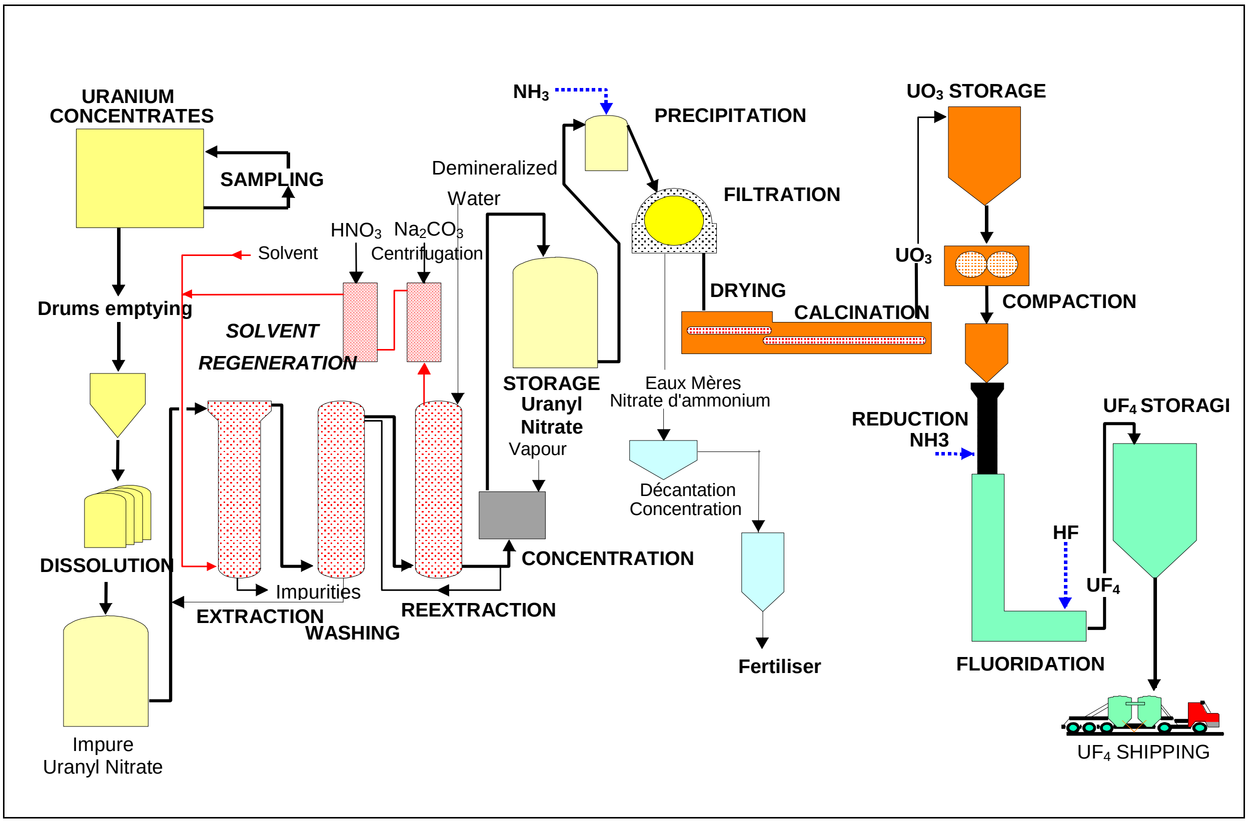


Figure 1 : Wet Process for refining/conversion of uranium mining concentrates

2.2 Dissolution

The drums of sampled concentrates are emptied into a silo. The concentrates are then dissolved with concentrated nitric acid (HNO_3) in a series of stainless steel tanks to produce an impure solution of Uranyl Nitrate ($UO_2 (NO_3)_2$).

2.3 Purification

The purification workplace uses a liquid-liquid exchange technique between the aqueous uranyl nitrate solution and the tri n-butyl phosphate (TBT) solution in dodecane that takes place in the largest purification column in the world, with a capacity of 14 000 t/year.

$2\ NO_3^- + UO_2^{2+} \leftrightarrow [UO_2 (NO_2)_2], H_2O \leftrightarrow [UO_2 (NO_3)_2] (TBP)_2$

This workplace comprises an extraction column, a washing column and a re-extraction column: The extraction column, where uranium is moved from the aqueous phase to the organic phase, receives at the top the impure uranyl nitrate solution and at the bottom the TBT solvent. The organic phase carries the uranyl nitrate/TBP complex and is collected at the top. The aqueous phase, depleted in uranyl nitrate but containing almost all the impurities present in the concentrate is collected at the bottom. In the washing column,the residual impurities are removed from the organic phase. In the re-extraction column uranium is removed from the organic phase to the aqueous phase. The organic phase, now depleted in uranyl nitrate, is collected at the top for further regeneration of the solvent while the aqueous phase with the purified uranyl nitrate, containing only some few ppm of impurities, is collected at the bottom of the column.

2.4 Precipitation/calcination

Gaseous ammonia (NH_3) is injected in the uranyl nitrate solution in order to produce an ammonium diuranate ($(NH_4)_2U_2O_7$) precipitate.

$2 [UO_2 (NO_3)_2] + 6 NH_4OH \rightarrow (NH_4)_2 U_2O_7 + 4 NH_4NO_3 + 3 H_2O$

The solid precipitate is separated from the water in a rotating filter operated under vacuum. The water constitutes a very pure solution of ammonium nitrate (NH_4NO_3) which is concentrated and used as liquid fertiliser. The ammonium diuranate falls directly from the filter on the moving conveyor belt of a drying and calcinating continuous furnace, where the filtration cake is passed through by a 500°C air flow.
$(NH_4)_2 U_2O_7 \rightarrow 2 UO_3 + 2NH_3 + + H_2O$

The resulting uranium oxide (UO_3) powder is stored and compacted before its introduction in the reduction/fluoridation furnaces.

2.5 Reduction/hydrofluorination

A parallel battery of several fluidised bed vertical furnaces is used to perform the reduction from uranium trioxide (UO_3) to uranium dioxide (UO_2), followed by the fluoridation of the uranium dioxide into uranium tetrafluoride (UF_4). The hydrogen required by the reduction of UO_3 into UO_2 is obtained *in situ* by the thermal cracking of gaseous ammonia (NH_3) on the uranium oxide bed heated up to 700°C.
$UO_3 + H_2 \rightarrow UO_2 + H_2O$

The UO_2 produced meets then the gaseous fluorhydric acid (HF) and produces UF_4 at a reaction temperature of 500°C.
$UO_2 + 4HF \rightarrow UF_4 + 2 H_2O$

The uranium tetrafluoride produced is finally stored in a silo from which it is loaded on special trucks for transport to the Pierrelatte COMURHEX plant.

2.6 Recycling

The recycling workplace receives all the uranium-bearing flows from the different workplaces and recycles them in the main production flow. This workplace processes also the uranium-bearing materials whose uranium grade is too low to enter directly the main flow. These materials come from the Pierrelatte plant as well as different installations (from France or foreign countries) that process natural uranium. The fluids that contain traces of non-reusable uranium are sent to decanting and evaporation ponds after having been neutralised with lime.

3 PROCESSING CAPACITY

With a yearly processing capacity of 14 000 t of uranium, COMURHEX supplies one third of the world UF_6 market and exports 40% of its production.

In 2001, the Malvési plant processed 12 000 t of uranium in the concentrates and produced the same quantity of uranium as UF_4. It used 16 000 t of nitric acid, 3 500 t of ammonia and 4 000 t of hydrofluoric acid, 3 500 t of gas oil and 29 000 million kWh.

4 IDENTIFICATION OF THE SAMPLING STATION

A study has been conducted in 1995 to estimate the annual external and internal exposure of the 170 exposed workers. Internal exposure by inhalation has been derived, from the data of daily averaged activity concentration measured by 26 Fixed Air Sampling (FAS) devices distributed among the several production units, and also, from an annual estimate of the time spent by each operator at the different workstations, together with the use of the ICRP 68 [1] dose coefficients appropriate to the solubility (moderate for uranates and slow for oxides) and the particle size distribution (Activity Median Aerodynamic Diameter (AMAD)=5µm) of the considered compounds. The results of this study showed that the annual collective effective dose (external+internal) of these 170 workers was 350 man.mSv, corresponding to an average annual individual effective dose of 2 mSv with an average contribution of the external exposure of 70%.

A more thorough study of these results showed that, 60% of the exposed workers were exposed to an annual individual dose below 2 mSv and most annual doses were below 5 mSv. However 6 workers from the sampling workplace (representing only 3% of the 170 exposed workers) received 12% of the plant collective dose, with corresponding annual individual doses between 6 and 12 mSv. In terms of internal exposure, those 6 workers were exposed to seven times more than the average and received about 25% of the plant annual internal collective dose, with corresponding annual individual doses between 1.5 and 6 mSv.

Finally, interpretation of the monthly urinary excreta as well as the yearly lung counting results of the sampling station workers for 1993 (with use of the ICRP 66 [2], 54 [3] et 68 [1] models as well as the LUDEP 2.0 code [4] for slow, 5µm AMAD compounds) showed that the annual dose estimates based on workplace air sampling could possibly underestimate the annual effective internal dose. Annual individual doses derived from urinary excreta ranged from 10 to 40 mSv, while doses derived from the yearly lung counting results - all below the detection limit – could nevertheless be compatible with annual doses as high as 50 mSv.

The results of this first study initiated efforts to better assess the dose of the workers of the sampling station as well as to study the principal characteristics of their exposure, in order to identify possible corrective actions and optimise the radiological protection of these workers. A comparison of the adequacy of various dose assessment methods for the optimisation of radiological protection in the case of exposure by inhalation to natural uranium compounds was then conducted in 1997. The best-adapted dose assessment methods were then used to conduct several measurement campaigns in 1997 and 1998 at the sampling workplace.

5 EXPOSURE ANALYSIS AND MEASUREMENT METHODS COMPARISON IN THE SAMPLING WORKPLACE

The workers of the sampling workplace take systematic samples of every drums of mining concentrate in order to analyse and record their uranium and impurities content. The successive steps of the process (see Figure 2) are the manual unbanding of the drum (unbanding stations), the - fully automated and confined - lid removal, drum emptying, primary (1%) and secondary sampling (1%) of the drum content, the automated filling and lid replacement of the drum (filling station), the manual removing of the secondary samples (secondary sampling station), the drum rebanding (rebanding stations 1 and 2), and finally the preparation of samples in a laboratory.

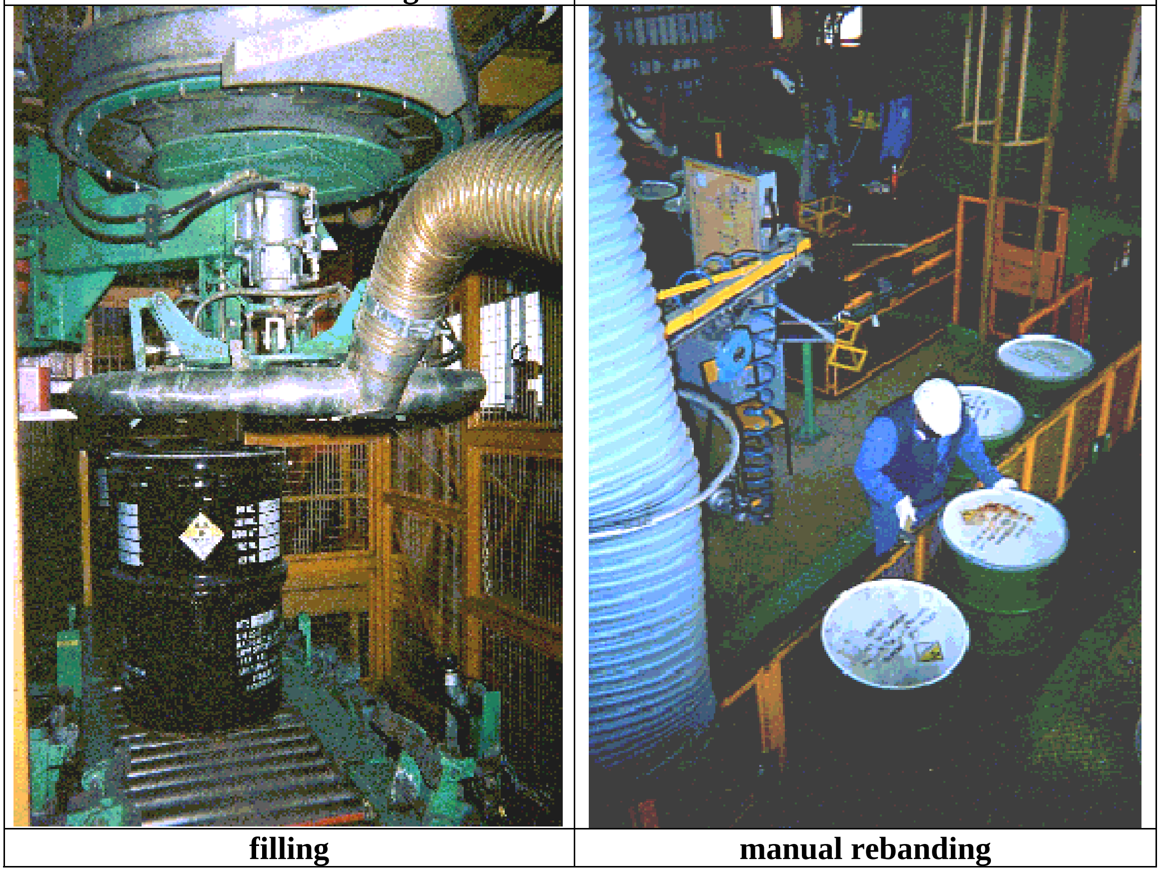
The study attempted to identify, through a number of measurement campaigns using personal and fixed air sampling apparatus, the operations that contributed the most to the exposure of operators at the sampling workplace. The study also included a comparison and analysis of the results of the different air sampling measurement methods, so as to determine which were, in this particular situation, the most suitable for analytical (task by task) estimation of individual doses with a view to optimisation of exposures.

This study relied on three types of sampling devices (see Figure 3) :

- Fixed Air Samplers (FAS) ; 1 200 $l.h^{-1}$ pump and 110 mm filter open sampling head ; Appareil de Prélèvement d'Air (APA), Merlin-Gerin. Most of those FAS were already present at the workstations for routine monitoring. Additional FAS were installed for this study at the sampling workplace.
- Low sampling rate Personal Air Samplers (PAS) ; 2 $l.h^{-1}$ centrifugal pump and 25 mm filter sampling head ; Integrated System for Individual Dosimetry (ISID), ALGADE. These light PAS (200 g) were originally designed for the monitoring of underground miners. The (integrated) pump and sampling head were worn on belt.

manual unbanding

lid removal



filling

manual rebanding

Figure 2: Sampling workplace process successive steps (floor 0)

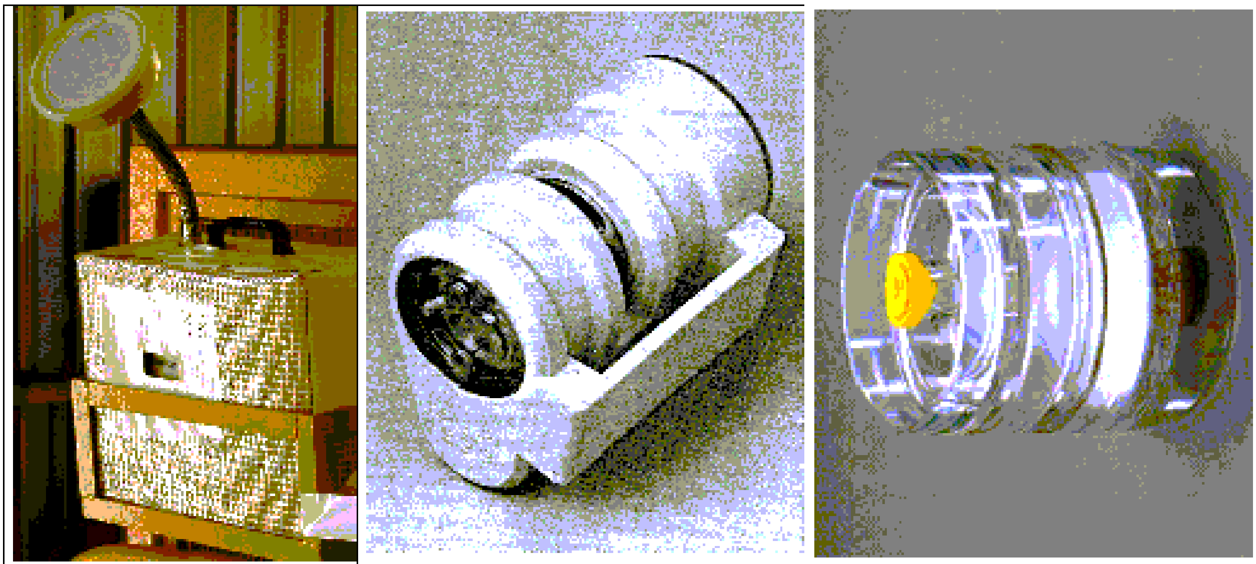
- High sampling rate Personal Air Samplers (HSR-PAS) ; 120 l.h^{-1} SKC pump and 37 mm filter plastic cassette SKC sampling head. This is the standard 37 mm cassette PAS. The pump was worn on belt and the sampling head in the operator's breathing zone.

The alpha activity on the filters from the FAS is measured with a large-area alpha counter with a detector diameter of 140 mm and an alpha background count rate of 1.5 cpm. The sample changer of the counting system allows 50 samples to be counted automatically. Routine counting times are 5 minutes. Filters from PAS were alpha counted on a low-background multi-detector alpha-beta counting system (IN20) with a background alpha count rate of 0.1 cpm. Usually eight filters were counted per day and counting times were extended to up to 20 hours.

The counting of filters on both counting systems was delayed to 20 hours after sampling to allow the decay of the short lived radon daughters.

9.1 Estimation of exposures per task with collective air sampling

Determination of per-task exposures by the combined use of fixed air sampling apparatus (FAS) (for the evaluation of daily average activity concentrations) and personal air sampling systems (PAS) assigned to each task (for evaluation of the daily work times at each station of a reference operator) has shown (see Table 2) that the workstations with the highest exposure in the months of May and June 1997 (excluding cleaning operations) were the rebanding stations (54%) and the unbanding stations (18%) (platform function) as well as the laboratory (14%) and the secondary sampling stations (8%) (laboratory function). It is interesting to note that the platform function which represents only 51% of the time spent, makes a 77% contribution to total exposure, which shows the more than average activity concentrations encountered at the corresponding workstations. Conversely, the laboratory function, which represents 49% of the time spent, represents only 23% of the total exposure excluding cleaning, which shows the less than average activity concentrations encountered there.



FAS
(APA, Merlin Gerin)

PAS
(ISDS, ALGADE)

HSR-PAS
(37 mm cassette, SKC)

Figure 3 : Fixed and personal samplers used in the COMURHEX case study

9.2 Estimation of exposures per task with individual air sampling

Comparison of the results of these exposure calculations with those of evaluations based on the one-month accumulated exposure readings of the PAS assigned to each of the tasks has shown (see last column of Table 2 and Table 3) that the latter indicated a similar ranking of the stations in terms of relative contribution to exposure with 86% of exposure for the unbanding and rebanding stations, and 14% for the secondary sampling station, which were the only two working stations for which the one-month integrated activity was greater than the detection limit.

However, it was found that the exposure estimates for May and June 1997 based on the PAS results for those two tasks were greater by a factor of 30 to 100 (45 to 70 for both months combined) than the corresponding estimates made using the FAS. Thus, the annual individual doses corresponding to exposure during these two months of the reference operator (calculated using a 1.2 m^3/h inhalation rate and a dose factor derived from ICRP Publication 68 [1] with the help of the LUDEP 2.0 software [4] for a compound of low solubility and an AMAD of 10 µm[7]) were 0.43 mSv/year and 16 mSv/year respectively, depending on whether they were determined using FAS or PAS.

The study then tried to determine the reasons for the significant difference between the measurements made by FAS and PAS, seeking to establish whether these differences result from the existence of air contamination peaks during operations (whose contribution is correctly integrated by the PAS but underestimated in the daily average of the FAS), the presence of systematic bias in the activity concentration measurement of either method, or the different sampling positions (distance and height) of both apparatus in relation to the sources of contamination.

Table 2: Contributions of tasks to total operation time and exposure

	Contribution to total operation time	Contribution to total exposure	
		(FAS)	(PAS)
Platform function			
Unbanding	**26%**	**18%**	**86%**
Rebanding	**17%**	**54%**	
Lid unsticking	3%	2%	BDL
Empty drums	1%	2%	BDL
Computer room	4%	1%	BDL
Laboratory function			
Computer room	3%	1%	BDL
Laboratory grinding	**5%**	**3%**	BDL
Laboratory heating	**36%**	**11%**	
Secondary sampling	**5%**	**8%**	**14%**
Total	100%	100%	100%
Platform function	**51%**	**77%**	**86%**
Laboratory function	**49%**	**23%**	**14%**

(BDL) One month integrated activity below detection limit

---

[7] Standard value close to the activity median aerodynamic diameter of 9 µm measured at the workstations.

Table 3: Dose estimates per task (2 months) by FAS and PAS

	Effective dose (Sv)		PAS / FAS
	FAS	PAS	
Platform function			
Unbanding	**$6.1\ 10^{-5}$**	**$2.7\ 10^{-3}$**	**44**
Rebanding			
Lid unsticking	$2.1\ 10^{-6}$	BDL	-
Empty drums	$1.5\ 10^{-6}$	BDL	-
Computer room	$1.1\ 10^{-6}$	BDL	-
Laboratory function			
Computer room	$5.8\ 10^{-7}$	BDL	-
Laboratory grinding	**$1.2\ 10^{-5}$**	BDL	-
Laboratory heating			
Secondary sampling	**$6.6\ 10^{-6}$**	**$4.6\ 10^{-4}$**	**69**
Total	**$8.6\ 10^{-5}$**	**$3.2\ 10^{-3}$**	
Total annual dose	**$4.3\ 10^{-4}$**	**$1.6\ 10^{-2}$**	

(BDL) One month integrated activity below detection limit

9.3 Testing for the existence of contamination peaks during operations

To determine whether any concentration peaks generated by the operations themselves could explain the disparity between the exposure evaluations made with FAS and PAS, the best approach appeared to be to study the correlation between the daily averaged activity concentrations measured with the FAS at the different workstations and the amount of time spent there by the operators.

This study showed a significant positive correlation between the daily average concentration at the unbanding station and the time spent by the reference operator at this place, as well as a significant negative correlation between the daily average concentration at the secondary sampling station and the time spent by the reference operator at this place. No significant correlation between the average concentration and the time spent by the operator were found for the other stations.

In order to interpret the observed correlations, we may try to formulate as follows the relation existing, at a given workstation, between average activity concentration measured by a FAS and activity concentrations existing at this station during and outside the operations conducted at this station:

$$C_{FAS} = (T_{work}\ C_{work} + (T - T_{work})\ .\ C_{T - T_{work}}) / T$$

with:

C_{FAS}	Daily averaged activity concentration measured by the Fixed Air Sampler (FAS)
C_{work}	Daily averaged activity concentration during operations
$C_{T - T_{work}}$	Daily averaged activity concentration outside operations
T	Daily measurement duration of the FAS
T_{work}	Daily operation duration

Similarly, activity inhaled during operations at a given workstation may be expressed as follows:

$$A = V_R\ .\ T_{work}\ .\ C_{work}$$

with:

A	Daily activity inhaled during operations
V_R	Ventilation rate

We may then test the impact on these formulations of three simple categories of activity concentration time profile during operations:

1 - Operations at a given workstation have no impact on the contamination of this workstation ($C_{FAS} = C_{work}$)
The average activity concentration and the operation duration are then independent and activity inhaled during operations at a given workstation may then be expressed as:
$A = V_R . T_{work} . C_{FAS}$

2 - Operations at the workstation are the only source of contamination of this workstation ($C_{T - T_{work}} = 0$)
The average activity concentration and the operation duration are then positively correlated and activity inhaled during operations at a given workstation may then be expressed as:
$A = V_R . T. C_{FAS}$

3 - The contamination of the workstation is null during operations ($C_{work} = 0$)
The average activity concentration and the operation duration are then negatively correlated for $C_{FAS} = (1 - T_{work} / T) C_{T - T_{work}}$ and activity inhaled during operations at a given workstation may then be expressed as:
$A = V_R . T_{work} . C_{work} = 0$

This formulation, together with the observed correlations between activity concentrations measured by the FAS and total duration of operations, allowed us to divide the workstations into three types:

1 - The rebanding workstation is characterised by the fact that the operations carried out there appear to be the main source of contamination of the station. The estimation of the exposure there using FAS could be thus carried out by simply multiplying the daily average activity concentrations measured by the sampling time per day. However, an exposure estimate of this type still remains lower by a factor of 10 than one using PAS.

2 - The secondary sampling station exhibits contamination which appears to diminish while operations are carried out there. The use of FAS measurements would appear to be ill suited for estimating the exposure received in such a station.

3 - Finally, it would appear that the operations carried out in all the other workstations have little impact on the contamination prevailing there and that the method consisting of multiplying the average daily activity concentration measured using FAS by the daily work duration appears to be the best suited for determining exposure on the basis of FAS measurements.

9.4 Testing for the existence of systematic bias in the activity concentration measurement methods

To detect systematic bias in FAS and PAS exposure estimates, two measurement campaigns were carried out (December 1997 and March 1998) to compare the monthly activity accumulated over eight hours per day by PAS and FAS placed at a distance of less than 30 cm and operated simultaneously. The results of these measurements have made it possible to observe differences of up to a factor of three (on one side or another) in exposure estimates made using FAS and PAS. In the light of these results, there is assumed to be no systematic overestimation of the measurement of activity concentration by PAS compared to FAS but an important variability which may be possibly due to high activity concentration gradients.

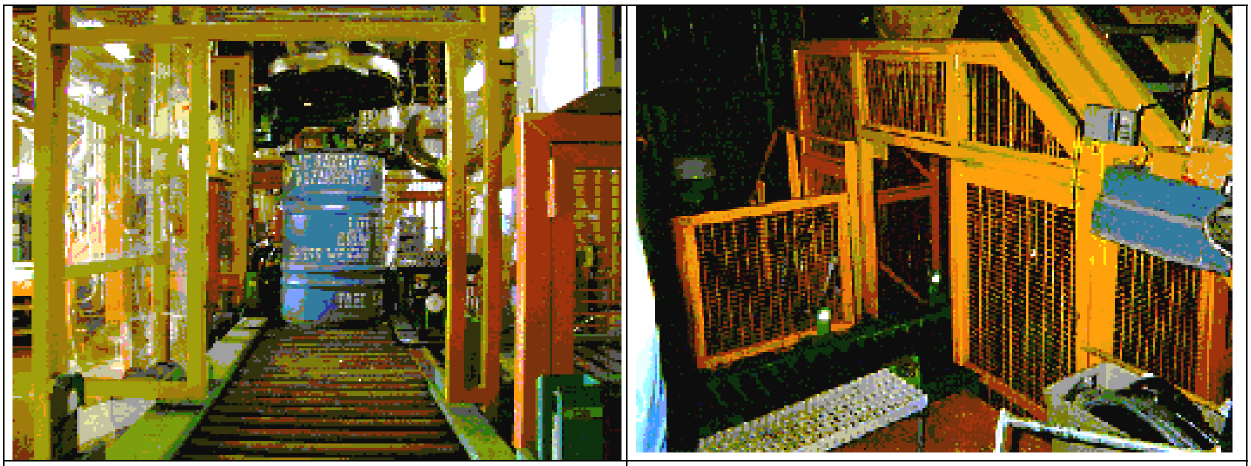
9.5 Testing for the importance of sampling position

Finally, the importance of the sampling point position relative to the sources of contamination and the operator's respiratory tract entrance was evaluated during a March 1998 measurement campaign to compare simultaneous estimations of exposure carried out using a PAS worn at the waist and a HSR-PAS, offering greater exposure estimation reliability, due to its higher sampling rate and its sampling point as close as possible to the entrance of the operator's respiratory tract. The results of this campaign have shown that for both platform and laboratory tasks, monthly exposure estimates made using PAS exceeded those made using monthly totals of the daily HSR-PAS measurements by a factor of two. That difference can be possibly explained by the greater proximity to the sources of contamination of the PAS, which is worn at the waist. These results confirmed thus the acceptable accuracy of the PAS measurements under these conditions and suggested the existence of important contamination gradients which may partly explain the still lower activity concentration measurements of FAS, which are further away from the sources of contamination and higher, compared to HSR-PAS.

10 EXPOSURE ANALYSIS IN THE SAMPLING WORKPLACE AFTER CONFINEMENT OF THE FILLING STATION

Following this first PAS measurement campaign, it was decided to implement two corrective actions at the filling station:

- the filling hopper was modified in order to eliminate frequent drum overfilling incidents that were the source of significant contamination.
- The filling station was confined, however with some unprotected openings (see Figure 4) allowing for the entrance of the empty drums and the exit of the filled drums to the rebanding workstations.



Empty drums entrance | **Filled drums exit**

Figure 4: Openings in the filling station confinement

10.1 First measurement campaign

A first measurement campaign was conducted during one month in October 2001 in order to estimate the impact on exposures (especially those received at the rebanding stations) of the filling station modification and to identify additional protection actions that would allow, if necessary, to decrease further the exposures.

For this purpose, three types of air sampling devices were used in combination (see Figure 5):

- Twelve FAS were allocated to the various workstations in the sampling-taking workplace. They were switched on during the whole work shift duration and measured thus the time-averaged concentration during the shift at the given location.
- HSR-PAS were used in the following way:

  - The two workers belonging to the platform function (and thus involved in the drums unbanding and rebanding operations) carried HSR-PAS that were switched on during their whole work shift duration and allowed thus to estimate during a shift the collective exposure and work duration associated with the operations of the platform function.
  - Three HSR-PAS were allocated to the most potentially exposed workstations (unbanding, rebanding 1, rebanding 2) and used as FAS. They were switched on[8] by the workers only when they carried out a task at the given workstation. These HSR-PAS allowed thus to estimate, for each of these three workstations, the collective working time spent during a shift at the given workstation, as well as the averaged activity concentration during the operations.
- A Continuous Air Monitor (CAM)[9] was used at various locations (inside the filling station and at the rebanding workstation) to record the time-profile of the airborne activity concentration.

Three sets of uranium oxide drums were sampled during the campaign:
- set 1: RANGER drums (524 drums, 16 days).
- set 2: PRIARGUNSKY drums (190 drums, 4 days) ; easily dispersible product
- set 3: MAC ARTHUR drums, (150 drums, 4 days) ; damaged drums

---

[8] using the Pause button in order not to reset the pump volumeter

[9] CAM with α, β real-time detection by silicium detectors on a paper filter, and dynamic compensation for α, β radon daughters ; ABPM 302 CAM, MGP Instruments (see Figure 5)

Figure 5: Detailed measurements with FAS, PAS, switched PAS, CAM and RTMD

The statistical comparison (comparison of means before and after protection of the filling station) of the daily average concentrations measured by switched HSR-PAS at the rebanding 1 station have shown that while the average daily concentrations measured by the FAS were not statistically different, the average daily concentrations measured by the switched PAS after protection were both much lower (by a factor of 10) and less dispersed than those measured before the protection measures were implemented.
In addition, one could observe that the daily averaged concentrations measured by APA at the rebanding 1 workstation were always lower (by a factor of 4 on average) than those measured inside the confinement of the filling station. Moreover, the ratio of the average activity concentration measured by switched HSR-PAS and APA has been found to be much lower (ratio of 1.5) for the rebanding 1 station than for the rebanding 2 and unbanding stations (ratios of 7 and 3).
The results of this analysis are coherent with the hypothesis that the confinement of the filling station has significantly reduced the contamination peaks from the filling station reaching the rebanding 1 station.

The daily averaged activity concentration at the rebanding station 1, measured either by a FAS or a switched HSR-PAS (see Figure 6) has been found to be highly variable from one day to another and a detailed statistical treatment (multiple mean comparison) of the measurements analysing the impact of the drums set processed showed that:

- the FAS activity concentration at the rebanding workstation was significantly different for the three sets of drum processed, with set 3 > set 2 > set 1
- the switched PAS activity concentration at the rebanding workstation was significantly different for the third set of drum, with set 3 > set 2 = set1

Further analyses have been thus conducted separately for each set of drums, in order to take into account the potential importance of the product dispersability characteristics and the condition of the on the workers exposure.

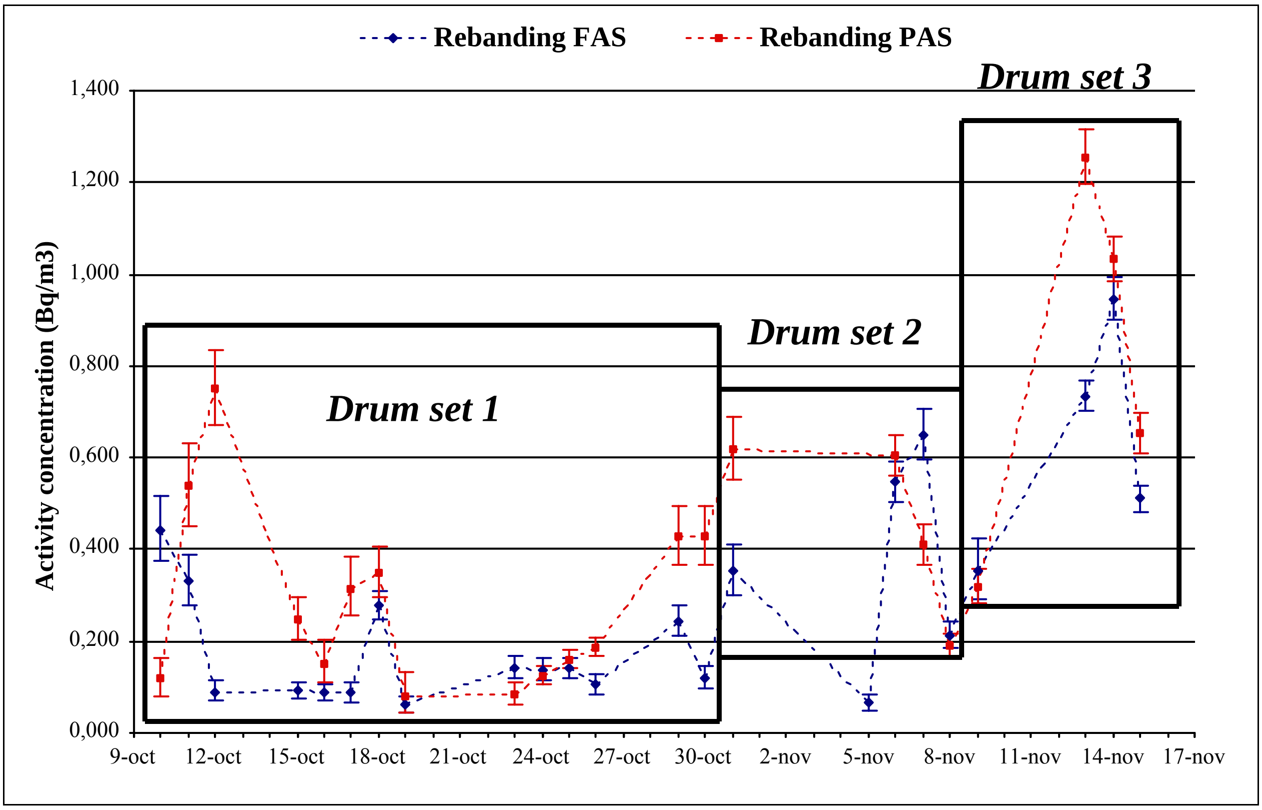


Figure 6: Comparison of the averaged activity concentration measured by FAS and switched PAS at the rebanding station

As shown in Table 4 the annual individual exposure estimated on the basis of the PAS worn by the workers PAS has been significantly reduced (by a factor of 6) by the modification and confinement of the filling station.

Table 4: Comparison of annual individual dose estimates before/after protection of the filling station

	Effective dose (Sv/year)	
	LSR-PAS	HSR-PAS
Before protection		
Platform function	16 10^{-3}	8 10^{-3}
After protection		
Platform function		
Drum set 1		1.1 10^{-3}
Drum set 2		1.7 10^{-3}
Drum set 3		1.3 10^{-3}
All sets average		1.2 10^{-3}

The expected annual collective exposure associated with the three sets of drums has not been found to be statistically different. However the comparison (for each set of drums) of the contribution of operations held at the unbanding and rebanding workstations to the collective work duration and exposure (measured by the switched HSR-PAS)has shown that these contributions did depend on the type of drums:

- After the implementation of protection measures, for drum sets 1 and 2 combined, the unbanding and rebanding workstations were no longer major contributors to exposure (they represent 29% of the exposure for 41% of the working time)
- in contrast,, for drum set 3, those workstations were still major contributors to exposure (they represent 61% of the exposure for 33% of the working time).

The results of this analysis, indicating that the rebanding operations (and to a less extent unbanding operations) could give rise to significant contamination releases when damaged drums were processed were found to be in good accordance with the observation of visible contamination releases from the damaged drums of set 3 during their rebanding.

10.2 Second measurement campaign

Finally, a three days measurement campaign was conducted in March 2002, in collaboration with the SERAC IRSN laboratory (see [5]), in order to:

- compare in a real working environment the performances of the air sampling devices used at COMURHEX with those of reference samplers (see Figure 7)
    - The APA FAS was compared with a CATHIA FAS
    - The 37 mm cassette HSR-PAS (closed and open) were compared with a button and IOM PAS, with the help of the CALTOOL device
- study the capabilities of a Real Time Monitoring Device (RTMD) (GRIMM G 1.108 eight channels optical particles counting device, GRIMM) to provide information on the air concentration time profile in order to better distinguish, at the rebanding station, the respective contributions to the airborne contamination of the contamination escaping from the filling station and from the rebanded drums (see Figure 5)

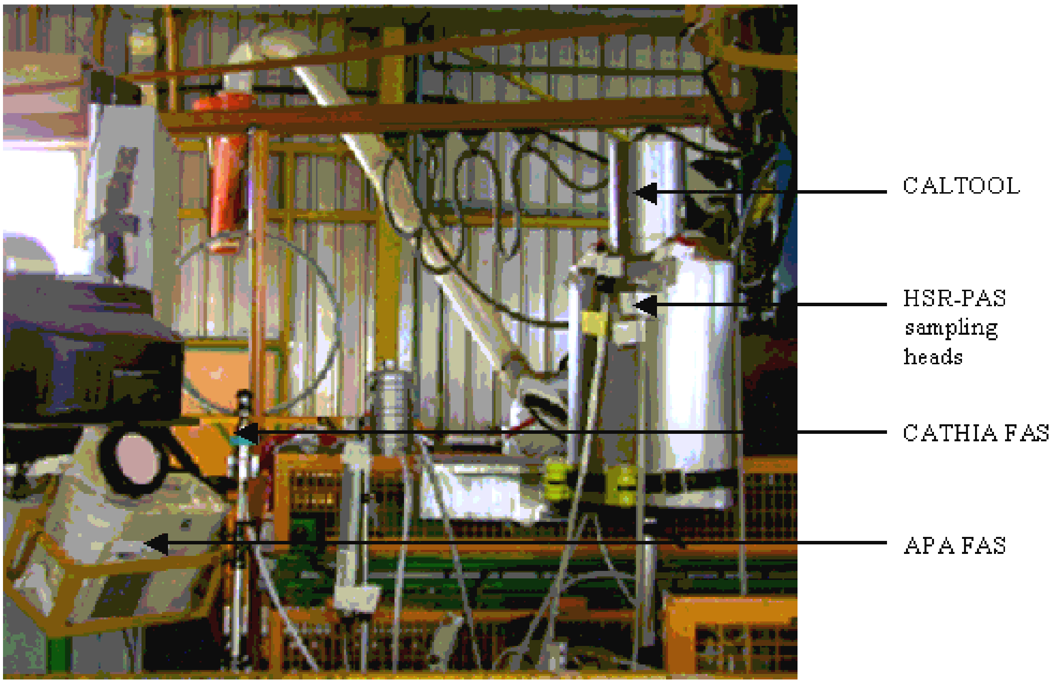


Figure 7: On-site comparison of air samplers with reference air sampling devices

Concerning the performance of the air sampling devices used at COMURHEX, the main results of this measurement campaign are as follows:

- activity concentrations measured by the APA FAS have been found to be very close to those measured by the reference CATIA FAS.

LSR-PAS

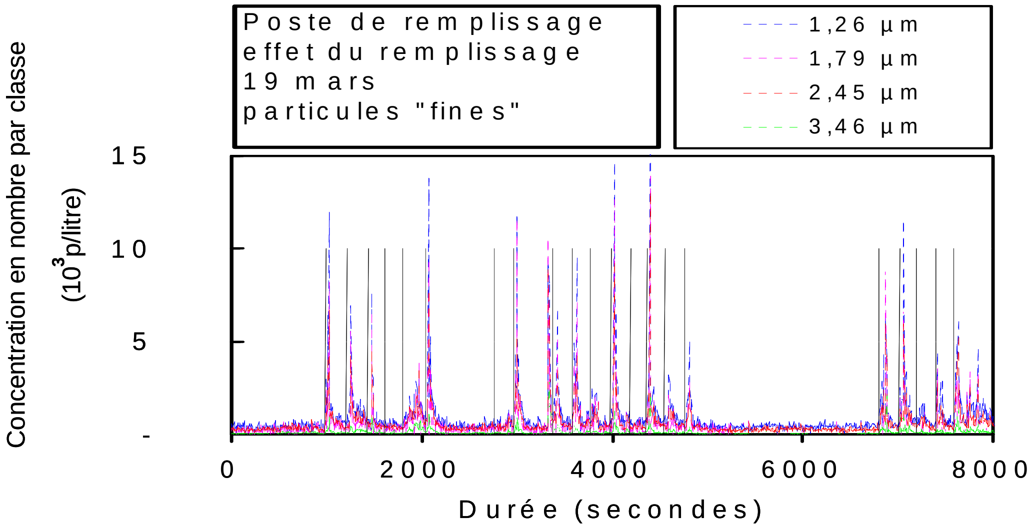
- activity concentrations measured by the HSR-PAS have also been found to be close to those measured by the reference CATIA FAS, but more dispersed than those measured with the APA. This comparison showed thus no systematic overestimation by the HSR-PAS of the activity concentration.
- activity concentrations measured by the IOM and Button PAS have been found to be very close to those measured by the reference CALTOOL PAS.
- Activity concentrations measured by the 37mm cassette (closed or open) have been found to be more dispersed, with activity concentrations measured with open face always higher than those measured with closed face. This comparison showed however no systematic overestimation by the HSR-PAS of the activity concentration.

The GRIMM real-time multi-channel optical particle counter was used for two days, in two locations (inside the filling station and at the rebanding workstation). The first day corresponded to a normal operation of the sampling station while the second one corresponded to separate filling and rebanding operations, in order to try to separate their contributions to the particle counts.

Inside the filling station (see Figure 8 and Figure 9), the measurements have shown a visible correlation of the particle counts with the filling operations (presented as vertical bars) that was more marked for fine particles (right side of Figures 8 and Figure 9) and bigger particles than for all sizes together (left side of Figure 8 and Figure 9), due to the important background of ultra fine particles. One can also note the visible impact on particle counts (see middle peak on Figure 9 for fine particles) of the resuspension of deposited contamination due to the entrance of an operator inside the confinement for maintenance purpose.

At the rebanding workstation (see Figure 10 and Figure 11), while particle concentrations peaks were still visible, these peaks were less pronounced and while the effect on particle counts due to dust resuspension by operators movements could be noticed, it was not possible to discriminate the contribution to these peaks of the filling and rebanding operations. Actually, for measurements held on March 20, the filling and rebanding operations were too close in time to allow any discrimination (see left part of Figure 10) and for measurements held on March 21, the background of ultra fine and fine particles (see left part of Figure 11) was so high compared to the process-related particles, that particle counts peaks could hardly be noticed, even for medium and bigger particles (see right part of Figure 11).

These measurements showed that contamination was released inside the filling station during the filling operations and that some contamination peaks (although much less important) were also present at the rebanding 1 workstation. They indicated not only the effectiveness of the filling station confinement on the contamination levels at this workstation, but also the existence of residual contamination peaks at the rebanding workstation, that could come both from the filling and rebanding operations. Lastly, these measurements highlighted the need for a multi-channel RTMD (that could differentiate particle sizes), in order to discriminate the process-related particles from the background particles.



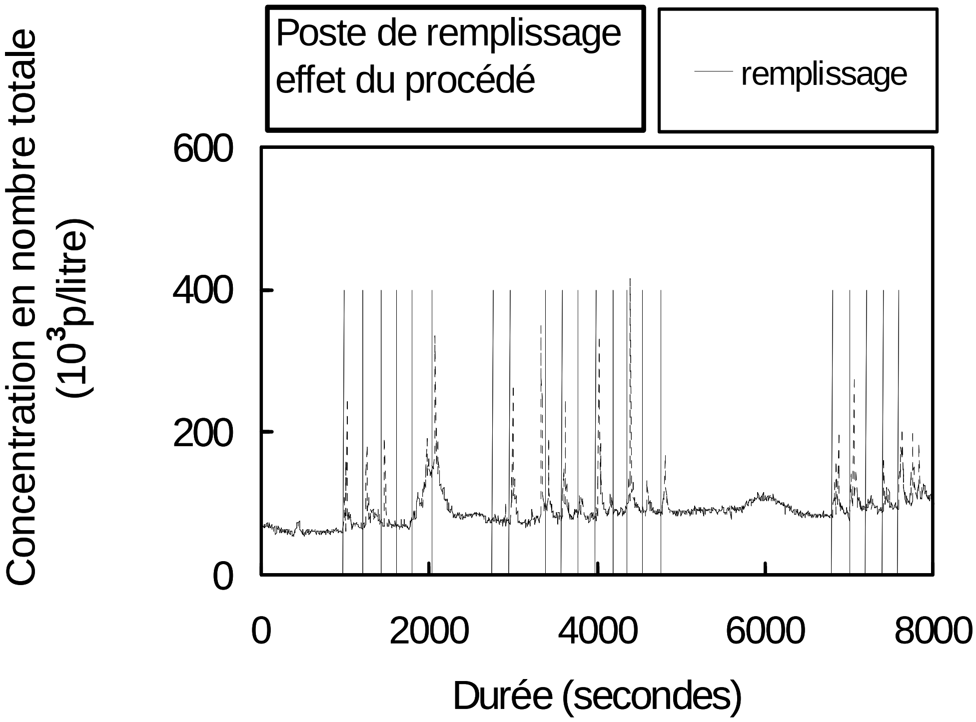


Figure 8: Particles concentration at the filling station (GRIMM, March 19). Fine particles above, all particles below.

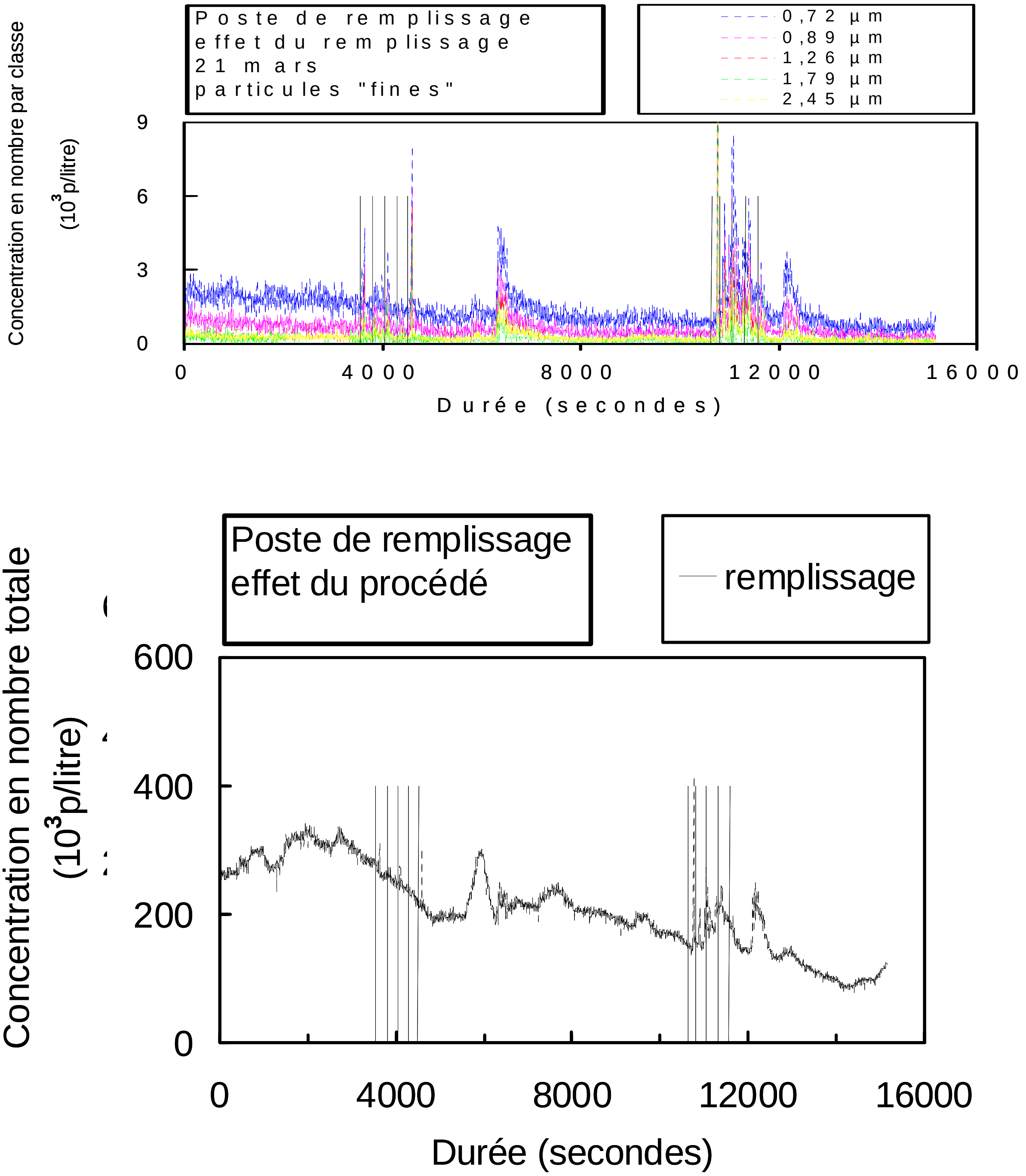


Figure 9: Particles concentration at the filling station (GRIMM, March 21). Fine particles above, all particles below.

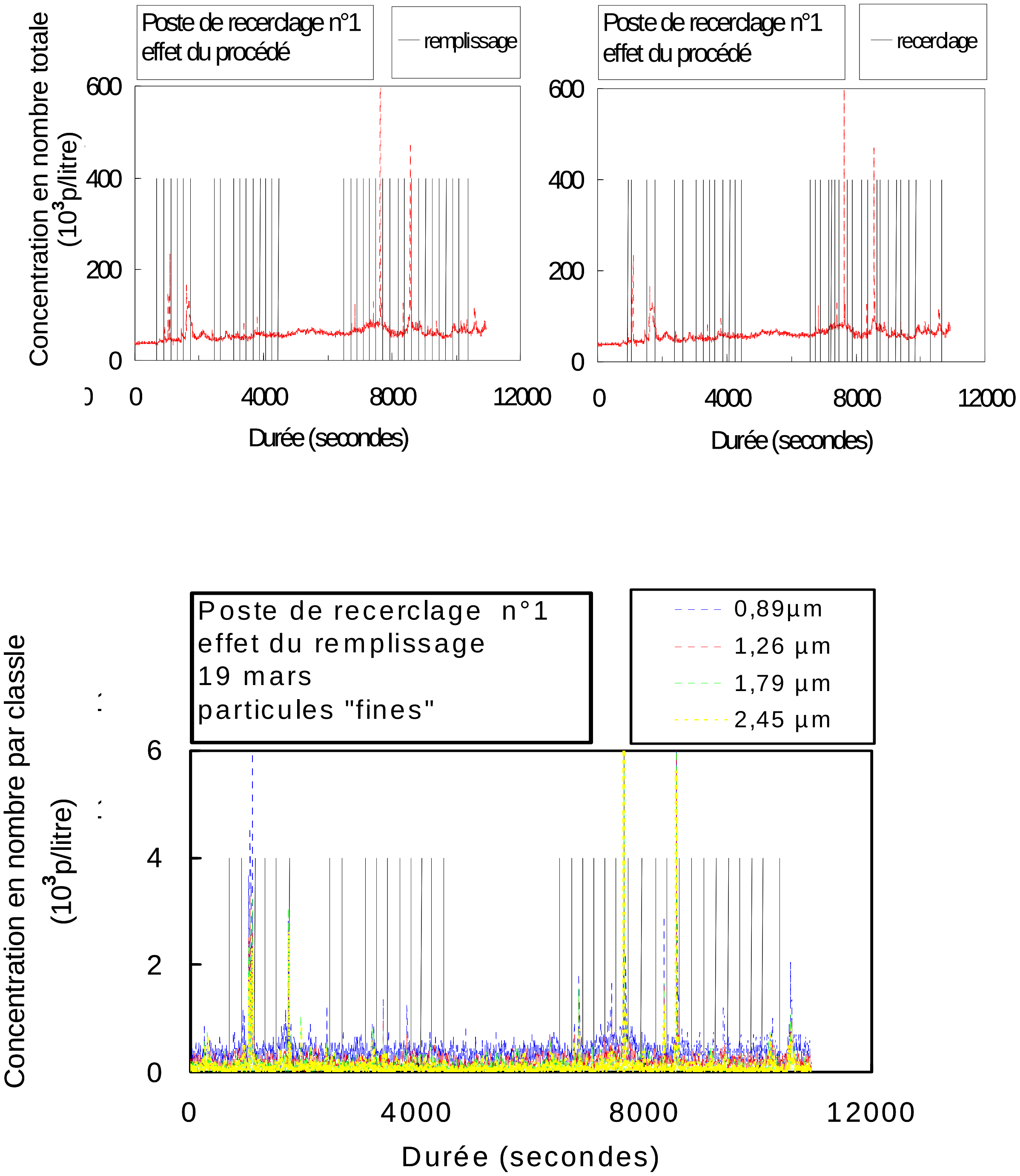


Figure 10: Particles concentration at the rebanding station (GRIMM, March 19). All particles above, fine particles below

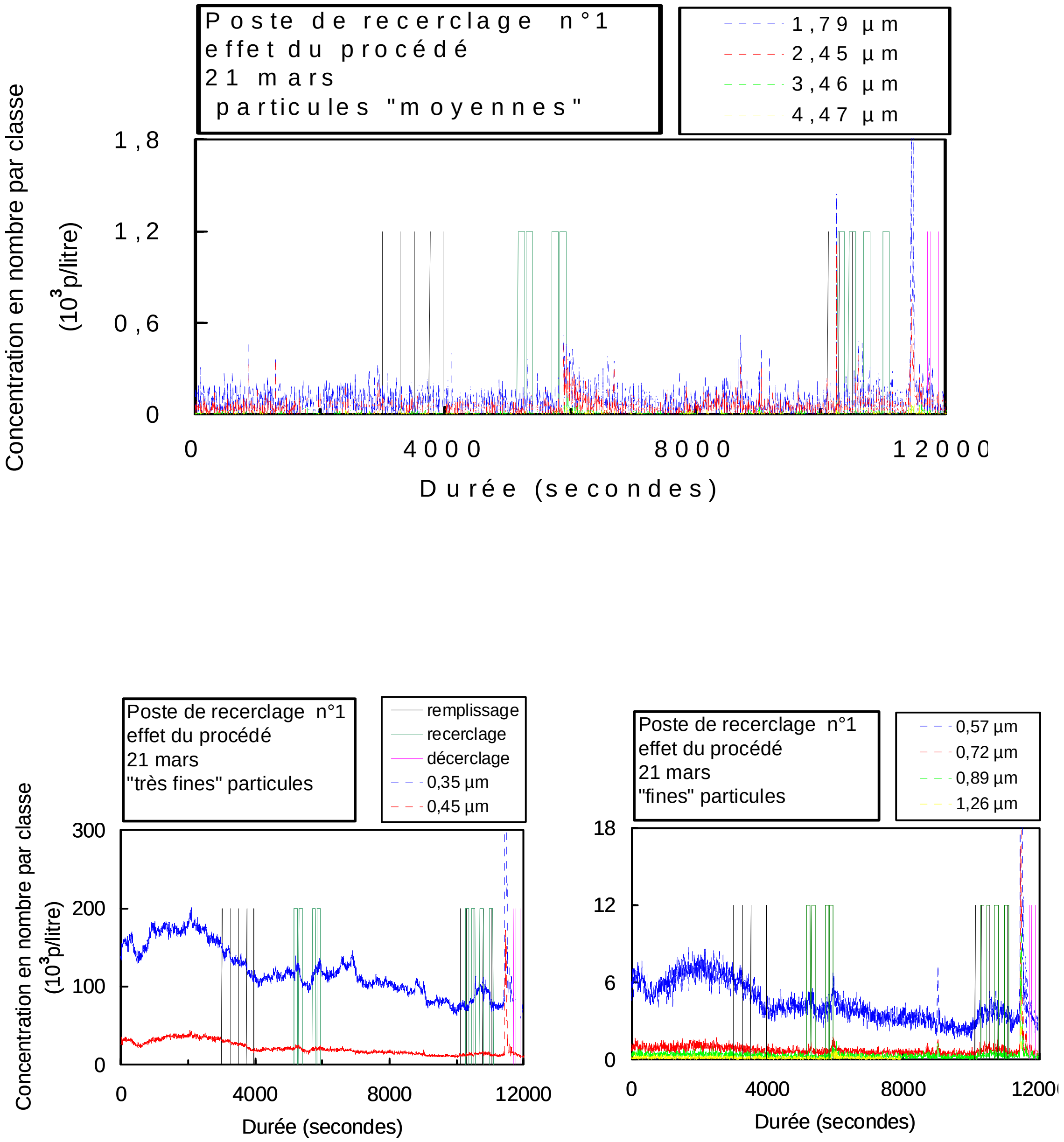


Figure 11: Particles concentration at the rebanding station (GRIMM, March 21). Medium particles above, fine and ultra-fine particles below.

11 ADDITIONAL PROTECTION ACTIONS

The two measurement campaigns following the introduction of protection measures at the filling station prompted two further protection actions that had been envisaged:

- the important contribution to exposure of rebanding operations with damaged drums led to a modification of the drums handling equipment.
- This latter fact, together with the identification of residual contamination peaks at the rebanding station, led to the removal of the rebanding workstation from the filling station, to the automated shutting of the lid during the rebanding operation, in order to avoid contamination releases, together with a dynamic confinement for this workstation (see Figure 12).

Figure 12 : New dynamically confined rebanding workstation, equipped with a lid shutting device

12 CONCLUSION

The different results of this case study have shown that although FAS may produce representative measurements of average daily activity concentrations at sampling points close to workstations, their use for the estimation of exposure (including the case where there is precise information on exposure times), is more uncertain and may result in substantial underestimation of exposure. This is because FAS measurements fail to properly reflect the dynamics of exposure, due to variation in contamination over time and space in the workstations and to operator movement.

As PAS are worn by operators, a more representative estimation of exposure is obtained, but their low sampling rate can provide, for reason of sensitivity, only monthly exposure estimates. Moreover, when this type of device is worn at the waist, a representative sample of the air inhaled cannot be obtained in the presence of high activity concentration gradients.

Due to their high sampling rate and their sampling point which is representative of the air inhaled, HSR-PAS make it possible to make sensitive estimates that are highly representative of daily exposure and appear to be the most suitable for analysis of exposures. The possibility of making daily measurements means that this device not only constitutes an operational dosimetry system but also a tool for analysing the causes and implementing corrective action in the event of abnormally high individual exposure. Its daily measurements could also be used to determine a realistic incorporation time-profile for the dosimetric interpretation of bioassays. Finally, the measuring campaigns carried out have demonstrated the feasibility of on-site daily measurement of the activity of the filters of the HSR-PAS. The main drawback of this system remains the fact that it is relatively heavy, weighing approximately one kilogram. However, the possibility of placing the sampling head at a distance from the main part of the equipment makes it possible to envisage a suitable carrying system.

The different measurements made with FAS and PAS have made it possible to establish the substantial contribution (more than half) of the rebanding station to the sampling workplace operators exposure. The study of correlation between activity concentration and operation duration permitted to postulate that most of the exposure at the rebanding station result from contamination peaks generated by the operations carried out there. And confirmed the decision to modify and confine the filling station.

Additional PAS (and switched PAS) measurements allowed an assessment of the efficiency of the filling station protection measures, and confirmed the need for additional protection actions (modification of drums handling equipment and modification, removal and dynamic confinement of the rebanding station). The use of a multi channels RTMD showed the usefulness of such devices in identifying contamination peaks and relating them to specific process steps, although such devices are more suited to situations with low specific activity materials.

Finally, this case study showed the significant day to day variability of the results, and the real importance of gathering numerous measurements and applying to them standard statistical analysis methods to obtain useful results. Furthermore, it put in evidence the practical interest of such measurement campaigns that have allowed to reduce significantly the exposure of the operators at the sampling station.

13 REFERENCES

[1] ICRP 68 International Commission on Radiological Protection: Dose coefficients for intakes of radionuclides by workers. ICRP publication 68. Annals of the ICRP 24 (4). Pergamon Press, Oxford,1994.

[2] ICRP 66 International Commission on Radiological Protection: Supporting guidance 3: Guide for the practical application of the ICRP Human Respiratory Tact Model, ICRP publication 66. Annals of the ICRP 32 (1-2). Pergamon Press, Oxford, 2002.

[3] ICRP 54 International Commission on Radiological Protection: Individual Monitoring for Intakes of Radionuclides by Workers: Design and Interpretation, ICRP Publication 54, Annals of the ICRP18, (1-4). Pergamon Press, Oxford, 1988.

[4] LUDEP 2.0, Jarvis, N.S., A. Birchall, A.C. James, M.R. Bailey, and M.-D. Dorrian. LUDEP 2.0: "Personal Computer Program for Calculating Internal Doses Using the ICRP Publication 66 Respiratory Tract Model.", National Radiological Protection Board, NRPB-SR287, Chilton, UK, 1996.

[5] S.Fauvel, G.Basso Et O.Witschger, Comparaison de techniques de prélèvement d'aérosols.atelier d'échantillonnage des fûts d'uranium de l'usine COMURHEX, Rapport DSU / SERAC / 03- 06, IRSN, 2003.