



# Radionuclide fluxes at a plant manufacturing dicalcium phosphate for domestic animals

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**Abstract.** The objectives of this study is to map out the fluxes of radionuclides from the  $^{238}\text{U}$  decay serie as well as estimate doses to workers at a dicalcium phosphate plant. At the studied plant phosphate rock is used for the production of dicalcium phosphate, which is a source of calcium and phosphorous for domestic animals. *A by-product in the manufacturing process is calcium chloride which is used in the oil industry, food industry and as road salt.* In the phosphate rock, the radionuclides were found in secular radioactive equilibrium with an average activity concentration of  $830 \text{ Bq}\cdot\text{kg}^{-1}$ . Separation and concentration processes was observed. Most of the  $^{226}\text{Ra}$  was found in the calcium chloride while the major part of  $^{238}\text{U}$  was found in the dicalcium phosphate, about  $950 \text{ Bq}\cdot\text{kg}^{-1}$ . The annual occupational effective dose to workers was found to be below the 1 mSv limit. The studie shows a good example of an important non-nuclear industry with a high input of natural radionuclides and several conceivable pathways to man.

## 1. Introduction

Phosphate rock of sedimentary origin is a main source of phosphorous for production of fertilizers and feed-supplements for domestic animals [1].

One feature of sedimentary phosphorite is its high abundance in natural radionuclides from the  $^{238}\text{U}$  decay serie. Using phospate rock of sedimentary origin as a raw material in an industry process thus will lead to an input of several different radionuclides with different chemical behaviour.

The objective of this study have been examine how radionuclides from the  $^{238}\text{U}$  decay serie are distributed in end-products, by-products and waste at the manufacturing process of dicalcium phosphate (DCP).

Effective doses to workers from inhalation of dust and radon have also been estimated.

## 2. Materials and methods

The DCP product is used as a supplement of phosphorous and calcium for domestic animals DCP can be provided to all kinds of animals but is primarily used as supplement for non-ruminant animals. Of the total food intake for the animals, DCP usually stands for 0.1–1 % of the weight.

The amount of phosphate rock used at the plant is 70300 tons per year.

At the initial step in the process the phosphate rock is partially dissolved in a hydrochloride acid solution. When  $\text{CaCO}_3$  has been added and the pH adjusted to  $\text{pH}=2$ , dicalcium phosphate is precipitated from the solution. The sludge (sludge 1) that is formed and separated in this step mainly consists of undissolved phosphate rock,  $\text{SiO}_2$  and flourid compounds as  $\text{CaF}_2$ . The remaining solution is used for production of calcium chloride in an adjacent plant. Before it enters this plant, mainly  $\text{Mg}(\text{OH})_2$  (sludge 2) is precipitated from the solution by changing the pH to  $\text{pH}=10$ . Both types of sludges are disposed close to the plant.

A scheme of the manufacturing process can be seen in fig.1.

The calcium chloride has many areas of use, mainly in the oil industry, food industry and as road salt. Several different qualities and concentrations are manufactured, both in soultions and solid forms. To produce calcium chloride of food quality, the solution of calcium chloride is purified by using active carbon.

$\text{CaCl}_2\cdot 6\text{H}_2\text{O}$  is obtained from a crystallization process where evaporation to saturation of the calcium chloride in the solution is followed by refrigeration.

Annual production of DCP, calcium chloride and different waste products is listed in table I.

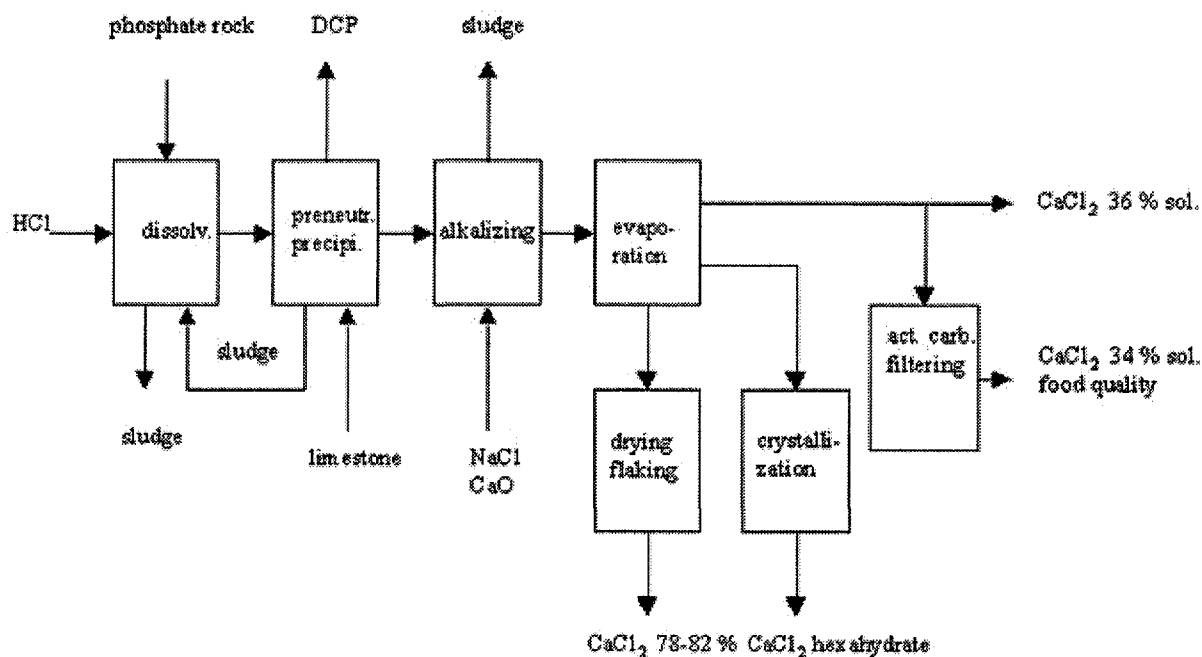


Figure 1. Schematic description of the manufacturing process.

Table I. Annual production of products and wastes

Material	Annual production [tons per year]
DCP	47100
Sludge 1	122000 (14600 dry weight)
Sludge 2	5500 (2000 dry weight)
CaCl <sub>2</sub> 36 % solution	42000
CaCl <sub>2</sub> 34 % solution (food quality)	6000
CaCl <sub>2</sub> ·6H <sub>2</sub> O	650
CaCl <sub>2</sub> 78–98 % (flakes and powder)	Approximately 70000

### 2.1. Radiochemical separation procedures and activity measurements

Slightly modified methods described by [2] were used for separation of uranium and thorium. The thorium was further purified from traces of uranium by ion-exchange (DOWEX, AG 1-4X, 100–200 mesh). As yield determinants <sup>232</sup>U and <sup>229</sup>Th was used.

Finally the uranium and thorium were electrodeposited on stainless steel disc at a current of 1 A for 1 hour from a sodium sulphate electrolyte [3].

For polonium methods described by [4] was used. From diluted hydrochlorid acid the polonium was spontaneously deposited on nickel discs at 65° C for 2 hours.

L-ascorbic acid was added to the sample to avoid deposition of Fe<sup>3+</sup> on the disc. As yield determinant <sup>209</sup>Po was used.

α-spectrometry was carried out with ion-implanted silicon detectors (FWHM 30–40 keV in the region 4.15 – 5.31 MeV).

<sup>226</sup>Ra was measured by sealing the sample in 200 ml radogas-tight steel containers. After 3 weeks storing when secular equilibrium was reached with its short lived decay products, the activity of <sup>226</sup>Ra was determined from the photopeaks of <sup>214</sup>Bi (609 keV) and <sup>214</sup>Pb (352 keV).

<sup>210</sup>Pb was measured from its 46.5 keV photopeak. After gamma spectrometric measurement of the sample, it was mixed with reference-ore (Canmet DH-1a) and measured again. From the results of both measurements <sup>210</sup>Pb concentration in the sample was calculated.

Gamma spectrometric measurements were carried out with an n-type HPGe-detector with 35 % relative efficiency and 1.8 keV FWHM at 1.33 keV.

Measurement times were sufficiently long to ensure the statistical counting errors to be less than 5 %.

## 2.2. Dose assessment and measurements

To estimate the annual effective dose from inhalation of dust, dose conversion factors were taken from [5] and [6].

Where information not have been available, as for particle size distribution, conservative assumptions have been made. The breath rate was set to  $1.5 \text{ m}^3 \cdot \text{h}^{-1}$ , corresponding to light exercise conditions [7].

According to information from the staff of the plant the average time spent per week in the production area is about 10 h.

The most dominating source for dust in the studied plant was where the DCP is dried after being filtered from the solution. Dust can also be released in connection with different interruptions in the operation of the plant. Most common is dust from the DCP-product. Interruptions producing DCP-dust is estimated to occur approximately 10 times per year while interruptions causing phosphate-dust occur approximately 5 times per year (duration 2 hours).

Concentration of dust in the air have been measured by the company at several occasions giving an average dust concentration of  $3.5 \text{ mg} \cdot \text{m}^{-3}$ , of which  $3 \text{ mg} \cdot \text{m}^{-3}$  has been assumed to origin from the DCP and  $0.5 \text{ mg} \cdot \text{m}^{-3}$  from the phosphate rock. Dust concentration in the control room was set to  $0.5 \text{ mg} \cdot \text{m}^{-3}$ . Maximum dust concentration measured in the plant is  $16 \text{ mg} \cdot \text{m}^{-3}$ .

The external dose measured at the plant was determined by using a doserate instrument (RADOS SRV-2000) calibrated in ambient dose equivalent ( $H^*(10)$ ). The calibration was traceable to the national standard laboratory at STUK (Finland).

The concentration of short lived radon daughters was measured at two occasions. One using the modified Tsivoglous method described by [8]. To calculate the radon gas concentration an equilibrium factor of 0.6 was assumed.

Radon has also been measured by track-etch detectors. Exposure times for the track-etch detectors were 12 days. The time between the two measurements was approximately 3 months.

The dose conversion factor for radon gas exposure ( $3.2 \cdot 10^{-6} \text{ mSv} \cdot \text{h}^{-1} \cdot \text{Bq}^{-1} \cdot \text{m}^3$ ) was taken from [9].

## 3. Results

See table II–VI.

Table II. Activity concentration [ $\text{Bq} \cdot \text{kg}^{-1}$  fresh weight]. The standard deviation are based on multiple analyses ( $n = 2$  or  $3$ ) for all radionuclides except  $^{210}\text{Pb}$  where it is based on results after repeated homogenizations of sample and reference ore. Dry weight to fresh weight ratios were measured to 0.12 for sludge 1, 0.37 for sludge 2 and 0.64 for active carbon

	$^{238}\text{U}$	$^{234}\text{U}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{210}\text{Po}$
Phosphate rock	832	830	816	$855 \pm 7$	$843 \pm 35$	820
DCP	$954 \pm 38$	$1012 \pm 42$	$10 \pm 1$	$15 \pm 1$	$169 \pm 7$	$350 \pm 2$
Sludge 1	$178 \pm 14$	$170 \pm 14$	$409 \pm 8$	139	$100 \pm 5$	-
Sludge 2	$8 \pm 0.5$	$8 \pm 0.2$	$12 \pm 4$	$78 \pm 8$	$3480 \pm 252$	-
CaCl <sub>2</sub> (82 %)	<0.01	<0.01	<0.01	$825 \pm 7$	$70 \pm 4$	-
CaCl <sub>2</sub> (78 %)	<0.01	<0.01	<0.01	$493 \pm 4$	$51 \pm 3$	-
CaCl <sub>2</sub> (36 %)	<0.01	<0.01	<0.01	$316 \pm 14$	$20 \pm 1$	-
CaCl <sub>2</sub> (stem solution 15 %)	<0.01	<0.01	<0.01	$138 \pm 4$	$100 \pm 9$	-
CaCl <sub>2</sub> ·6H <sub>2</sub> O (50 %)	<0.01	<0.01	<0.01	$21 \pm 1$	<5	-
CaCl <sub>2</sub> (food quality 34 %)	<0.01	<0.01	<0.01	$280 \pm 8$	$10 \pm 1$	-
Active carbon	$10 \pm 5$	$10 \pm 5$	4	147	$114 \pm 5$	-

Table III. Activity concentrations [ $\text{Bq}\cdot\text{kg}^{-1}$ ]. For active carbon the  $^{222}\text{Rn}$  concentration is expressed as Bq per kg fresh weight. The ratio dry weight to fresh weight was measured to 0.64

	$^{232}\text{Th}$	$^{40}\text{K}$	$^{222}\text{Rn}$
Phosphate rock	5	4	-
Active carbon (4 h after filtration)	-	-	31000

Table IV. Measured ambient dose equivalent rates [ $\mu\text{Sv}\cdot\text{h}^{-1}$ ] at different locations after background subtraction

Location	Dose rate [ $\mu\text{Sv}\cdot\text{h}^{-1}$ ]
DCP-plant (production area)	0.1-0.2
Phosphate mill house (1 m from the mill)	0.1
Outside phosphate storage silo (4500 ton)	0
Surface of active carbon storage container (height 1.5 m, diameter 1m and 0.5 cm steel walls)	1.5-2
Active carbon storage container (1 m distance)	0.1-0.3
Active carbon (surface)	7-8

Table V.  $^{222}\text{Rn}$  gas concentration

Location	Track-etch detector results [ $\text{Bq}\cdot\text{m}^{-3}$ ]	Modified Tsivoglous method results [ $\text{Bq}\cdot\text{m}^{-3}$ ]
DCP-plant (production area)	<70	8
Phosphate mill house	<70	3
$\text{CaCl}_2$ -plant	<70	1

Table VI. Estimated annual occupational effective doses for a worker at the DCP-plant

Origin	Annual occupational effective dose (mSv)
Dust inhalation (DCP and phosphate rock)	0.06
External exposure	0.1
Radon ( $70 \text{ Bq}\cdot\text{m}^{-3}$ )	0.1

#### 4. Discussion and conclusions

The average activity concentration for all measured radionuclides in the uranium decay series is  $833 \text{ Bq}\cdot\text{kg}^{-1}$  while the concentration of  $^{232}\text{Th}$  and  $^{40}\text{K}$  in the phosphate rock was relatively low.

For uranium, almost 70 % of the total activity ends up in the DCP product. According to [10] uranyl ions can be precipitated as  $\text{UO}_2\text{HPO}_4$  from acid (pH 1.2–2.3) solutions. The pH of the solution at the time when the dicalcium phosphate precipitates falls within this range and it is thus possible that the uranium coprecipitates as  $\text{UO}_2\text{HPO}_4$  with the dicalcium phosphate.

Almost all of the remaining uranium can be found in the sludge consisting of undissolved phosphate rock,  $\text{SiO}_2$  and fluoride compounds.

Sludge 1 contains almost all of the  $^{230}\text{Th}$  that enters the process. Of the total amount only about 1 % could be found in the DCP product. According to [11] Th has a high ability to adsorb on colloid surfaces which could explain the high concentration of  $^{230}\text{Th}$  in the sludge.

The  $^{226}\text{Ra}$  present in the process seems to behave similar as its chemical analogue calcium. The major part of the  $^{226}\text{Ra}$ , about 75 % of the total output, can be found in the calcium chloride solution where the concentration  $^{226}\text{Ra}$  in the different products is more or less proportional to the concentration of calcium chloride. The only exception was the  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  where the concentration of  $^{226}\text{Ra}$  was considerable lower. Differences in solubility between calcium- and radium chloride or rejection of the radium ions in the formation of the crystals is probably the explanation for this.

Almost all of the remaining radium ends up in the sludge consisting of undissolved phosphate rock,  $\text{SiO}_2$  and fluoride compounds.

Fresh samples of active carbon, used for the purification of  $\text{CaCl}_2$ , showed high concentration of short lived radon daughters,  $31000 \text{ Bq} \cdot \text{kg}^{-1}$ . The activity in the sample decreased with a half-life of about 4 days showing that the parent-nuclide was  $^{222}\text{Rn}$ .

As a percentage of the total input,  $^{210}\text{Pb}$  is more uniformly distributed between different products and wastes than the other measured nuclides. Noticeable is however the high concentration that was found in the sludge consisting of mostly  $\text{Mg}(\text{OH})_2$ , probably caused by coprecipitation of lead as the slightly soluble  $\text{Pb}(\text{OH})_2$ . This sludge constitute only about 2 % of the output mass from the process but contains approximately 45 % of the total amount of  $^{210}\text{Pb}$ .

The concentration of  $^{210}\text{Pb}$  in the  $\text{CaCl}_2$  was not proportional to the concentration of the  $\text{CaCl}_2$  as for  $^{226}\text{Ra}$ . The highest concentration was found in the stem solution having the lowest concentration of  $\text{CaCl}_2$  (15 % solution). The reason for this is that the concentration of particles and different impurities are high in the stem solution. In the solution holding 36 %  $\text{CaCl}_2$  the major part of the particles have been removed by sedimentation, and the lower concentration of  $^{210}\text{Pb}$  shows that a large part of the  $^{210}\text{Pb}$  is associated with these particles.

The concentration of  $^{210}\text{Pb}$  in the  $\text{CaCl}_2$  holding 78 and 82 % are also lower than was measured in the stem solution. Since purification by sedimentation is not carried out for this  $\text{CaCl}_2$  quality, the reason for this is different storage time for the stem solution, leading to different degree of sedimentation, before it enters the production line of 78 and 82 %  $\text{CaCl}_2$ .

Polonium has only been measured in the phosphate rock and in the DCP product showing that about 25 % of the total input ends up in the DCP.

Calculating a budget for inflowing and outflowing radioactivity for the process gives a inflow/outflow ratio between 0.70 and 1.14 for all nuclides (polonium excluded).

The annual effective dose for a worker at the DCP-plant is below the dose limit of 1 mSv when the plant is runned without too many interruptions that produces dust and force workers to spend time in the production area.

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