TECHNOLOGY FOR REUSE OF CONTAMINATED CONCRETE CONSTITUENTS

I.P. BINKHORST, H.A.W. CORNELISSEN
Environmental Technology Department, KEMA,
Netherlands

Abstract

During decommissioning activities of nuclear installations, large amounts of contaminated concrete will have to be processed. All this concrete has to be treated and stored as radioactive waste, which implies major economical and environmental consequences.

It was shown that the contamination is mainly concentrated in the porous cementstone. By separating this cementstone from the clean dense aggregate particles, a considerable volume reduction can be reached. KEMA has developed, designed and constructed a pilot plant scale test installation for separation of aggregate from contaminated concrete. The separation is based on a thermal treatment followed by milling and sieving.

The clean aggregate can be re-used in concrete, whereas the (slightly) contaminated cementstone could be upgraded to a binder for concrete used in the nuclear industry.

INTRODUCTION

In a nuclear installation, concrete in various building structures may get contaminated during operation. When the installation is withdrawn from service and eventually dismantled the contaminated concrete has to be conditioned and disposed off as radioactive waste. In many countries the disposal of waste coming from nuclear power plants is a major point of concern. Therefore, research is necessary to look into the possibilities for volume reduction and the re-use of material as an altemative solution for "waste" storage.

It was found that volume reduction of contaminated concrete can be achieved by separation of the fine cement stone and coarse gravel (Cornelissen, 1995). Subsequently the possible re-use of the cement stone (being fine material) was investigated. The fine material (waste) was upgraded for re-use as a cementitious binder or as a filler in building materials.

In the framework of the European Communities Programme on Decommissioning, KEMA (Netherlands) cooperated with CEA-UDIN (France) and BNFL (UK) in the project called RE-BONDIN.

BACKGROUND AND OBJECTIVES OF THE RESEARCH PROJECT

KEMA has developed, designed and constructed a pilot plant scale test installation for volume reduction of contaminated concrete. The solidification of the residual waste was studied by Taywood Engineering. From Versuchs Atomkraftwerk Kahl support was given to test the installation under actual conditions. The project was performed in the period 1989 - 1994 (Cornelissen, 1995).

In a nuclear installation, concrete in various building structures may get contaminated during operation. When the installation is withdrawn from service and eventually dismantled the contaminated concrete has to be conditioned and disposed off as radioactive waste. Global calculations indicate that per reactor about 3000 to 4000 tons will have to be conditioned.

In many cases, mainly the surface layer of the concrete structure will be contaminated. So a huge volume reduction can be obtained by removing this layer. The remaining structure can be treated as a clean building. Depending on environmental and economical conditions the concrete of the surface layer can be processed in a second step in order to gain maximum volume reduction of contaminated concrete (see figure I).

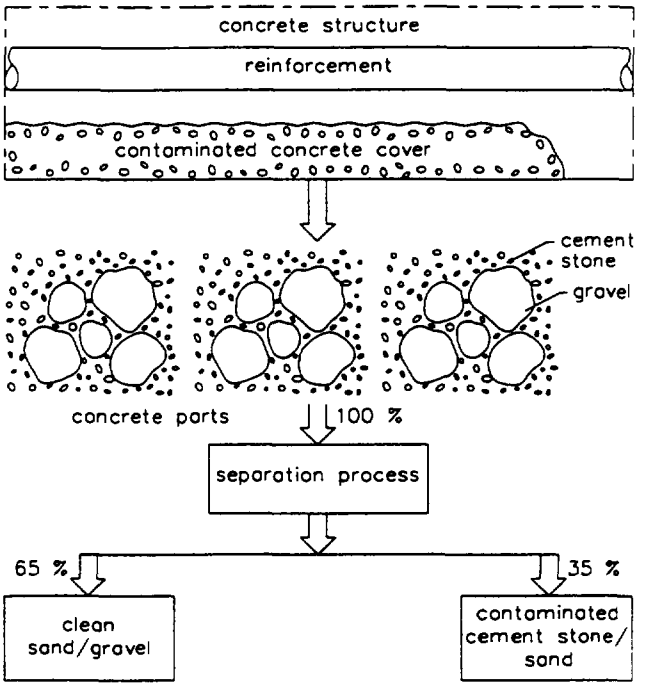

Figure I Removing the contaminated concrete layer followed by separation

After processing, the gravel can be re-used. In the on-going project, in which KEMA cooperates with CEA and BNFL, the possibilities for re-use of cementstone are being tested. The use of this material as binder for concrete in the nuclear industry seems promising.

The ultimate objective of the project is to reduce the volume of contaminated concrete, by separation techniques and re-use for the residues.

TECHNICAL APPROACH

Concrete contamination and activation

In normal quality concretes, the volume of the porous cementstone is approximately 30%, while the remaining part consists of dense aggregates such as quartz and limestone. Tests have shown that contamination primarily penetrates in the cementstone (see figure II). Sepa-

ration of the porous and dense components of concrete will therefore result in substantial volume reduction of radioactive waste. This is beneficial for economical and environmental reasons.

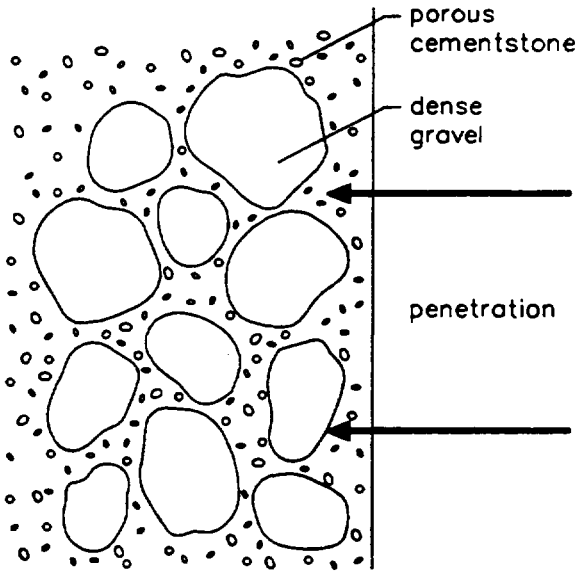

Figure II Contamination of the porous component of concrete

In order to verify the assumption that mainly porous cementstone is contaminated, concrete samples were supplied by the Borssele and Dodewaard nuclear power plants in the Netherlands. The Borssele sample was taken from a concrete element which was used in a room were the handling with radioactive fluids took place.

The main nuclide was ^{60}Co, which caused a total radioactivity of 120 kBq (0,23 kBq/g). The Dodewaard sample, from a core, was especially contaminated for these tests. therefore the core was submerged in radioactive water (150 kBq/l) consisting mainly of ^{137}Cs, ^{60}Co and ^{54}Mn. The total amount of radioactivity of the sample measured with a Germanium detector was 137 Bq for ^{60}Co (0,34 Bq/g), 700 Bq for ^{137}Cs (1,76 Bq/g) and 827 Bq for ^{54}Mn (2,1 Bq/g).

Both concrete samples were separated according to the following procedure:

a grinding and separation by sieving
b washing in HNO_3
c grinding again and separation by sieving
d washing in HCl
e selection (visual) of aggregates just covered with a low or no percentage of cementstone remainings.

After each separation step the activity of the components was measured. The results with respect to ^{60}Co are given in table I.

With respect to ^{60}Co, it can be derived from table 1, that the remaining activity of the aggregates after process step d is about 10 times smaller than the activity of the concrete samples, being 120 kBq and 137 Bq for the Borssele and Dodewaard sample respectively.

Table I Separation of contaminated and non-contaminated parts (activity due to ^{60}Co)

Borssele sample	aggregates (kBq)		cementstone (kBq)		residue* (kBq)
separation step					
a	59	(0,15)**	65	(0,50)	-
b	19	(0,05)	-		34
c	14	(0,04)	-		5
d	12	(0,04)	-		3
e	4	(0,03)	-		-
Dodewaard sample	aggregates (Bq)		cementstone (Bq)		residue* (Bq)
separation step					
a	59	(0,20)	84	(0,85)	-
b	13	(0,06)	-		49

* cementstone, leaching fluid, filter residue

** specific activity (kBq/g and Bq/g)

For the other nuclides, reduction factors were found being 5 for ^{137}Cs and 16 for ^{54}Mn. in terms of specific activity the reduction factors turned out to be 6 for ^{60}Co, 3 for ^{137}Cs and 9,5 for ^{54}Mn.

From the verification tests it can be concluded that the contamination of concrete is mainly concentrated in the porous cement stone.

In these tests the separation process was not yet optimized, therefore further improvement of the separation can be expected by the application of an appropriate technique as described in the following chapters.

Also the possible activation of concrete was tested. Therefore the various concrete components were subjected to a neutron fluency of $2,5 \times 10^{23}$ n/m^2. Ordinary Portland Cement (OPC) and Portland Blastfurnace Cement (PBC) were used. The tested aggregates were quartz, limestone and barite. The results as presented in table II show that because of their chemical composition, quartz gravel and limestone are less susceptible to activation than cements, while barite shows the opposite. From the tests it can be concluded that separation of contaminated concrete is effective. This is also true for activated quartz and limestone concretes.

Basics of separation

Separation of concrete into its components gravel, sand and cementstone is based on the reduction of bond between the cement matrix and the aggregates. The bond can be reduced by temperature induced mechanical stresses. Two methods were tested in this research programme. Cooling down by liquid nitrogen and heating up in an oven. The latter method has an additional chemical effect because of decomposition of the cementstone.

Table II Results of irradiation tests (2,5 x 10^{23} n/m^2)

component	activity after 2y decay (MBq/kg)
cement:	
Ordinary Portland	88
Portland blast furnace	84
aggregate:	
quartz	5
limestone	27
barite	122

Typical results of both temperature treatments are presented in table III in terms of the separation efficiency, E_d, defined as:

$E_d = A_s / A_o$

In this formula A_s stand for the separated material smaller than 1 mm, while A_o represents the original amount of cementstone and sand smaller than 1 mm (the separated "waste"). It can be seen that heating up is more effective.

Table III Effect of type of temperature treatment on separation

thermal treatment	E_d (%)
heating up (650 °)	80
cooling down (liquid N_2)	39

In the research programme, important concrete and process variables on concrete separation were investigated. This finally led to a setup for a separation plant as schematically presented in figure III. In this figure, four main steps can be distinguished. In the first step concrete parts are crushed in order to extend the surface assessable for the subsequent treatments. By means of heating up, the bond between aggregate and cement matrix is reduced and in the next step separation is realized by mechanical forces in a turning mill. Then a selection has to be made between contaminated and clean material. It was decided from preceding tests, to sieve the material over 1 mm sieves. The material < 1 mm turned out to contain the powdered cementstone and consequently the contamination.

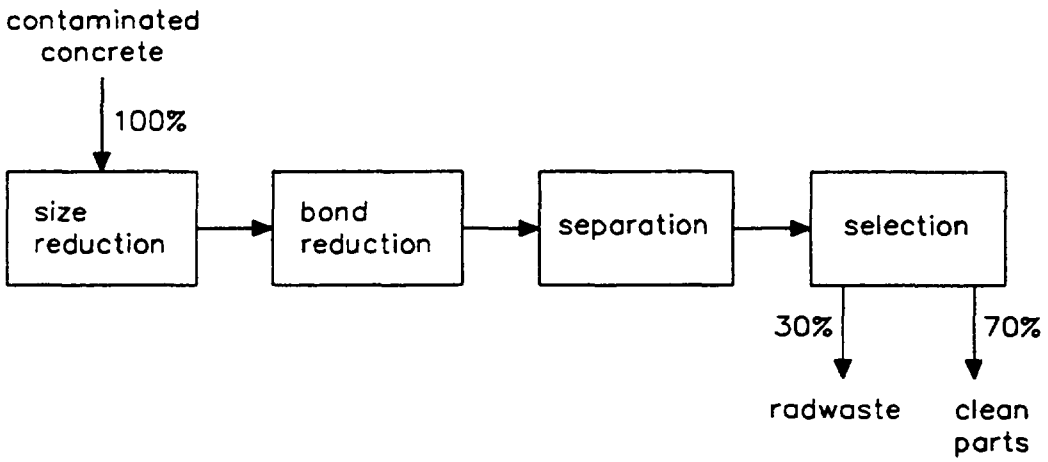

Figure III Flow sheet of concrete separation process

Pilot plant scale test installation

The approach as presented before in figure III formed the basis for the design of a pilot plant scale test installation for separation of contaminated concrete.

In order to be able to use standard components, a batch-wise process was developed. Much attention was given to dust-free operation, which resulted in the introduction of closed process containers and a filtering system connected to all individual components. In the process flow diagram of figure IV, the various components and the process are shown. An additional important feature of this installation is that all process parameters can be investigated in a wide range.

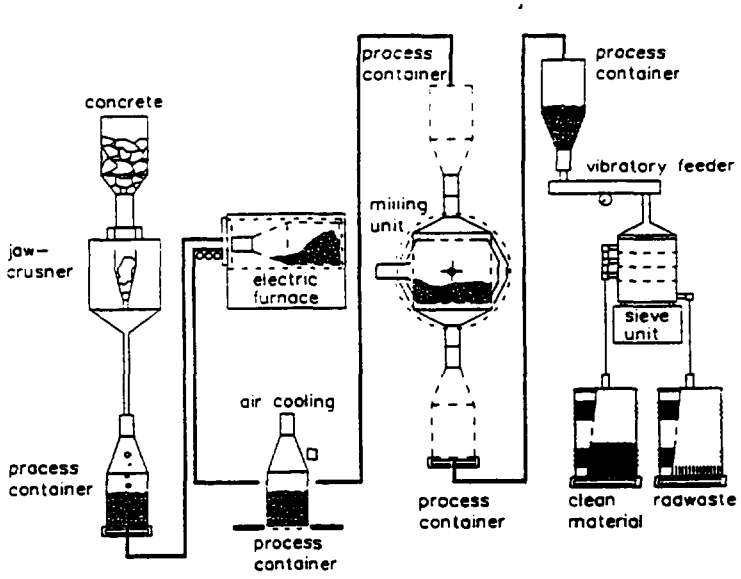

Figure IV Process flow diagram of the test installation

In the jaw-crusher the input concrete is crushed to about 40 mm diameter parts, which are then transported in a specially designed closed process container to the electrical oven for a temperature treatment at about 650 °C. After cooling down of the concrete, the mill (in vertical position) is loaded and then operated (in horizontal position). In the last step the milled material is led to the sieve unit, where the cementstone and fine sand < 1 mm is collected as radwaste in a storage drum. The material > 1 mm is also collected for possible reuse as concrete aggregate. A top view of the installation as erected in the KEMA laboratories is shown in figure V.

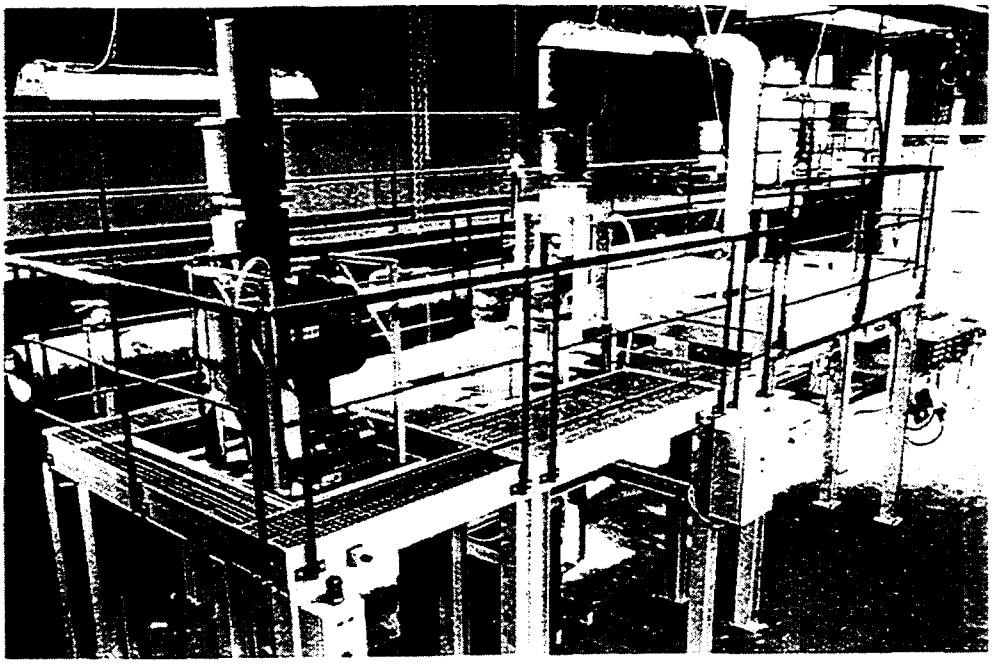

Figure V Top view of the KEMA test installation

Test-runs

The first test-runs with the installation showed that some minor modifications proved to be necessary for dust-free operation. This mainly concerned the valve construction and operation of the process containers.

Well defined, not contaminated, concrete (150 mm) cubes were made with maximum grain size of 31,5 mm. The 28 days compressive strength was about 40 N/mm^2. From the concrete composition and the sieve line of the quartz aggregate, the amount of cementstone and sand < 1 mm can be estimated. The findings are given in table IV.

It was calculated that the amount of fine material < 1 mm was 35% of the total mass of concrete. The specific mass of the concrete was taken as 2400 kg/m^3.

Test-runs were executed, in which the concrete parts were subjected to temperatures in the range of 650 - 700 °C for 3 to 4,5 hours. The milling time was set between 1 and 2 hours. After sieving over 1 mm, the amount of "clean" material proved to be 63%, and the amount of "contaminated" residue was 37% (standard deviation 3%). Because of crushing of some aggregate particles during operation, this ratio of 37% is slightly higher than the theoretical value as given in table IV.

Table IV Data of concrete mix used for the test-runs

component		amount
1	ordinary Portland Cement	320 kg/m^3
2	quartz sand < 1 mm	450 kg/m^3
3	formed cementstone (calculated)	400 kg/m^3
cementstone and sand < 1 mm (2 +3)		850 kg/m^3
fine material ratio*		35%

* (850/2400) x 100%

It can be concluded from the results that by separation, the original amount of "contaminated" concrete was reduced to 37% of the input material. This corresponds with a volume reduction of about 2,5.

An impression of separated concrete samples can be got from figure VI. Material smaller than 1 mm as well as material that retained on 1 mm sieves is shown. Note the remaining dust layer on the aggregate particles (> 1 mm). During the continuation of the project this layer could be removed by wet sieving.

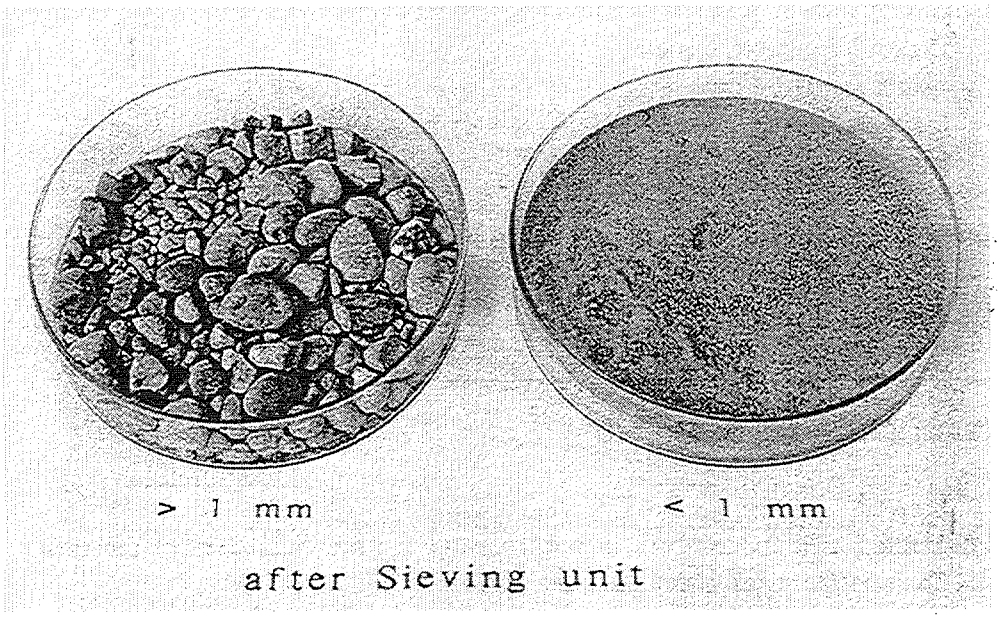

Figure VI Concrete separated in clean aggregate (> 1 mm) and contaminated fines (< 1 mm)

Separation and production of fine material

The present separation process was optimized for the production of clean aggregates (> 1 mm). A further improvement is the reduction of volume of the fine 'clean' material, quartz. In this paragraph a general description is given about the concrete separation process and the process variables which will be maintained for processing of fine material out of the concrete of CEA-UDIN and BNFL (Peeze Binkhorst, 1997).

For the research programme, the settings of process variables for processing of the different types of concrete from the nuclear facilities of CEA-UDIN and BNFL were selected:
- temperature heating 700 ^{0}C
- cooling down for 8 hours
- milling time 1 hour
- sieve size 0,5 mm and sieving time 1 hour.

Normally the process parameters have to be changed with the composition of the concrete, because these parameters effect the separation efficiency. However, the objective of this part of the project is to investigate the opportunities of the re-use of the fine ('rad waste') material of < 1,0 and material < 0,5 mm.

For the study of the separation of quartz (SiO_2) from the fine material (being cementstone plus quartz), a start was made by the production of 85 kg of fine material < 1.0 mm out of 245 kg concrete available at KEMA. After that KEMA received 170 kg of inactive concrete core samples, taken out of the Sea Tank Building located at Sellafield, from BNFL. This concrete was also processed in the separation installation of KEMA. The material was sieved over sieve 0.5 mm, see table V. The material < 0.5 mm contains cementstone agglomerates and quartz. The material > 0.5 mm was sieved over sieve 1.0 mm. As proved before, this aggregate > 1.0 mm mainly contains quartz.

Table V Results separation concrete BNFL

concrete BNFL	run 1	run 2	run 3	run 4	run 5	run 6
weight	33,094	33,589	34,164	32,941	33,976	33,713
after heating	30,491	30,930	31,636	30,493	31,415	31,220
weight loss dry (%)	8,54	8,60	7,99	8,03	8,15	7,99
after milling and sieving						
< 0,500 mm > 0,500 mm	6,353 23,412	6,359 24,730	5,908 25,246	7,034 23,924	6,707 24,930	6,182 25,000
% < 0,500 mm % > 0,500 mm	21,34 78,66	20,45 79,55	18,96 81,04	22,72 77,28	21,20 78,80	19,83 80,17
total	29,765	31,089	31,154	30,958	31,637	31,182
loss loss in %	0,726 2,44	-0,159 -0,51	0,482 1,55	-0,465 -1,50	-0,222 -0,70	0,038 0,12

note: weight in grams

Electrostatic separation

Electrostatic separation of particles also called "high voltage separation" is a separation method which is based on the differences in polarity (positive and negative charges) of electric charged particles, influenced by an electric field. The separation condition is that the different particles should have a different electrostatic property. The result of the inventory study of CEA-UDIN showed that electrostatic separation is used in the mineral industry. KEMA experiences are based on electrostatic separating of different synthetic materials. From this point of view it was decided to focus on electrostatic separation of cement stone based on electrophoresis.

Electrophoresis is the movement of a charged particle influenced by an electrical field (figure VII).

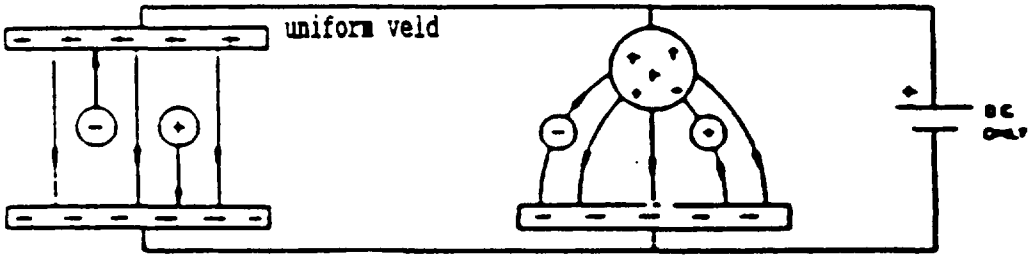

Figure VII Electrophoresis

There are three methods to charge of the particles, known by:
- corona charging
- induction charging
- contact charging.

Separation by means of a corona charging is most common. By corona charging all particles are charged with the same polarity. By moving the particle on a grounded (neutral) surface the conductive particles are neutralised and the separation can be realised between conductive and non-conductive particles.

A conductive particle which is located on a grounded plate under an electric field will be charged by the polarity of the electrode. The charged particle lifts from the surface attracted to charged electrode, Non-conductive particles are not charged.

With contact charging or piëzo charging the particles are charged by moving the particle along each other. When the particles enter a separator with a potential difference (between a negative and a positive electrode), the particles are attracted to the electrode of opposite potential.

KEMA developed and constructed a small scale electrostatic separator as shown in figure VIII. A standard electrical power supply is attached with a maximum of 30 kV. The separator has a lay out to explore the three different methods for separation as mentioned above.

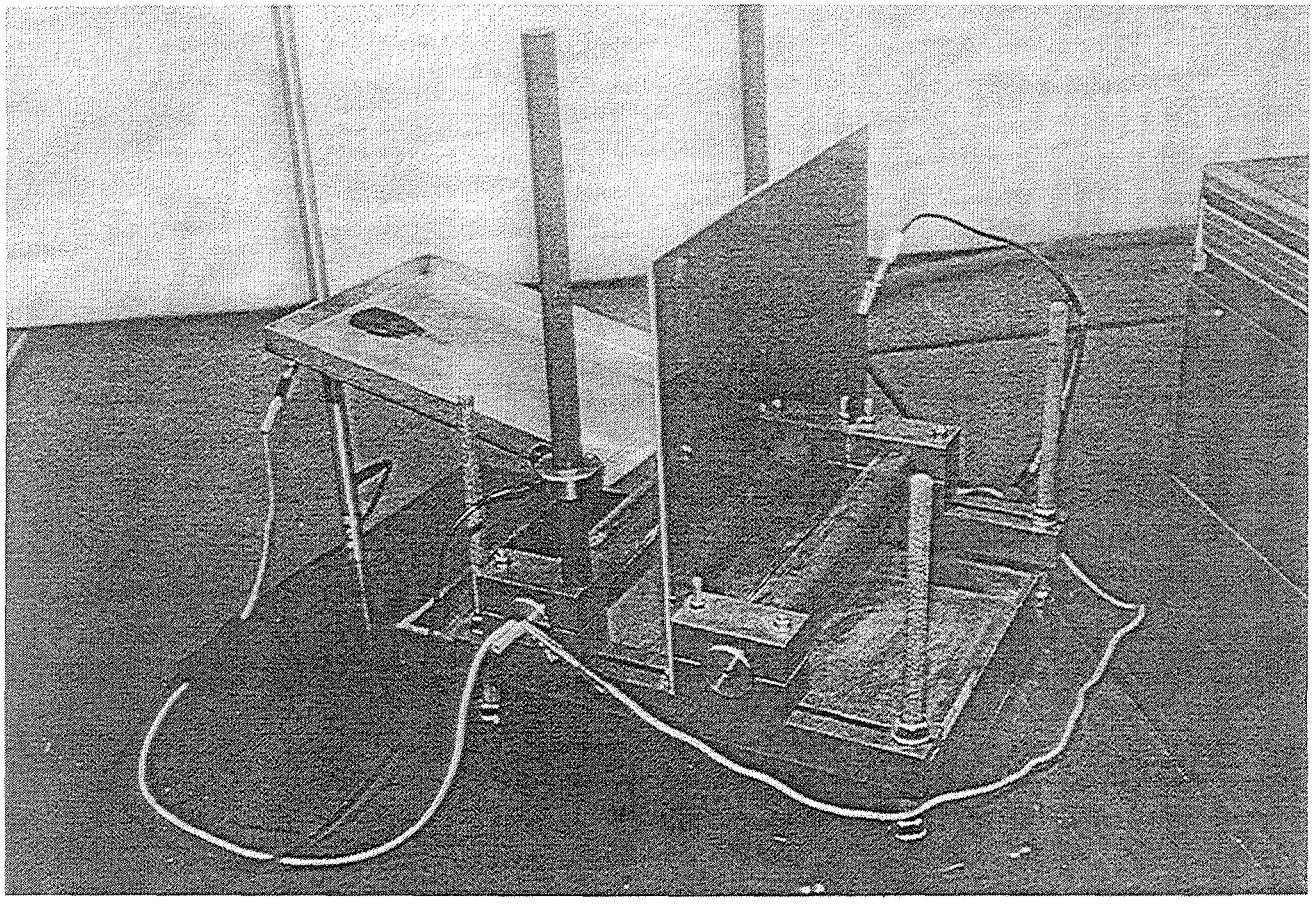

Figure VIII Small scale electrostatic separator for cementstone with quartz

ACCOMPLISHMENTS

The experiments are performed to assess the necessary parameters, to confirm the separation method and to verify the separation possibilities. The fine material (cement stone) used for electrostatic separation is processed in the KEMA separation installation and has been provided by BNFL.

An indication and the planning for the next series of experiments with material like pure sand and cement also different process parameters (corona string, grounded surface and different electrodes) are examined such as:

1 non-charged fine material
2 charged fine material by contact charging (minimal shaken)
3 fine materials charged on a grounded plate
4 non-charged fine material on an isolated grounded plate
5 negative and positive electrodes changed
6 lay out static separator: a plate and one roll charged negative and positive
7 lay out static separator: two rolls charged negative and positive
8 lay out static separator: a roll and feeder charged negative and a roll positive
9 lay out static separator: with corona string
10 lay out static separator: without corona string.

During the tests it was observed that:

- a high voltage increases the rebound of material against the (plate) electrode
- cement is attracted to negative charged electrode

- the corona string is not affective
- the minimal "shaken" material (for contact charging) is charged insufficient. It is also possible that the particles loose their charge in a humid environment.

It was shown from the results and observations of separation with corona charging (ion bombardment) and conductive charging, that these two are not a real option for further investigations. A small range in the granulometry improves the separation of different particles (cement stone and quartz) on specific gravity (density) and the dielectric value.

The observations have shown that during additional milling to break the cement stone agglomerates, the particles became static by contact charging.

Generally it can be concluded that contact charging is a favourable option. Further experiments in combination with optimisation of contact charging by milling could result in a separation (efficiency) of the quartz and the cement from fine material.

The current knowledge of inadequate for prediction of the charging of cement stone and quartz particles. Industrial implementation is necessary to assess the influence of the humidity, temperature and the size of the electric field (the polarity) and the extend of the charge.

5 SUMMARY AND CONCLUSIONS

Contamination of concrete is mainly concentrated in the porous cementstone and not in the dense aggregates like quartz gravel and limestone.

Depending on the concrete composition, volume reduction of at least a factor 2, and sometimes a factor 4, can be reached of material that has to be treated and stored as radioactive waste.

Concrete can be separated in contaminated and clean parts by means of a process based on heating, milling and sieving over 0.5 - 1 mm. The KEMA test installation showed that separation is feasible on small scale. Full scale concrete separation seems beneficial for economical and environmental reasons.

The aggregate is clean and can be re-used, whereas the cementstone can be solidified with only minor volume increase. A better option is to use this cementstone as a binder. Therefore the contaminated cementstone must be separated to enable its use as binder for concrete in the nuclear industry. This separation technology needs further optimization.

By volume reduction of contaminated concrete and re-use of the residues, a considerable contribution can be given to environmentally and economically sound assessment of the consequences of nuclear power generation up to decommissioning.

BIBLIOGRAPHY

CORNELISSEN, H.A.W., "Test Installation for Volume Reduction of Contaminated/Activated Concrete," KEMA-report 40913-KET/R&B 95-4078, September 1995.

PEEZE BINKHORST, I.A.G.M., "Rebondin Intermediate Report part 1 and part 2," KEMA-report 00332-KST/MAT 97-6632, November 1997.