

## **ENVIRONMENTAL CERTIFICATION OF BOTTOM ASHES FROM COAL FIRED POWER PLANTS AND OF BOTTOM ASHES FROM MUNICIPAL WASTE INCINERATION**

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### **ABSTRACT**

Environmental certification is the preferable method for building materials producers to demonstrate that their products comply with the relevant environmental legislation. A procedure for environmental certification according to the Dutch Building Materials Decree is described for granular materials. The operation of this procedure is shown for two granular products, namely bottom ashes from conventional coal fired power plants and bottom ashes from municipal waste incineration.

### **1 INTRODUCTION**

In the Netherlands, an aspect of growing importance for building materials in their utilization is the environmental quality. In 1995 the so called Building Materials Decree has been issued by the Dutch Ministry of Housing and the Environment.

In this Decree, that is part of the Soil Protection Law, rules are set towards the environmentally responsible utilization of building materials. For this purpose, demands are set regarding the immission of 21 inorganic components from a building material into the soil. The immission into the soil is calculated from the results of laboratory leaching tests. Based on the level of measures against infiltration into the soil of leachate, two utilization categories are distinguished, with different emission boundaries:

Category 1 - no restrictions and an estimated infiltration of 300 mm/year

Category 2 - restricted utilization, estimated infiltration of 6 mm/year.

Apart from that, compositional limits are set regarding the content of a set of organic components. In table 1 an overview is given of the calculated emission demands for Category 1 and Category 2 granular building materials, for a height of respectively 1.5 m (relevant for bottom ashes from coal fired power plants) and 50 m (relevant for bottom ashes from municipal waste incineration). For granular building materials the column test is the compulsory test method.

The emission and composition boundaries will be implemented in 1998. The building materials producers have had the opportunity then to make sure that they can meet with the demands. In the explanatory note to the Building Materials Decree, the Ministry of VROM states that environmental certification is the main acceptable proof that the demands of the Building Materials Decree are met.

Table 1            Calculated leaching limits for Category 1 and Category 2 Building Materials, for granular materials, for a utilization height of respectively 1,5 and 50 m (relevant for CF-bottom ashes and MWI-bottom ashes)

Component	Category 1 Granular material, leaching values in mg/kg	Category 2 Granular Materials leaching values in mg/kg
As	0.86	7.0
Ba	3.4	55
Cd	0.026	0.061
Co	0.30	2.3
Cr	0.69	11.7
Cu	0.47	3.3
Hg	0.018	0.075
Mo	0.21	0.84
Ni	0.85	3.5
Pb	1.3	8.1
Sb	0.035	0.41
Se	0.036	0.094
Sn	0.15	2.3
V	1.3	32
Zn	2.9	14
Br	2.7	4.0
Cl	580	8800
CN-complex	0.032	0.35
CN-free	0.006	0.07
F	7.2	96
SO <sub>4</sub>	1100	22000

A general framework for the environmental certification of granular materials is described and subsequently illustrated for bottom ashes from coal fired power plants (CF-bottom ashes) and bottom ashes from municipal waste incineration (MWI-bottom ashes). Both the Dutch Fly Ash Corporation (CF-bottom ashes) and the Waste Processing Association (MWI-bottom ashes) are developing certification procedures for their materials.

## 2 FRAMEWORK FOR ENVIRONMENTAL CERTIFICATION

### 2.1 General

For a certificate of environmental quality, two possible schemes can be followed:

- lot by lot inspection; every lot is tested and evaluated separately
- production certification; a certificate is issued regarding the expected quality of the production process. The production certification is based on the so-called moving average. If the moving average exceeds the limits of the category in which the building material is utilized than correction measures are taken to improve the quality of the building material. An example of a moving average chart is given in figure 1.

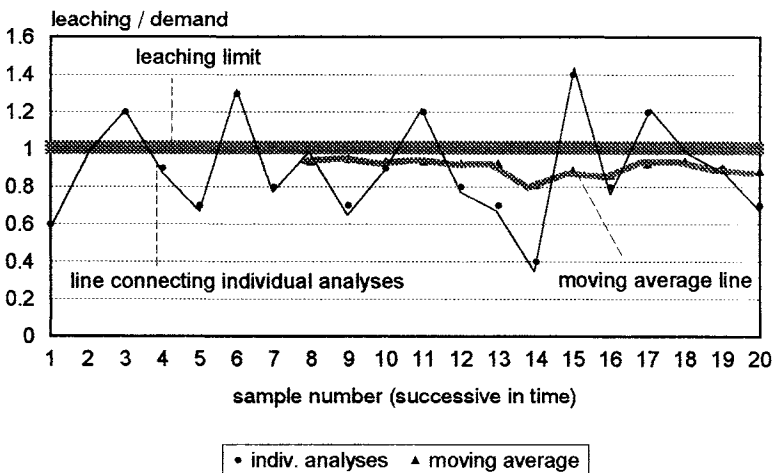


Figure 1 Example of a moving average chart for quality control of granular building products

For most building materials producers production certification is the preferable method for a certificate of environmental quality. Production certification safeguards a stable supply to the market and makes long term supply contracts possible.

The following aspects play an important role with production certification of building materials in general:

- reduction of errors due to variation in the total analytical procedure
- representative sample taking and sample preparation
- selection of critical elements
- a test scheme that meets with the quantities that are produced of the specific material and with the risks that the emission limits are exceeded
- statistically based interpretation of data, based on consumers risks and producers risks
- the use of short tests to predict the results from the compulsory test.

## 2.2 Reduction of errors

The total standard error in leaching results is built up from the following elements:

$$S_{\text{total}} = \sqrt{S_{\text{sample}}^2 + S_{\text{preparation}}^2 + S_{\text{leaching analysis}}^2}$$

where:

- $S_{\text{total}}$  = the total standard error in leaching analyses
- $S_{\text{sample}}$  = the standard error during sampling (both due to inhomogeneity of the lot and due to the influence of the sample size)
- $S_{\text{preparation}}$  = the standard error during sample preparation (milling, comminution, preparation of a laboratory sample)
- $S_{\text{leaching analysis}}$  = the standard error during the leaching procedure and subsequent chemical analysis of the leachate.

By increasing the number of increments per sample, by using a sample splitting apparatus and by analysing several samples, the influence of the standard error on the final result can be lowered.

## 2.3 Representative sample taking and sample preparation

Representative sampling is dependant of the following factors:

- grain size of the material
- percentage of the material that contains the critical element
- variation inside the lot.

Based on the formulas for sample size derived from NEN 7301 a minimum sample size is calculated.

Variation inside the lot can be counterbalanced by taking one sample in several increments. The necessary increment size is dependant on the grain size of the building material. If possible, the increments are taken from a moving stream.

#### 2.4 Selection of critical elements

Based on a statistically relevant number of samples (minimum 10) a selection is made of the critical elements. For as specific building material critical elements are those elements that lead potentially to exceeding of the relevant limits. They are described as elements with  $X_{\text{average, leaching}} > 25\%$  of the relevant limit of the Building Materials Decree.

For production certification only the critical elements should be analyzed on a regular basis. For the critical elements the distribution of  $X_{\text{leaching}}$  is established (normal, log normal or undefined) to be able to choose a method of assessment of the leaching results against demands from the Building Materials Decree.

#### 2.5 Testing scheme

Based on the quantity of building material that is produced and based on the chance that a limit is exceeded the testing scheme is chosen. In the testing scheme the number of leaching analyses per quantity of building material is established.

#### 2.6 Producers risk and consumers risk

The consumers risk and the producers risk are defined as:

- the risk that a defect lot is incorrectly approved (consumers risk)
- the risk that a correct lot is incorrectly rejected (producers risk).

During production certification both the producers risk at a specific percentage of defects (higher than 50%) and the consumers risk at a specific percentage of defects (lower than 50%) are brought down to an acceptable low level.

The risks are determined by the number of samples that is analyzed and by the rejection limit that is chosen. The rejection limit can be generally written for normal distributions as  $X_{\text{rejection}} = \text{limit Building Materials Decree} + k \cdot \text{standard error}$  ( $k$  can both be positive and negative). For log normal distributions the formula is slightly different.

## 2.7 Short tests

The compulsory column test takes 21 days. This makes it impossible to take quick correcting measures after the start of deterioration of the quality of a granular building product. The use of short tests such as the test developed by CEN TC 292 or the Dutch Cascade Batch test can offer possibilities to reduce the necessary time-span for analyses. The possibilities to do that are largely dependant on  $X_{\text{average}}$  for the most critical component in relation to the limit from the Building Materials Decree and on the relation between the short test and the compulsory test.

## 3 BOTTOM ASH FROM COAL FIRING (CF-BOTTOM ASHES)

### 3.1 General

CF-Bottom ash is the bottom ash that originates from coal combustion in dry bottom boilers. It exists of coarse ash particles that have been coagulated and sintered and subsequently quenched in the water basin that acts as a water lock for the boiler. Yearly about 80,000 tons of CF-bottom ashes are produced. CF-bottom ash is almost exclusively used in granular form as embankment material or road base material. The material is used up to a height of 1.5 m as a light embankment material in weak soils and because of that comes into contact with the ground water. This means that it can be only utilized as a category 1 building material. If category 1 is exceeded only utilization in concrete is possible for which momentarily no market exists in the Netherlands.

### 3.2 Critical elements

In 1990 and 1991, the composition and leaching behaviour of 40 CF-bottom ashes was determined. Between 1991 and 1996 quality improvement measures were carried out and two new power plant lines were started.

In 1996 a new testing series was started to get actual information about leaching of the CF-bottom ashes per power plant.

In table 2, the leaching in the column test of 40 CF-bottom ashes (1990-1991) is shown. As can be seen in table 2, the variation in leaching behaviour is large, with variation coefficients running up to 275%. This is partly due to the fact that leaching from the CF-bottom ashes is relatively low. From table 2 it can be deduced that barium, molybdenum, selenium, antimony, sulphate and vanadium are potential critical elements.

Table 2 The leaching behaviour of 40 Dutch CF-bottom ashes

Component	Average leaching (mg/kg)	Standard deviation (mg/kg)	Limit Category 1 BMD (mg/kg)	Variation coefficient (%)
As	0.113	0.0929	0.86	82.24
Ba	3.145	2.862	3.4	91.01
Cd	0.002	0.003	0.026	148.26
Co	0.039	0.109	0.30	276.49
Cr	0.013	0.007	0.69	54.49
Cu	0.044	0.117	0.47	262.74
Hg	0.0025	0.0005	0.018	20
Mo	0.120	0.097	0.21	80.8
Ni	0.0855	0.195	0.85	228
Pb	0.015	0.005	1.33	33.3
Sb	0.015	0.0063	0.035	40.7
Se	0.053	0.052	0.036	97.8
Sn	0.025	0.005	0.15	20
V	0.253	0.169	1.3	67
Zn	0.241	0.301	2.9	124.45
SO <sub>4</sub>	538	607	1100	112.7

The classification of CF-bottom ashes is therefore uncertain. From table 2 it appears that about 50% will fall in category 1 - which means unhindered utilization and 50% will fall in category 2 (isolation demands). Specifically for selenium the leaching often lies at the boundary of category 1 / category 2.

### 3.3 Procedures for certification

Based on the data from 1990-1991 a provisional assessment guideline for certification was drafted in 1996. This consists of the following elements:

- method of sampling                      moving stream
- sample size                                25 kg
- number of increments                    20
- sample frequency                        1 sample per 2000 tons
- certification method:                    lot by lot
- rejection limit                            every analysis has to comply with the limits from the Building Materials Decree
- critical elements                         Ba, Mo, Sb, Se, SO<sub>4</sub>, V

### 3.4 Actual status of certification

Testing of the possibilities for certification was started with the CF-bottom ashes of two power plants. The CF-bottom ashes of one of those two Dutch power plants comply with the demands for certification. These ashes are supplied to the market with a certificate. For the CF-bottom ashes from the other power plant quality improvement is necessary. Momentarily research is carried out regarding the quality of the CF-bottom ashes from the other power plants. Preliminary results show that for a number of power plants quality improvement of the CF-bottom ashes is called for.

### 3.5 Further development of certification

The following aspects for CF-bottom ash certification are under development;

- development of a short test. The possibilities of the CEN TC 292 test as a short test for quality control are tested. Preliminary results for selenium leaching show a good correlation between the column test and the CEN-TC 292 test as shown in fig. 2
- quality improvement measures for the other power plants
- actualization of the provisional scheme for certification. Attention will be given towards the statistical basis for evaluation of the analytical results (can we make use of a moving average system?)

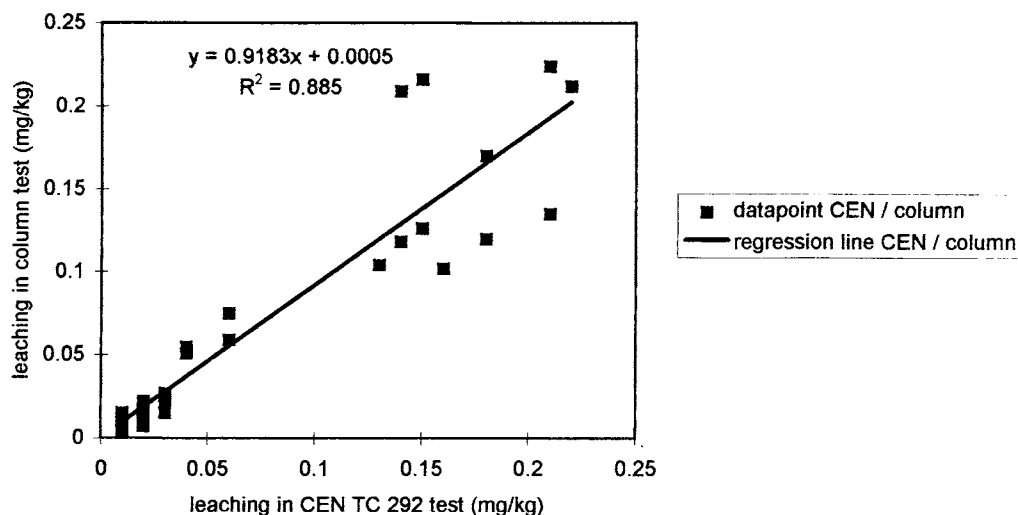


Figure 2 Leaching behaviour of selenium from CF-bottom ashes of 6 power plants, tested both in the compulsory column test NEN 7343 and in the CEN TC 292 short Batch test

#### 4 BOTTOM ASH FROM MUNICIPAL WASTE INCINERATION (MWI-BOTTOM ASH)

##### 4.1 General

MWI-bottom ash is the solid residue from combustion of municipal waste or in a Municipal Waste Incineration Furnace. Often MWI-bottom ashes have been subjected to a post treatment consisting of magnetic separation of iron and sieving and comminution of particles > 40 mm. Fly ashes from Municipal Waste Incineration are kept separate from the MWI-bottom ash. In the Dutch situation it is forbidden to prepare mixed ashes from fly ash and bottom ashes. In 1996 800,000 tons of MWI-bottom ash were produced in the Netherlands. The last years MWI-bottom ash is utilized for 100%, primarily in granular form as embankment material up to a height of 10 m or more or as a road base material.

MWI-bottom ashes are supplied to the market with a certificate for its technical and environmental behaviour. The environmental part of this certificate is based on "old" legislation. MWI-bottom ashes up to now always comply with the demands for environmental certification.

The Building Materials Decree enforces more severe demands than the present regulations. Because of that a large part of the MWI-bottom ashes does not comply with the demands from the Building Materials Decree. To safeguard its outlet to the market the Dutch Ministry of the Environment has developed a "Special Category for MWI-bottom ashes". In this category MWI-bottom ashes can be utilized under a set of isolation measures. With the Municipal Waste Incineration sector the appointment has been made to pursue steady quality improvement of its byproducts so that MWI-bottom ashes can be utilized as Category 2 Building Materials in future.

#### 4.2 **Critical elements**

Since 1987 MWI-bottom ashes have been subjected to a regular quality control from which the environmental part is based on the serial batch test NEN 7349. This test is however not the compulsory test for the Building Materials Decree. Since 1991 all the Dutch Municipal Waste Incineration plants have also carried out column tests (the compulsory test for the Building Materials Decree) on their MWI-bottom ashes. The purpose was to build up sufficient leaching data to be able to prepare environmental certification according to the Building Materials Decree and to show the extent of quality improvement that has been realized in the run of years. In table 3 the leaching data for 1996 are shown.

Table 3 Leaching data for 26 column tests from MWI bottom ashes during 1996

Component	Average leaching (mg/kg)	Standard deviation (mg/kg)	Limit Category 2 BMD (mg/kg)	Variation coefficient (%)
As	0.054	0.195	7.0	361
Cd	0.003	0.003	0.061	105
Cr	0.077	0.22	11.7	291
Cu	1.96	1.27	3.27	65
Mo	2.09	2.91	0.84	139
Ni	0.17	0.30	3.5	176
Pb	0.16	0.42	8.2	260
Sb	0.20	0.15	0.42	72
Zn	0.16	0.24	14	149
Br	10.4	6.0	4.0	58
Cl	3040	n.a.	8800	n.a.
SO <sub>4</sub>	5360	n.a.	22000	n.a.

From table 3 it can be concluded that the following critical elements exist for MWI-bottom ashes: Cu, Mo, Sb and Br. Based on the average leaching of chloride  $> 0.25 \cdot U_2$ , chloride could also be considered as a critical element. However, during the total period 1991 - 1996 the leaching limit for category 2 has only once been exceeded.

A significant reduction in copper leaching has been effected between 1991 and 1996. For the critical elements the distribution of the leaching data has been established. The data can both be described by a normal and a log normal distribution. Because the fitting for a normal distribution seemed slightly better, the testing criteria have been based on a normal distribution of the results.

Based on the leaching behaviour of bromide, presently all MWI-bottom ashes should be considered as MWI-bottom ashes. For most Municipal Waste Incineration plants also the leaching of molybdenum exceeds the Category 2 limits.



MWI-bottom ashes of all Municipal Waste Incineration plants should be considered then as Special Category MWI-bottom ash. This is based on the leaching behaviour of bromide (always) and molybdenum (for most Municipal Waste Incineration plants) during 1996.

#### 4.5 Further development of certification

The following aspects for MWI-bottom ash certification are under development;

- development of a short test. The possibilities of the CEN TC 292 test as a short test for quality control are considered. A comparison of the results from the column test and the serial batch test (from which a large set of data is available) has been carried out in 1996. More than 50% of the datasets batch-test / column test were not fit for comparison. A translation serial batch - column seems possible, but appears not reliable enough in the case of data near a leaching limit
- demonstrations with quality improvement measures are carried out (for instance accelerated aging).

## 5 DISCUSSION

Both CF-bottom ashes and MWI-bottom ashes show a leaching level for the most critical element around one of the leaching limits. Because of that aspect, production certification is preferred; lot by lot inspection may lead to a high percentage of rejection, whereas a production certificate safeguards a more continuous supply. Leaching levels exceeding the limit set by the Building Materials Decree are allowed, provided they are compensated by other parts of the production, showing a lower leaching level.

The use of short tests as an alternative for the compulsory column test is under development. The inherent lower reliability that is caused by the translation of one test to another may be "smoothed out" in the case of a moving average method.

**LITERATURE**

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