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Waste Materials in Construction: Putting Theory into Practice

PREDICTION OF ENVIRONMENTAL QUALITY OF BY-PRODUCTS OF COAL-FIRED POWER PLANTS

ELEMENTAL COMPOSITION AND LEACHING

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ABSTRACT

In the Netherlands the elemental compositions of the various streams of coal-fired power plants are well recorded. The information of these studies is used to calculate enrichment factors for the trace elements in ash, the vaporization percentage of minor and trace elements in flue gases, the degree of removal of gaseous minor and trace elements from flue gases in flue-gas desulphurization installations and the leaching percentage of the elements in ash. These relative parameters combined with trace-element analyses of the coals are used to predict the concentrations of trace elements in the ash, in the leachate and in the flue gases in the gaseous phase. The model is also valid for co-firing with secondary fuels.

1 INTRODUCTION

In 1995 29% of electricity in the Netherlands was generated using coal. Only imported bituminous coal is fired. Coal is imported from all over the world. Major suppliers are Australia and the USA. Other suppliers are Colombia, South Africa, Indonesia, Poland and China. Today mostly blends are fired. In the Netherlands the only boilers installed are pulverized coal-fired dry bottom types. The flue gases are cleaned by high-efficiency cold-side electrostatic precipitators (ESPs) and by flue-gas desulphurization (FGD) installations of the lime(stone)/gypsum process. Table 1 shows some typical values for a 600 MWe coal-fired power plant in the Netherlands. The by-products are bottom ash, collected ash, gypsum and sludge of the waste-water treatment plant. The collected ash from the electrostatic precipitators (ESPs) is called pulverized fuel ash (PFA) in the UK and fly ash in the USA. In this paper it will be called PFA.

The policy in the Netherlands is in principle not to produce waste, but to produce usable residues (for the environmental legislation in the Netherlands see the paper by Van der Poel (Van der Poel, 1997). The electricity generating companies in the Netherlands founded a special firm for the marketing of the coal-firing residues: "de Vliegasunie" (Dutch Fly Ash Corporation). This firm also stimulates research of and experiments with applications. Long-term disposal of coal-firing residues is impossible at present. So far the Dutch Fly Ash Corporation has realized almost 100% utilization of all by-products. For more information on this subject see the paper by Van den Berg (Van den Berg, 1997).

Table 1 Averaged mass flows at a modern coal-fired power plant of 600 MWe

description	unit		description	unit	
net capacity	MWe	600	ratio bottom ash		12/88
full load hours	$h \cdot a^{-1}$	6,000	bottom ash	$ton \cdot a^{-1}$	15,600
thermal efficiency	%	40.5	PFA	$ton \cdot a^{-1}$	115,000
energy demand	$MJ \cdot a^{-1}$	$3.2 \cdot 10^{1}$	gypsum	$ton \cdot a^{-1}$	41,000
coal demand	$ton \cdot a^{-1}$	$1.2 \cdot 10^{6}$	sludge	$ton \cdot a^{-1}$	600
coal, ash content	% (w/w)	11	coal, caloric value	$MJ \cdot kg^{-1}$	27
coal, sulphur content	% (w/w)	0.7	fly dust emission	$ton \cdot a^{-1}$	60
desulphurization efficiency	%	92	process water FGD	$m^3 \cdot h^{-1}$	100
collection efficiency ESP	%	99.75	limestone demand	$ton \cdot a^{-1}$	24,000

2 MEASUREMENTS PERFORMED AT COAL-FIRED POWER PLANTS IN THE NETHERLANDS

2.1 Introduction

In this chapter an overview is given of the research in the field of (trace) elements performed at coal-fired power plants in the Netherlands. It concerns complete mass balance studies, studies limited to some streams and leaching studies.

2.2 Mass balance studies at power plants in 1980-1992

Following the reintroduction of coal as a fuel for power plants, the environmental consequences for electricity generation have been thoroughly studied; for instance in the Dutch National Coal Research Programme (NOK). A fairly important environmental aspect is trace elements. The concentrations and distributions of trace elements in coal, ash, and in flue-gas (in the vapour phase) were determined in sixteen mass balance studies in coal-fired power plants.

The first flue-gas desulphurization (FGD) system was installed in the Netherlands in unit 13 (CG-13) of the Gelderland power plant in 1985. Extensive testing was performed at this unit in the following year (1986) in order to study the fate of (trace) elements in a coal-fired power plant equipped with a wet flue-gas desulphurization facility of the limestone/gypsum type. This aspect was researched in detail (Meij, 1989).

An important aspect in these mass balance studies are the relations between the various streams, from which relative parameters could be deduced.

2.3 Studies at some related streams at power plants in 1988 and 1993-1995

Trace elements are emitted into air in solid (fly ash) and gaseous states. The emissions in the solid state are low due to their high degree of removal in ESPs. The emissions in the gaseous phase are relatively more important. In a plant with FGD equipment both emissions are further diminished. Hence, from an environmental point of view, the gaseous emissions require further research. Consequently, in 1988 the removal of gaseous minor and trace elements in FGD plants was studied at all Dutch units equipped with FGD systems. The concentrations of the gaseous trace elements were measured in the flue gases both upstream and downstream of FGD installations together with the concentrations in the feed coal. The relative parameters which could be deduced were the vaporization percentage and the removal in the FGD installation.

In the years 1993-1995 26 samples of feed coal with the corresponding pulverized fuel ash were analyzed for their elemental composition. It concerns mostly blends and represents the recent Dutch policy of coal purchase.

2.4 Studies of the leaching behaviour of bottom ash and fly ash in 1991-1995

Leaching behaviour of by-products has been studied at KEMA since 1980. However old data are not useful, because different leaching tests were used. It was KEMA who took the initiative to standardize leaching tests. Nowadays the column test and the availability test are mostly used in the Netherlands.

In 1991 and 1995 45 bottom ash samples were studied: elemental composition and leaching behaviour established by the column test.

In 1993-1995 26 fly ash samples were studied: elemental composition and leaching behaviour. The elemental composition was fixed after an aqua regia digestion and after a total digestion or INAA (instrumental neutron activation analyses; method without digestion). The leaching behaviour was established by the column test and the availability test.

2.5 Studies of the leaching behaviour of fly ash under field conditions

The leaching behaviour of pulverized fuel ash under field conditions has been studied in large lysimeters (height 3m80 and 0m95) at the KEMA premises since 1993. This project should lead to a better understanding of the leaching process in field condition and therefore a lot of parameters are monitored: water balance, composition of pore water and leachate, including pH, Eh and speciation of As, Cr and Se (Meij, et al., 1994; Van der Hoek et al. 1995).

2.6 Studies at power plants during co-firing in 1993-1996

In the years 1993-1996 11 test series were performed at coal-fired power plants (7x) and at a test facility at KEMA (4x) during co-firing secondary fuels such as sewage sludge, paper sludge, wood and petroleum-coke. In these test-series all the relevant streams were monitored and compared with the situation without co-firing including leaching behaviour.

3 PARAMETERS DEDUCED FROM STUDIES AT COAL-FIRED POWER PLANTS

3.1 Introduction

The studies mentioned in chapter 2 yield typical parameters that provide the relations between the streams concerned. These parameters are independent of the situation at that particular moment and can be used in a general way in models for predicting the composition of the streams and the leaching behaviour of the by-products (Meij, 1994).

3.2 Relation between elemental coal composition and elemental ash-composition

After combustion of the coal, ash remains. In general the ash contains the same elements as were present in the coal, but enriched in the ash by a factor equal to 100/(ash content in %).

Three types of ashes are to be considered:

- ash collected on the down side of the boiler and called bottom ash or slag
- ash collected in flue gases by flue gas control devices, such as electrostatic precipitator (ESP), this type of ash is named pulverized fuel ash (PFA) in the UK and fly ash in the USA
- ash that escapes the flue-gas control devices and will be emitted through the stack, called fly ash.

In this paper the three types of ash are called bottom ash, PFA and fly ash, respectively.

The enrichment in the ash depends on the type of ash and the particular element. The term "relative enrichment" was introduced to properly describe the behaviour observed (Meij et al., 1983). The relative enrichment factor (RE) is defined as:

$$RE = \frac{\text{(element concentration in ash)}}{\text{(element concentration in coal)}} \bullet \frac{\text{(\% ash content in coal)}}{100}$$

Table 2 Classification of elements based on their behaviour during combustion in boiler and ducts with their Relative Enrichment factor (RE)

class	bottom ash	PFA	fly ash[1)]	behaviour in installation
I	≈1	≈1	≈1	not volatile
IIc IIb IIa	<0.7 <0.7 <0.7	≈1 ≈1 ≈1	1.3<..≤2 2<..≤4 >4	volatile, but condensation within the installation on the particles
III	<<1	<1		very volatile, hardly any condensation

[1)] emitted fly ash and PFA from last hopper of ESP (finest fraction)

Based on the RE factor, elements can be grouped into three classes. The background of the classification is the behaviour of the elements during combustion in the boiler and further behaviour in the ducts, air preheater and ESP. The three classes are given in table 2. Class II is further divided into three subclasses. These subclasses refer to the degree of volatility.

For the three types of ash of each element studied the RE factors have been established in studies mentioned in chapter 2. All these RE factors are combined in a database. In table 3 the elements are classified into the three classes as mentioned in table 2.

Table 3 Classification of elements based on research performed in the Netherlands

class	I	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th and Ti
class	IIc	Ba, Cr, Mn, Na and Rb
	IIb	Be, Co, Cu, Ni, P, U, V and W
	IIa	As, Cd, Ge, Mo, Pb, Sb, Tl and Zn
class	III	B, Br, C, Cl, F, Hg, I, N, S and Se

Class I elements are defined as elements that do not vaporize during combustion. Their concentration in all ash types is the same (see table 2). The RE factor is about one.

However, for some elements there is a redistribution among the various ash types, i.e. bottom ash, PFA (collected) and fly ash (in the flue gases downstream of the ESP). Those elements are vaporized in the boiler. Concomitantly with the route of the flue gases through the boiler, ducts, air preheater and ESPs, the temperature decreases from about 1600 °C to about 120 °C. Depending on the chemical compound, the dew point will be passed somewhere on this route and condensation will start. Condensation occurs on the surface of the fly ash particles. Also, particles can form through nucleation of vaporized material and growth through coagulation and heterogeneous condensation. The smallest particles have the largest specific areas. Therefore, on a weight basis, the condensing elements are found in greatest concentrations on the smallest particles. All elements that condense within the installation are grouped in **class II**. The RE factor of the bottom ash is less than 0.7 because elements originally present in the vapour phase have no chance of condensing on the bottom ash particles. The RE factor of the PFA from the collection tank is about one for elements of class II; the factor for the smaller particles exceeds 1.3. The smaller particles are found in the last two hoppers of the ESP and in the flue gases downstream of the ESP.

Elements that occur in compounds with a low dew point condense only partly within the installation and, in the absence of an FGD plant, they are totally or partly emitted in the vapour phase.

They are grouped as **class III**. Their RE factor is very small (<< 1), especially in the bottom ash and to a lesser extent in the PFA of the collection tank. The RE factor of the smallest fly ash particles, as found in flue gas downstream of the ESP, can be high (see table 2).

3.3 Relation between elemental coal composition and concentrations of gaseous elements in the flue gases

In chapter 3.2 the relation between the elemental concentrations in coal and the various ashes are discussed. Class III elements are generally for a small part present in ash. The largest part is present in the vapour phase. Just as RE factors, a parameter is introduced for these elements: the vaporization percentage (Meij et al., 1983).

Based on research as mentioned in chapter 2, the class III elements can roughly be divided into three groups (Meij, 1994):
- displaying almost complete vaporization (Cl, F, I)
- with a typical vaporization of about 50% (B, Br and Hg)
- with low vaporization (Se and As = class IIc).

However, since the introduction of FGD, the major part of these elements is removed in the FGD. Another parameter, also based on research as mentioned in chapter 2, is introduced: the degree of removal. The results are (Meij, 1994):
- B, Br, Cl and I are removed for >80-90%,
- F, Hg and Se are removed for >50%.

3.4 Relation between ash-composition and leaching

The leaching of elements, as mentioned in chapter 2.3, is studied together with the elemental composition of the ash. The parameter, which could be deduced from these studies, is the leaching percentage relative to the composition. This is done for bottom ash with respect to the column test and for the pulverized fuel ash with respect to the column test and the availability test. The results are given in figure 1. The Dutch leaching test and other test are discussed in detail by Van der Sloot (Van der Sloot, 1991) and also by Meij et al. (Meij et al., 1994).

Thus the leaching percentage of a great number of ashes are obtained. The mean value can be used to predict the leaching behaviour of future ashes of that order. However the range of the mean leaching percentage is fairly large. It is not possible to predict leaching behaviour in detail with a straightforward parameter. There are more parameters concerned. In the lysimeter project (Meij et al., 1994) more information is obtained about the leaching mechanism. However, profound knowledge of a particular pulverized fuel ash is not sufficient to predict leaching of other pulverized fuel ashes. Nevertheless a prediction of leaching behaviour of an arbitrary pulverized fuel ash could be possible in combination with an evaluation of the data in the file "Database Leaching".

It has to be said that an accurate prediction is not always needed. Only when it is really necessary, for instance when the concentration of a particular element comes close to a standard. In that case an advanced model for predicting the concentrations of that particular element is needed.

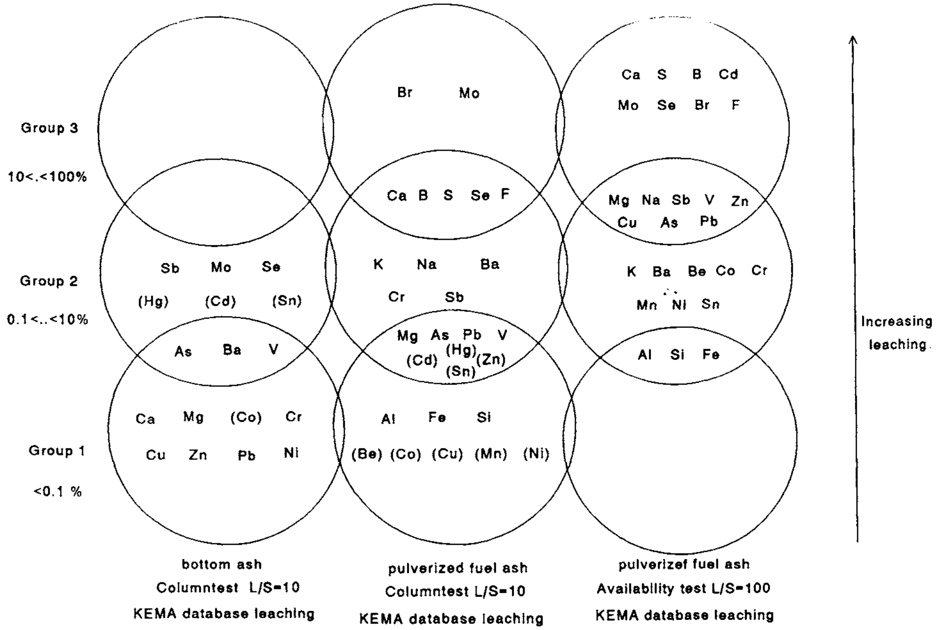

Figure 1 Leaching behaviour of elements in bottom ash and pulverized fuel ash as produced in Dutch coal-fired power plants in different leaching tests. The relative leaching with respect to the composiotion of the ash grouped into three classes. The figures in brackets are derived from detection limits

4 DATABASES

4.1 Introduction

The measurements, as mentioned in chapter 2, and the deduced relative parameters, as mentioned in chapter 2, are recorded in databases. The databases are (see also figure 2:

a database Coal: elemental composition, ash content and other quantities
b database Bottom ash: elemental composition and RE factors
c database Pulverized Fuel Ash (PFA): elemental composition and RE factors
d database fly ash (emitted into air): elemental composition and RE factors

e database Gaseous Elements (emitted into air): concentrations in the flue gases, vaporization percentages and degree of removal in FGDs
f database leaching bottom ash: composition of the leachate, pH and leaching percentages
g database leaching pulverized fuel ash: composition of the leachate, pH and leaching percentages
h database Co-firing: all the data and relative parameters as mentioned in the databases a up to and including g, but classified according to the secondary fuels.

The foremost database is the one concerning the coal composition. Therefore the next section more detail will provide on this database.

4.2 Database coal

It appears that the differences in elemental concentration between lots from the same geographical region is relative small. Therefore all the samples from one region are combined. For one country of origin the mean value together with the standard deviation will used henceforth. The weighted averaged coal composition, as fired in coal-fired power plants in the Netherlands in a particular year, can be calculated, based on the origin of the coal for that year, together with the standard deviation.

5 PREDICTION OF ENVIRONMENTAL QUALITY OF BY-PRODUCTS

The databases as mentioned in chapter 4 contain data on the composition and leaching of various streams of the Dutch coal-fired power plants. Because of this one can get information of the composition (mean and standard deviation) in the past. One can extrapolate into the future.

However, besides composition, relative parameters are always as well recorded. These relative parameters can be used to predict the composition of the various streams. A general scheme is presented in figure 2. The basis is the coal composition. If one knows the coal composition, the composition of the various ashes and flue gases can be calculated.

If the coal composition is not known but the origin of the coal is known, the coal composition can be taken from the database. This latter approach will yield a fairly good prediction.

This approach is also valid for blends and was tested in practice with 21 samples from 6 different Dutch power stations in 1993 and 1994. A comparison between the measured and the predicted values of the coal composition (42 elements) yields a mean R^2 value of $93 \pm 7\%$. The same procedure was followed for the composition of the pulverized fuel ash: it yields a mean R^2 value of $93 \pm 8\%$ The prediction for some individual elements can be less accurate, such as (in decreasing order) Hg>Br>Be,Se>Cd,Zn.

The origin of the coal in a particular year is well recorded, so for that year the averaged composition together with the standard deviation of the various streams can be calculated. Hence, the representative figures for that particulate year are obtained.

It turns out that all the relative parameters also apply to co-firing, at least for the study cases, in which at the most 10% of the coal was replaced by a secondary fuel. So the model is also useful in predicting the consequences of co-combustion.

The prediction of leaching is only indicative, as discussed in section 3.4. However, in many cases this is sufficient.

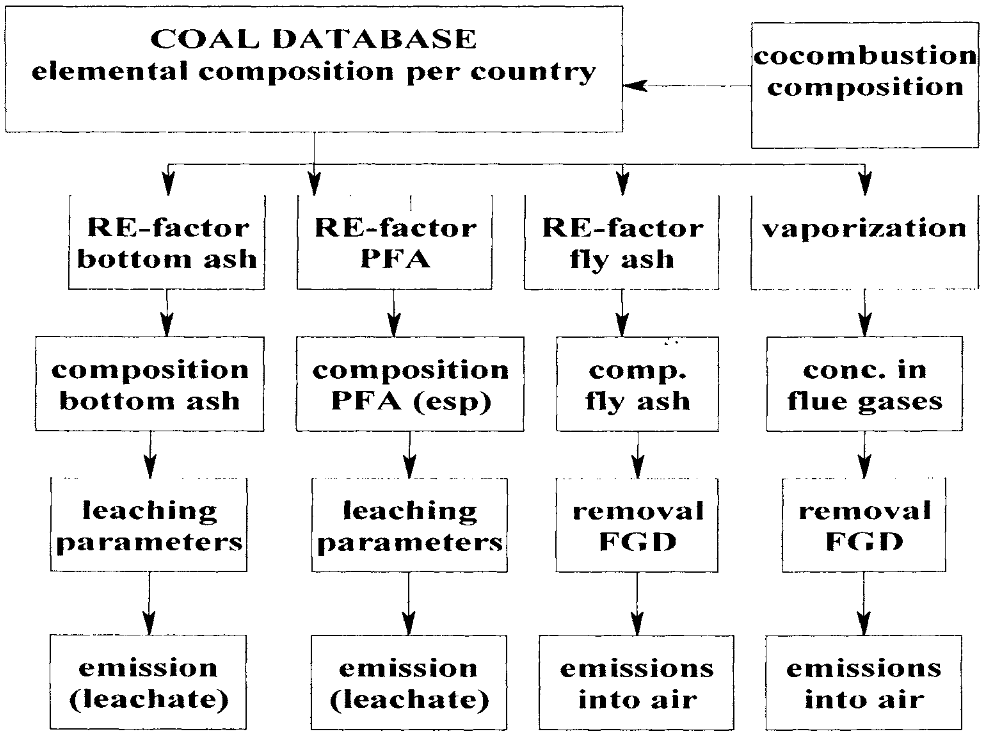

Figure 2 Scheme for prediction of the composition of the various streams a coal-fired power plants

6 CONCLUSION

- the elemental composition of coal and the outgoing streams, such as bottom ash, pulverized fuel ash (ESP-ash), emitted fly ash, flue gases and leachate, is recorded in databases
- besides elemental composition of the outgoing streams, relative parameters are also deduced. These parameters are: relative enrichment factors, vaporization percentages, removal percentages and leaching percentages
- these relative parameters also apply to co-firing
- the elemental compositions of coal blends are on average easy to predict

- the elemental compositions of the outgoing streams are on average easy to predict, assuming a known coal composition or a predicted coal composition. Some elements are less well to predict in ash, such as mercury and bromine
- the prediction of the elemental composition of leachate is only indicative. This is due to the fact that leaching depends on several parameters. However, for most cases it can be sufficient. If necessary, e.g. when the leaching is close to a standard, an advanced model for predicting the concentrations of that particulate element is needed. This model can be made based on information derived from the database and from the lysimeter experiment.

7 ACKNOWLEDGMENTS

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