PD CEN/TR 16443:2013

BSI Standards Publication

Backgrounds to the revision of EN 450-1:2005+A1:2007 — Fly ash for concrete

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National foreword

This Published Document is the UK implementation of CEN/TR 16443:2013.

The UK participation in its preparation was entrusted to Technical Committee B/517/4, Additions for concrete.

A list of organizations represented on this committee can be obtained on request to its secretary.

Published by BSI Standards Limited 2013

ISBN 978 0 580 78799 7

ICS 91.100.30

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 30 April 2013.

Amendments issued since publication

Date	Text affected

TECHNICAL REPORT
RAPPORT TECHNIQUE
TECHNISCHER BERICHT

CEN/TR 16443

March 2013

ICS 91.100.30

English Version

Backgrounds to the revision of EN 450-1:2005+A1:2007 - Fly ash for concrete

Contexte de la révision de l'EN 450-1:2005+A1:2007 - Cendres volantes pour béton

Hintergründe zur Überarbeitung der EN 450-1:2005+A1:2007 - Flugasche für Beton

This Technical Report was approved by CEN on 29 October 2012. It has been drawn up by the Technical Committee CEN/TC 104.

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EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. CEN/TR 16443:2013: E

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Foreword

This document (CEN/TR 16443:2013) has been prepared by Technical Committee CEN/TC 104 “Concrete and related products”, the secretariat of which is held by DIN.

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Introduction

Following five years of experience using EN 450-1, it was clear that some clauses need improvement within the standards. In the existing standards the maximum amount of fly ash from co-combustion was limited to certain proportions. Experience gained with fly ashes conforming to a European Technical Approval (ETA), where higher co-combustion amounts were permitted, showed that the requirements in the corresponding Common Understanding of Assessment Procedure (CUAP) were sufficient guarantee for fly ashes to produce excellent performance in concretes, mortars, grouts and cements. As agreed in CEN/TC 104, the experience gained with ETA fly ashes should be incorporated in the revision of EN 450-1.

In this background report it is proved that wider ranging limits and types of co-combustion materials can be safely applied in the revised EN 450-1. It is also shown that in practice some requirements in EN 450-1 have been proven to be unrealistic. Improvements have been proposed for the definition of fly ash, the loss on ignition, free calcium oxide, reactive silicon dioxide and the limits for phosphate.

The conformity procedures have also been evaluated, especially the assessment procedure for inspection by variables. Based on this evaluation work, modifications are needed for the LOI 1) classes B and C.

The revised version of the standard incorporates the European Technical Approvals (ETA) and EU members experience gained with fly ash in concrete. The requirements of the revised standard will result in fly ashes which will perform similarly to those conforming to EN 450-1:2005.

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1) LOI – Loss on ignition.

1 Scope

This Technical Report describes the backgrounds to the revision on EN 450-1:2005+A1:2007, *Fly ash for concrete — Part 1: Definition, specifications and conformity criteria*.

2 List of relevant references

The following references are covered by the present document:

- EN 450-1:2005+A1:2007, *Fly ash for concrete — Part 1: Definition, specifications and conformity criteria*;
- EN 450-1:2012 (revised EN 450-1 [2]), *Fly ash for concrete — Part 1: Definition, specifications and conformity criteria*;
- EN 450-2:2005, *Fly ash for concrete — Part 2: Conformity evaluation*;
- EN 196-2, *Methods of testing cement — Part 2: Chemical analysis of cement*;
- EN 197-1:2000, *Cement — Part 1: Composition, specifications and conformity criteria for common cements*;
- EN 14588:2010, *Solid biofuels — Terminology, definitions and descriptions*.

3 General

3.1 General and objective

Fly ash has been used for many decades in concrete as an addition for its positive influence on workability, heat of hydration, strength development and durability. After the encouraging pilot projects some decades ago with positive results, licenses for regular use and later on technical approvals were granted by the national building authorities, certificates and standards. Today, regulations and standards exist for the use of fly ash in mortar and concrete.

In 1995, the first EU standard was published, namely EN 450, *Fly ash for concrete — Definitions, requirements and quality control*. This edition was followed up by a harmonised standard based on Mandate M 128 in 2005 (EN 450-1:2005), together with a second standard (EN 450-2:2005), specific for conformity evaluation.

The scope of EN 450-1:2005 states that fly ashes with percentages of co-combustion material higher than those covered in EN 450-1:2005, Clause 4 or with other types of co-combustion material are outside the scope of EN 450-1:2005.

In some countries, the use of fly ash with a higher percentage of co-combustion material was already common practice and it was not accepted by these countries that these fly ashes, containing higher amounts of co-combustion and other co-combustion materials, were excluded from CE marking.

It was agreed that European Technical Approvals (ETAs) could be granted for this product according to Article 8.2 of the Construction Products Directive. The mandate M 128 was updated with the clarification that fly ash produced with other types than those covered by EN 450-1 and fly ash produced with a percentage of co-combustion material outside the limits defined in EN 450 (all parts), can be subject to ETAs, in order to allow these products to be CE marked. The experience gained with the fly ashes conforming to these ETAs has been used for the next revision of EN 450-1.

Due to the regular five-year revision, WG 4 of CEN TC 104 incorporated the knowledge gained with the fly ashes conforming to these ETAs with EN 450-1. Other issues for the revision were identified as a lack of clarity regarding the conformity evaluation and some of the other requirements.

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2) In this present Technical Report a reference to the revised EN 450-1 always refers to EN 450-1:2012.

The objective of this report is to provide insight into the background to the modifications that have been taken up in EN 450-1:2012 (revised EN 450-1) and of those requirements that have been deleted from EN 450-1:2005+A1:2007

3.2 Structure of the report

Clause 4 provides an overview of the requirements of EN 450-1:2005+A1:2007 and EN 450-1:2012. In Clause 5 the background for the modifications of the requirements within EN 450-1 is described. Clause 6 gives the background for the statistical evaluation for assessment procedure by variables, Clause 7, the background for the required test methods, regarding chemical composition and the determination of fineness. In Clause 8, an overview how fly ash quality is assured within the production process itself, the quality control system and the conformity evaluation of toxicological and environmental aspects is given. Clause 9 deals with the impact of co-combustion on the release of regulated dangerous substances.

More background information about the generation of fly ash can be found in Annex B.

4 Overview of requirements in EN 450-1:2005+A1:2007 and EN 450-1:2012

An overview of the requirements in the revised EN 450-1 is presented in Table 1. The requirements are related to fresh and hardened concrete. The chemical requirements concern Loss On Ignition (LOI), chloride (Cl), reactive and free Calcium Oxide or lime (CaO), reactive Silicon Dioxide (SiO_2), the sum of SiO_2 + Al_2O_3 + Fe_2O_3, Magnesium Oxide (MgO) and soluble Phosphorus Pentoxide (P_2O_5). The physical requirements concern (or: are related to) fineness and the maximum deviation of particle density. The performance based requirements are water requirement, initial setting, activity index and soundness.

In relation to the previous standard, the following changes have been adapted:

- The definition of fly ash has been modified (EN 450-1:2012, 3.2).
- The permitted amount and type of co-combustion materials have been changed (EN 450-1:2012, 4.1).
- The requirement for the lower limit of LOI for category B and C fly ash has been deleted (EN 450-1:2012, 5.2.2).
- The requirement for free lime (CaO) has been changed (EN 450-1:2012, 5.2.5).
- The amount of total phosphate has been limited by a new requirement (EN 450-1:2012, 5.2.11).

Table 1 — Properties and requirements of fresh and hardened mortar and concrete

Phase	Property	Unit	EN 450-1:2005+A1:2007	EN 450-1:2012
workability	loss on ignition (LOI) class A class B class C	% by mass	≤ 5,0 2,0 – 7,0 4,0 – 9,0	≤ 5,0 ≤ 7,0 ≤ 9,0
	water requirement [a]	%	≤ 95	n.m. [e]
	fineness fraction > 45 µm	% by mass	≤ 40 (cat. N) [d] ≤ 12 (cat. S)	n.m. [e]
initial strength development	soluble phosphate (P_2O_5)	mg/kg	≤ 100	n.m. [e]
	total phosphate (P_2O_5)	% by mass	—	≤ 5,0
	initial setting	min.	2C [b]	n.m. [e]
strength development	sum $SiO_2 + Al_2O_3 + Fe_2O_3$	% by mass	≥ 70	n.m. [e]
	reactive SiO_2	% by mass	≥ 25	n.m. [e]
	activity index 28 days 91 days	%	≥ 75 ≥ 85	n.m. [e] n.m. [e]
alkali silica reaction (ASR)	total content of alkalis (Na_2O equivalent)	% by mass	≤ 5,0	n.m. [e]
	reactive calcium oxide (CaO)	% by mass	≤ 10,0	n.m. [e]
soundness/ durability	sulphuric anhydride (SO_3)	% by mass	≤ 3,0	n.m. [e]
	free calcium oxide (CaO)	% by mass	≤ 2,5 [c]	[f]
	soundness	mm	≤ 10	n.m. [e]
	magnesium oxide (MgO)	% by mass	≤ 4,0	n.m. [e]
	chloride (Cl^-)	% by mass	≤ 0,10	n.m. [e]

[a] Only applicable for category S fly ash.

[b] Initial setting of fly ash cement paste shall not be more than twice as long as the initial setting time of the test cement alone.

[c] If the content of free lime is greater than 1,0 % by mass, the fly ash shall be tested for conformity to the requirement for soundness.

[d] The fineness shall not vary by more than ±10 % from the declared value.

[e] n.m. = not modified.

[f] If the content of free lime is greater than 1,5 % by mass, the fly ash shall be tested for conformity to the requirement for soundness.

5 Background for modification of the requirements in EN 450-1

5.1 Definition of fly ash

5.1.1 Text of EN 450-1:2005+A1:2007

Fine powder of mainly spherical, glassy particles, derived from the burning of pulverised coal, with or without co-combustion materials, which has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3. The content of reactive SiO_2, as defined and described in EN 197-1 being at least 25% by mass.

5.1.2 Text of EN 450-1:2012 (revised EN 450-1)

Fine powder of mainly spherical, glassy particles, derived from the burning of pulverised coal, with or without co-combustion materials, which has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3.

5.1.3 Background

The requirement of reactive SiO_2 has been deleted in the definition of the revised EN 450-1, but still exists as requirement for initial type testing (EN 450-1:2012, 5.2.7).

By definition fly ash has to be derived from the burning of pulverised coal and co-combustion materials. This is only possible in dedicated boilers where combustion of finely ground fuel takes place in a cloud, with combustion temperatures of 1 300 – 1 500 °C. This means that ashes from other boilers like grate-fired and fluidised bed combustion boilers do not meet this definition. In other words, the definition guarantees that combustion takes place at high temperature, which is high enough to facilitate glass formation in the fly ash.

The definition includes co-combustion, but, in EN 450-1:2012, 4.1, the amount and type of combustion material are further restricted. Also, as noted in EN 450-1, municipal and industrial waste incineration ashes do not conform to the definition of this clause. This implies that the fuel always contains coal. Coal contains mineral matter that will form the glass phase during combustion. Also part of the secondary fuel also contains mineral matter that contributes to glass formation. On a performance level, the requirement for the activity index after 28 and 91 days provide enough assurance for a sufficient pozzolanic behaviour of the fly ash. The presence of the glass phase is further assured by the requirement for the minimum total amount of $SiO_2 + Al_2O_3 + Fe_2O_3$ (as a main fraction of potential glass forming matter).

5.2 Co-combustion materials

5.2.1 Text of EN 450-1:2005+A1:2007

Fly ash from co-combustion as defined in 3.2 is obtained from pulverised coal fired simultaneously with co-combustion materials as listed in Table 1 (Table 2 of this report). The minimum percentage, by dry mass, of coal (K_c) shall not be less than 80 % and the maximum proportion of fly ash derived from co-combustion materials (M) shall not be greater than 10 % when calculated from Formula (1).

Table 2 (Table 1 of EN 450-1:2005+A1:2007) — Types of co-combustion materials

1	Vegetable material like wood chips, straw, olive shells and other vegetable fibres
2	Green wood and cultivated biomass
3	Animal meal
4	Municipal sewage sludge
5	Paper sludge
6	Petroleum coke
7	Virtually ash free liquid and gaseous fuels

5.2.2 Text of EN 450-1:2012 (revised EN 450)

Fly ash from co-combustion as defined in 3.2 is obtained from pulverised coal fired simultaneously with or without co-combustion materials as listed in Table 1 (Table 3 of this report). The minimum percentage, by dry mass, of coal (K_c) shall be not less than 60 % or 50 % if the co-combustion material is only green wood. The maximum proportion of ash derived from co-combustion materials (M) shall not be greater than 30 % by dry mass when calculated from Formula (1).

Table 3 (Table 1 of the revised EN 450-1) — Types of co-combustion materials

1	Solid Bio Fuels conforming to EN 14588:2010 including animal husbandry residues as defined in 4.3 and excluding waste wood as defined in 4.40, 4.107 and 4.136
2	Animal meal (meat and bone meal)
3	Municipal sewage sludge
4	Paper sludge
5	Petroleum coke
6	Virtually ash free liquid and gaseous fuels

NOTE Other types of co-combustion materials not included in Table 3 (Table 1 of the revised EN 450-1) may be subject to an ETA.

5.2.3 Background

The classification of secondary fuels has been changed in the revised EN 450-1. The secondary fuels listed in line 1 and 2 of table 3 have been merged as these are from the same origin and compiled in EN 14588. As “green wood” is not defined in that report a definition was added in the revised EN 450-1 as:

"3.13
green wood
green wood is wood originating from trees, bushes and shrubs created when processing wood as cross-cut ends, planings, saw dust and shavings used in the form of dust, chips and pellets".

The minimum proportion of coal has been decreased from 80 % by mass to 60 % by mass. Further, the maximum proportion of ash derived from secondary fuels has been increased from 10 % to 30 % by mass.

Since 2005, ETAs have been used for testing the technical and environmental suitability of fly ash from co-combustion for use as addition in concrete. Generated fly ashes from co-combustion exceeding the co-combustion limits of EN 450-1:2005+A1:2007 were tested according to these ETAs. Before ETAs were available, Dutch fly ashes from co-combustion were tested according to CUR recommendations (since 1999). The tested fly ashes are presented in Annex C.

Co-combustion may increase the content of Ca, K, P and Mg in some cases. The other macro elements (Fe, Al, Si, Na, and Ti) are mainly indirectly influenced by becoming impoverished due to the enrichment of other macro elements. In most secondary fuels from vegetable and animal origin these macro-elements are present in low concentrations (ash based), related to coal. The situation in fuels from industrial origin may be different like the presence of Al, Si, Fe and Ti in demolition wood, Al, Si and P in sewage sludge and Al, Si and Ca in paper sludge. The revised EN 450-1 contains an adequate set of requirements that covers these influences; see Table 5. As can be derived from this table the influence of Ca, K, Mg and P is directly covered by at least one requirement of the revised EN 450-1.

Table 4 — Requirements for fly ash for fresh and hardened concrete in relation to the effects of co-combustion

Phase	Requirement of EN 450-1	Main influence co-combustion			
		Ca	K	Mg	P
workability	LOI	—	—	—	—
	water requirement	—	—	—	—
	fineness fraction > 45 µm	—	*V*	—	—
initial strength development	soluble P_2O_5	—	—	—	*VV*
	total P_2O_5	—	—	—	*VV*
	initial setting	—	—	—	*VV*
strength development	sum $SiO_2 + Al_2O_3 + Fe_2O_3$	*V*	*V*	*V*	*V*
	activity index	—	—	—	*V*
Alkali Silica Reaction	Na_2O equivalent	—	*VV*	—	—
	reactive CaO	*VV*	—	—	—
soundness/ durability	SO_3	—	—	—	—
	free CaO	*VV*	—	—	—
	Soundness	*V*	—	—	—
	total MgO	—	—	VV	—
	Cl^-	—	—	—	—

Key

VV direct relation between the requirement and the influence of co-combustion
V in-direct relation between the requirement and the influence of co-combustion
— no relation

The test results showed that in nearly all cases, the chemical requirements of the ETA were met with one exception, which in that case fly ash was rejected for use in concrete. This can be explained by the fact that the co-combustion amount was adjusted to the chemical requirements or to operational conditions (fuel feed, slagging, corrosion, etc.). An overview of limiting parameters for co-combustion materials is given in Table 5.

The results showed also that the XRD analyses of fly ash did not provide any extra information for quality control purposes. In all cases no minerals were identified other than listed in the ETA. Therefore this criterion was not included in the revised EN 450-1.

For a selection of these fly ashes, concrete specimens were produced to check if the proposed test methodology is adequate. The performance of the concrete did not show significant influence of co-combustion. The results are described in several reports and presentations (see CUR, 2003; Sarabèr, 2004; Sarabèr and Van den Berg, 2005; Sarabèr and Van den Berg, 2006; CTSC, 2008). It was shown that the performance of fly ash obtained from different co-combustion materials could be explained by the mineralogical composition of the fly ash and that this could be related to the origin of the co-combustion material. It was shown that depending on the origin of the fuel high co-combustion percentages are possible up to 25 % by mass.

Table 5 — Limiting parameters for co-combustion materials (basis Table 1 of the revised EN 450-1)

	Type	Limited by
1	**Solid Bio Fuels conforming to EN 14588:2010 including animal husbandry residues as defined in 4.3 and excluding waste wood as defined in 4.40, 4.107 and 4.136.**	
	green wood 1	Co-combustion fuel based
	green wood 2	Co-combustion fuel based
	green wood 3	Co-combustion fuel based
	bark wood	reactive CaO
	Cacao shells	Na_2O equivalent (K)
	palm kernels	total P_2O_5
2	**Animal meal (meat and bone meal)**	
	Meat and bone meal	total P_2O_5
3	**Municipal sewage sludge**	
	Municipal sewage sludge	total P_2O_5
4	**Paper sludge**	
	Paper sludge	CaO
5	**Petroleum coke**	
	Petroleum coke	—[a]
6	**Virtually ash free liquid and gaseous fuels**	
	Industrial HC liquid	Co-combustion fuel based

[a] Prevented by National environmental regulations.

As already stated, the actual amount of co-combustion material is not only limited by the maximum requirement for co-combustion, but also by the chemical requirements of EN 450-1. This means that in practice, the actual amount of coal combustion (K_c) will be higher than 60 % by mass and the maximum proportion of ash derived from co-combustion materials (M) will be less than 30 % by mass. To illustrate this, the maximum amount of co-combustion has been studied in relation to the chemical requirements (KEMA, 2008). The minimum proportion of coal combustion and the maximum proportion of ash derived from co-combustion materials (M) adjusted to meet the requirements of EN 450-1 by calculating chemical compositions using the "KEMA TRACE MODEL®"3) The study shows that co-combustion of most secondary fuels will be limited by the chemical requirements or by the definition regarding the fuel based maximum co-combustion. In Annex D all results are summarised.

5.3 Loss on ignition

5.3.1 Text of EN 450-1:2005+A1:2007

The loss on ignition shall be determined in accordance with the principles of the method described in EN 196-2 but using an ignition time of 1 h, and shall fall within the limits of the categories specified below:

Category A: Not greater than 5,0 % by mass

Category B: Between 2,0 % and 7,0 % by mass

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3) KEMA TRACE MODEL® is the trade name of a product. This information is given for the convenience of the users of this Technical Report and does not constitute an endorsement by CEN of the product named. Similar products may be used if they can be shown to lead to equivalent results.

Category C: Between 4,0 % and 9,0 % by mass

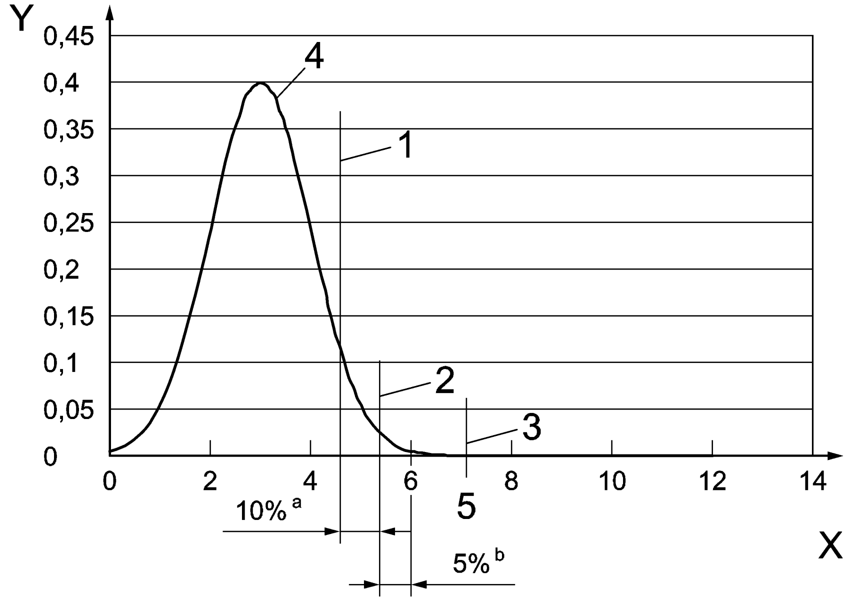
5.3.2 Text of EN 450-1:2012 (revised EN 450-1)

The loss on ignition shall be determined in accordance with the principles of the method described in EN 196-2 but using an ignition time of 1 h, and shall fall within the limits of the categories specified below:

- Category A: Not greater than 5,0 % by mass
- Category B: Not greater than 7,0 % by mass
- Category C: Not greater than 9,0 % by mass.

5.3.3 Background

LOI of fly ash is an important quality parameter. LOI may influence several properties of concrete like workability, interaction with organic admixtures, strength development, durability and visual aspects.



Key

1 LOI(mean) = UL – $k_a \cdot s$
2 upper limit
3 single result limit
4 Prob.
5 LOI
[a] PR
[b] CR

Figure 1 — Producer and consumer risk in statistical evaluation

With the introduction of the revised EN 450-1:2005, three categories of LOI were introduced, each covering a range of 5 % by mass but only category A with a lower limit of zero. The statistical assessment has to be evaluated by variables. The system used is designed for normally distributed data sets and acceptability constant together with producer and consumers risk. The system was established by D.B. Owen in 1962, but for one sided evaluations only.

An example for producer and consumer risk in statistical evaluation is given in Figure 1. The consumer risk of 5 % is the right tail of the curve, the producer risk of 10 % is under the curve between UL and UL- $k_A \cdot s$. For LOI category A no result can exceed the single result limit of 7 % LOI. The area under the normal curve at the zero point is negligible for category A fly ash as its not possible to have an LOI value < 0 %. But for category B or category C fly ash the lower limits of 2 or 4 % by mass cause compliance problems and reduce the possible mean LOI between category A and B. By this category B fly ash can only be produced in a very small and non-practical production window.

Based on the well proven systems of assessment by variables (see chapter 4) the lower limits need to be deleted as the evaluation is valid for one-sided systems only.

As a result of these changes, in practical terms the quality in terms of LOI of the fly ash complying with Category A, B or C will not change. This is demonstrated with the following examples using a typical SD of 1,0 and a typical k_A of 1,61 (for 60 – 69 results):

Cat A: Limit 5 %; mean value 3,0 %, follows: range is limited to 1,4 % to 4,6 %

Cat B: Limit 7 %; mean value 5,0 %, follows: range is limited to 3,4 % to 6,6 %

Cat C: Limit 9 %; mean value 7,0 %, follows: range is limited to 5,4 % to 8,6 %

The quality of fly ash in respect of consistency of LOI will not be negatively influenced with the deletion of the lower limits, as the inherent statistical evaluation procedures required will still ensure a low standard deviation for LOI will be achieved.

5.4 Free calcium oxide

5.4.1 Text of EN 450-1:2005+A1:2007

The content of free calcium oxide shall be determined by the method described in EN 451-1 and shall not be greater than 2,5 % by mass. If the content of free calcium oxide is greater than 1,0 % by mass, then the fly ash shall be tested for conformity to the requirements for soundness in 5.3.3.

5.4.2 Text of EN 450-1:2012 (revised EN 450-1)

The content of free calcium oxide shall be determined by the method described in EN 451-1. If the content of free calcium oxide is greater than 1,5 % by mass, then the fly ash shall be tested for conformity to the requirements for soundness in 5.3.3.

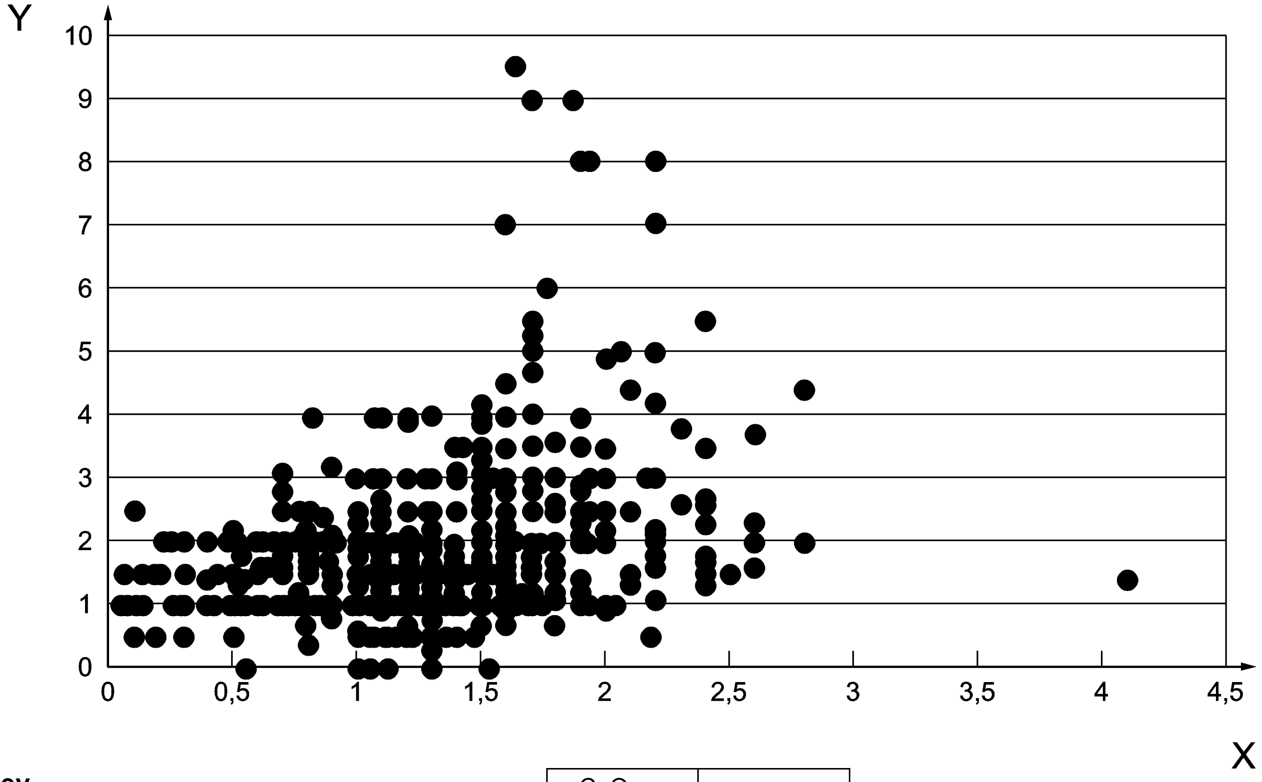
5.4.3 Background

The minimum free lime content above which soundness has to be tested has been increased from 1 % by mass to 1,5 % by mass. Further, the maximum amount of free lime of 2,5 % by mass has been deleted.

Free lime present in fly ash and cement will convert into Portlandite sooner or later if it comes into contact with water, according to the reaction:

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2}$$

This conversion is accompanied by heat generation and by an increase in its solid volume. This process is sufficiently powerful to generate large expansive forces, which may cause failure within the concrete. It has been found that unsoundness of cement in the Le Chatelier test occurs appreciably when the free lime content is in excess of 2 % by mass (Lea, 1970). A statistical analysis of data delivered from members of the CEN working group was performed (ECOBA, 2008). Data not conforming to EN 450-1 are also included within this dataset for demonstration purposes. See Figure 2. The results show that for up to 1,5 % by mass free CaO, soundness expansion is minimal. Above this content the soundness values may increase, but still hardly any fly ash exceeds the limit of 10 mm. Based on these data it is concluded that for only above 1,5 % by mass free lime, soundness has to be proven. The soundness criteria together with the reactive CaO criteria provide enough insurance that further limitation of the amount of free CaO is superfluous.



Key

X CaO$_{free}$ [% by mass]

Y soundness [mm]

	CaO$_{free}$	soundness
min	0,05	0,00
max	4,1	9,5
mean	1,28	1,86
s	0,49	1,10
n	734	734

Figure 2 — Relation between free lime and soundness (LeChatelier test)
(format modified acc. ISO 128 (all parts) and ISO 129 (all parts))

5.5 Reactive silicon dioxide

5.5.1 Text of EN 450-1:2005+A1:2007

The amount of reactive silicon shall be analysed in accordance with EN 197-1:2000 and shall not be less than 25 % by mass. Only fly ash from the combustion of pulverised coal shall be deemed to satisfy this requirement.

5.5.2 Text of EN 450-1:2012 (revised EN 450-1)

In the initial type test for fly ash from co-combustion (4.2) the amount of reactive silicon shall be determined in accordance with EN 196-2 and shall not be less than 25 % m/m. Fly ash obtained from combustion of pulverised coal only shall be deemed to satisfy this requirement.

5.5.3 Background

Reactive SiO_2 together with reactive Al_2O_3 are the main components in the glass phase, and these form the basics for the pozzolanic reaction, together with the $Ca(OH)_2$ from the hydration reactions of the cement. So it is an essential compound in EN 450-1 fly ash. The requirement of reactive SiO_2 is always met for coal fly ash.

NOTE ECOBA has produced a guidance document which details the test procedure for determining reactive SiO_2, which is available for download from the ECOBA web site (www.ecoba.org).

5.6 Phosphate

5.6.1 Text of EN 450-1:2005+A1:2007

The content of soluble phosphate (P_2O_5) shall be determined in accordance with EN 196-2 and shall not be greater than 100 mg/kg. Fly ash obtained from combustion of pulverised coal only shall be deemed to satisfy this requirement.

5.6.2 Text of EN 450-1:2012 (revised EN 450-1)

The content of total phosphate (P_2O_5) shall be determined in accordance with EN 196-2 and shall not be greater than 5,0 % by mass. Fly ash obtained from combustion of pulverised coal only shall be deemed to satisfy this requirement.

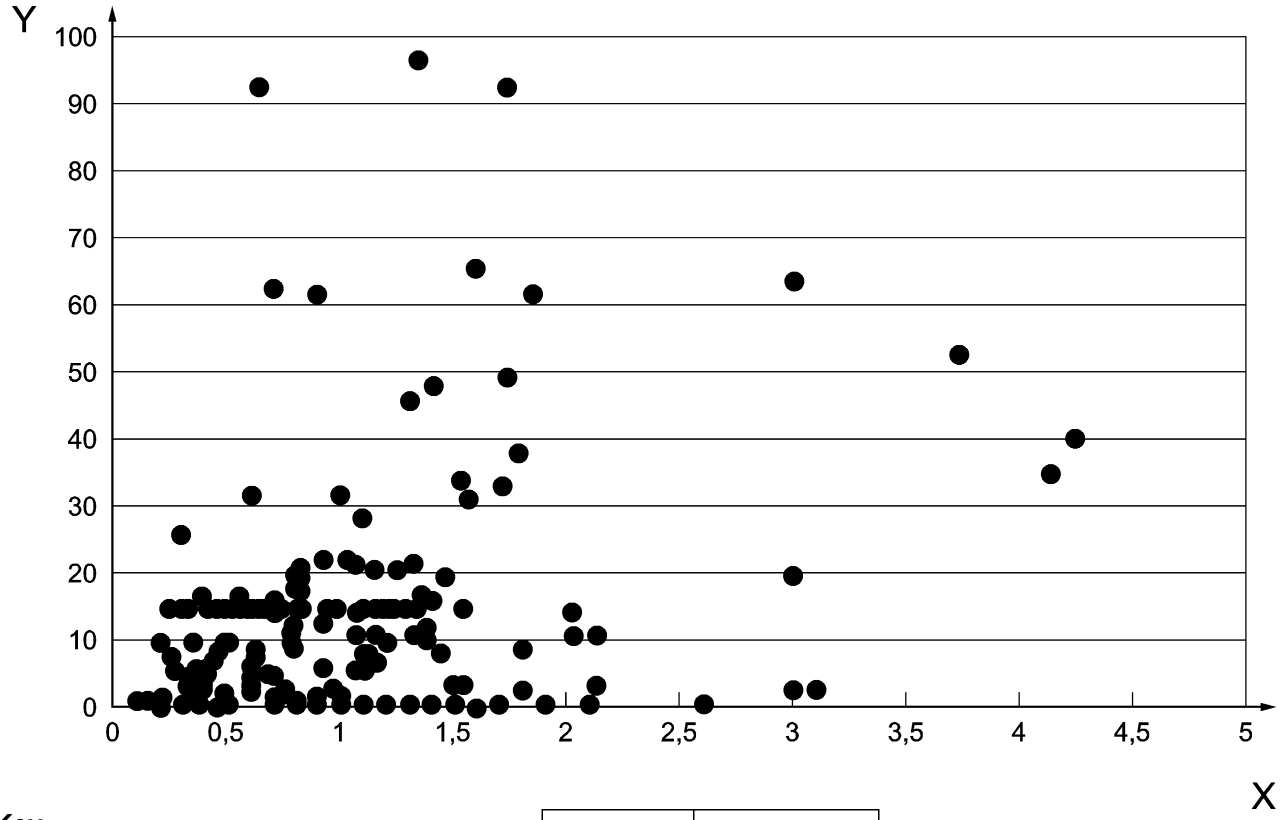
In the initial type test for fly ash from co-combustion (4.2) the content of soluble phosphate (P_2O_5) shall be determined in accordance with the method descried in Annex C and shall not be greater than 100 mg/kg.

5.6.3 Background

The requirement for phosphate has been extended with a requirement for total phosphate (maximum content of 5 % by mass).

As already stated, phosphate is a compound that is normally present in fly ash from 100 % coal in low concentrations; normally below 1 % by mass. Co-combustion of specific co-combustion materials, as are listed in Table 1 will cause an increase of the phosphate content, e.g. animal meal, municipal sewage sludge and solid bio fuels like cacao residues and wheat husks. The research data concerning the performance of concrete with phosphate enriched fly ash is up to approximately 5 % by mass P_2O_5, originating from different co-combustion materials. The assessment involved workability, strength development, freeze-thaw resistance and chloride permeability. There were no specific effects identified caused by phosphate on concrete performance. Therefore, it is concluded that fly ash may contain up to 5,0 % by mass P_2O_5.

In Figure 3, the relation between total and soluble phosphate is shown. It shows that up to 5% total P_2O_5 no fly ash exceeds the limit of 100 mg/kg soluble P_2O_5. As the analysis of soluble phosphate is a labour-intensive procedure and needs specific training to obtain realistic figures the analysis of the total phosphate content by means of X-ray fluorescence analysis is strongly recommended for autocontrol testing.



Key

X total P_2O_5 in [% by mass]

Y soluble P_2O_5 in [mg/kg]

	total	water soluble
min	0,1	0,2
max	0,6	2,7
mean	4,3	97
s	0,69	16,3
n	209	209

Figure 3 — Relation between the content of total phosphate and soluble phosphate

6 Background for the statistical evaluation for assessment procedure by variables

The Statistics Sub-group of TC 104/WG 4 carried out a comprehensive review of the compliance criteria of EN 450-1:2005+A1:2007 and EN 450-2:2005. A detailed report is available separately from the WG 4 secretariat.

The conformity criteria within EN 450-1:2005 were simply adapted from text within EN 197-1. There was little information as to the basis for the compliance criteria within EN 197-1 and TC 51 members were asked to provide the source information. It transpired the statistics adopted had been used for many years prior to the development of EN 197-1. The system is based on the assumption there is no information about the mean value or standard deviation of the data being analysed. At the time of drafting EN 450-1:2005 there was little or no consideration as to the differences between cement and fly ash and the limiting criteria. The relatively low standard deviation in comparison with the mean value for common cements, coupled with the relatively wide limits for compliance makes it possible for cement production to easily comply, whereas fly ash will find it much harder in some circumstances, particularly, as it transpired, in relation to Loss On Ignition (LOI).

One issue studied was whether the frequency distributions of data were in fact ‘normally’ distributed or better represented by the more complex ‘gamma’ function. The EN 197-1 statistics are based on normal distributions and would be invalid if non-normal or gamma functions were found. A detailed analysis of data on fineness, LOI and to a lesser extent parameters tested by attributes on data provided by ash suppliers throughout the EU were carried out. There was some evidence that LOI distributions were ‘non-normal’, but for all practical purposes this could be ignored. However, compliance with the criteria for LOI subsequently proved to be a significant issue due to the large statistical margins demanded by the compliance criteria.

There was evidence that some power stations were finding compliance with the LOI criteria difficult. This was because their particular mean LOI coupled with the categories for LOI and the large margins, resulted in too narrow a compliance band and in some circumstances proving completely impossible to comply. This was especially true for new ash sources that had low numbers of results. As the mean LOI is a function of the station, furnace, coals, etc., which ash producers are unable to change, this problem needed to be rectified. After a more detailed analysis of these data it became clear the application of the EN 197-1 statistics were never designed for such narrow bands within category B and C with LOI and two tail tests being impossible to comply with. After a series of discussions, it was agreed the solution was to delete the lower limits for categories B and C.

The quality of fly ash in respect of consistency of LOI will not be negatively influenced with the deletion of the lower limits, as the inherent statistical evaluation procedures required will still ensure a low standard deviation for LOI will be achieved (see 3.3).

One issue reviewed but not changed was the quoted producer and user risk values, P_k and C_R. These are somewhat misleading within EN 450-1:2005, as the actual failure rates for population distribution required are considerably lower, in order to comply with EN 450-1, Tables 3 and 4. This is particularly true for testing by attributes where low numbers of results are available, which results in compliance difficulties even in a system fully statistically compliant. This is a result of the statistics adopted, which assume no knowledge of the data mean and standard deviation, resulting in very high operating margins (k_A).

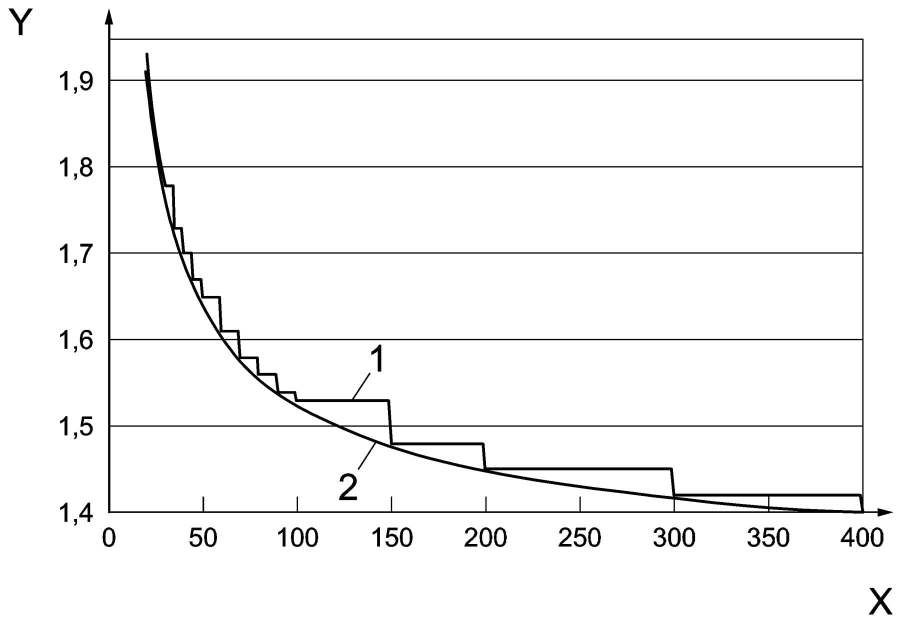
There was little known about the original source of the statistics. It transpired that the tables within EN 197-1 and EN 450-1 were extracted from previous cement standards, which in themselves had been adapted from a textbook by Owen (Owen, 1962). Further work by N. Bech within the statistics sub-group showed that k_A can be evaluated using the following one sided approximation postulated by M. Natrella (Natrella, 1963).

$$k_\mathrm{A} = \frac{z_{1-\mathrm{p}} + \sqrt{z_{1-\mathrm{p}}^2 - ab}}{a} \quad \text{where}$$

$$a = 1 - \frac{z_{1-\gamma}^2}{2(n-1)} \quad \text{and} \quad b = z_{1-\mathrm{p}}^2 - \frac{z_{1-\gamma}^2}{n}$$

The concept of producers and consumer risk in relation to fly ash is questionable and adoption of a single compliance value of a 5 % failure rate (one tailed test) for all variables would simplify the statistics. However, the sub-group in conjunction with Sector Group 2 agreed that to change the basis for compliance criteria away from that within EN 197-1 was a step too far. However, it was agreed that values for the margins could be calculated by computer using the Natrella approximation, allowing compliance monitoring spreadsheets to be created and removing the rather stepped function seen in the table within EN 450, see Figure 4.

In conclusion the decisions taken have removed the main problems associated with statistical compliance for LOI within EN 450-1. However, it is recommended that the basis of compliance both within EN 197-1 and EN 450-1 should be reviewed again in any post 2010 revisions.



Key

1 EN 450-1:2005
2 calculation (Natrella)
X number of results in analysis
Y value k_a

Figure 4 — Comparison between EN 450 and Natrella approximation

7 Background for modification of test methods in EN 450-1

7.1 Chemical composition

7.1.1 Text of EN 450-1:2005+A1:2007 and Text of EN 450-1:2012 (revised EN 450-1), 5.2.8 and 5.2.10

"The content of silicon dioxide (SiO_2), magnesium oxide (MgO), aluminium oxide (Al_2O_3), and iron oxide (Fe_2O_3) shall be determined in accordance with EN 196-2, modified as indicated in [EN 450-1,] 5.2.1. (…)"

NOTE Text remained unchanged.

7.1.2 Background

The new standard EN 196-2 allows for using methods other than the classical chemical methods, namely X-ray fluorescence analysis (XRF-EN196-2.2). By this, the use of XRF to determine the oxides need no longer to be classified as alternative method with the proof of equivalent results but can be used directly as a reference method.

7.2 Fineness wet/dry

7.2.1 Text of EN 450-1:2005+A1:2007, 5.3.1

The fineness of fly ash shall be expressed as the mass proportion in percent of the ash retained when wet sieved on a 0,045 mm mesh sieve and determined in accordance with EN 451-2 and shall fall within the limits of the categories specified below:

Category N: The fineness shall not exceed 40 % by mass, and it shall not vary by more than ± 10 percentage points from the declared value.

Category S: The fineness shall not exceed 12 % by mass. The ± 10 percentage points variation in fineness does not apply.

7.2.2 Text of EN 450-1:2012 (revised EN 450-1), 5.3.1

The fineness of fly ash shall be expressed as the mass proportion in percent of the ash retained when sieved on a 0,045 mm mesh sieve. The sieving can be determined in accordance with EN 451-2 or by airjet sieving according EN 933-10 and shall fall within the limits of the categories specified below:

Category N: The fineness shall not exceed 40 % by mass, and it shall not vary by more than ± 10 percentage points from the declared value.

Category S: The fineness shall not exceed 12 % by mass. The ± 10 percentage points variation in fineness does not apply.

In case of dispute the wet sieving method shall be used as the reference method.

7.2.3 Background

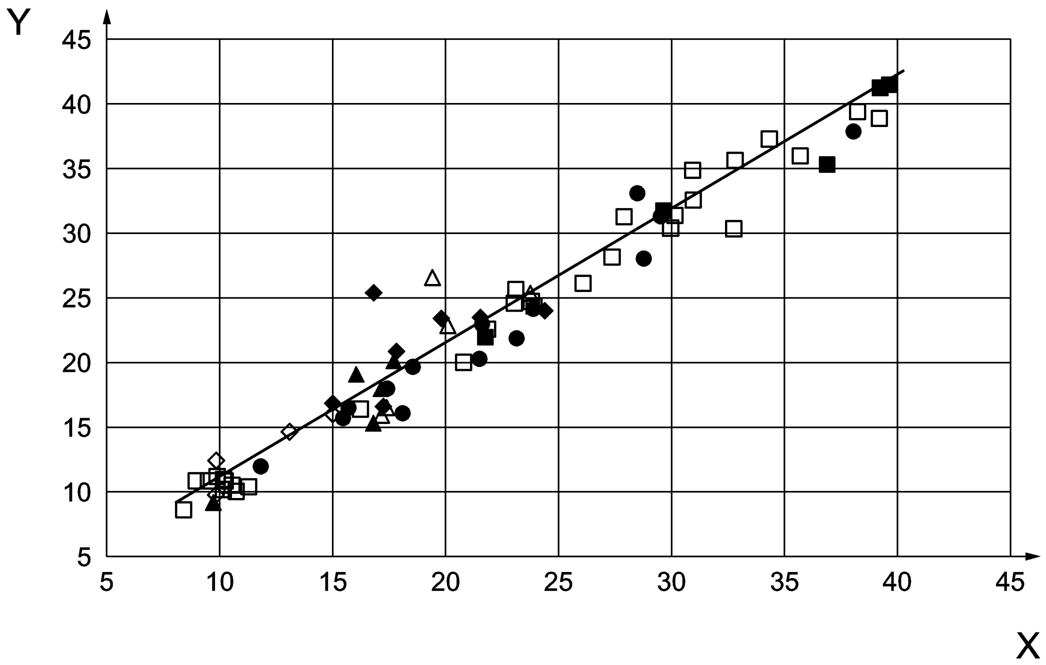
The fineness test is a control parameter in the power plant and needs to be performed at least once a day. As the wet-sieving analysis is time consuming the procedure is not the most favourable for autocontrol testing. As a result, the dry sieving analysis, namely airjet sieving, is used in more than 90 % of all power plants and in certified laboratories in Europe.

As the revision of EN 450-1 shall reflect the common practice it is important to integrate this in the revised standard. The principle has already been tested in 1990 within the preparation of the first version of EN 450-1. Round robin testing from 8 countries (Austria, Belgium, Germany, Denmark, United Kingdom, Italy, Netherlands and Norway) on chemical and physical parameters was performed. The important aim of the tests was the evaluation of different test methods for fineness, especially wet and dry sieving methods. It concluded that wet sieving produced the best correlation between the laboratories. By this, the wet sieving procedure was proposed to be the reference method in the future EN standard for fly ash for concrete.

The airjet sieving with a 45 μm sieve led to nearly the same results, only the standard deviation is higher.

In the report it is also noted that airjet sieving with 40 and 45 μm sieves lead to only small differences. As the 45 μm sieve was regulated in ISO 565, the 45 μm sieve will be used in the future fly ash standard.

In a new comparative testing programme the same dependencies were discovered as found in the previous round robin. The tests on 45 μm sieve for wet and dry analysis are given in Figure 5.



Key

◆ Producer A
■ Producer B
▲ Producer C
◇ Producer D
△ Producer E
● Producer F
□ Producer G

X residue wet sieving 45 μm [% by mass]
Y residue dry sieving 45 μm [% by mass]

trendline for all data sets $y = 1{,}0105x + 0{,}7584$
$R^2 = 0{,}9566$

Figure 5 — Test results for wet and dry sieving – data compilation from seven producers
(45/45 μm sieve)

8 Measures within EN 450-1 to assure fly ash quality

8.1 Production process

In each step of the fully controlled chain from fuel to fly ash, measures are taken to assure fly ash quality:

- Intake of the fuels. Fuels that will be fired in a dry bottom boiler shall not only have a minimum caloric value, but also a limited content of compounds regarding fly ash quality.

  Also, in relation to avoid any corrosion, slagging and fouling in the boiler, these compounds have to be limited.

  For each type of fuel the producer needs a permit in respect of emission limits. The procedure to get the permissions is time consuming and costly. As a result, there is no possibility to burn a fuel for which no permits have been granted.

- The suitability of fly ash obtained from combustion of coal with co-combustion materials shall be established and documented by the producer. An initial co-combustion in the furnace using the highest intended amount of co-combustion material shall be performed. A representative sample of fly ash taken from this co-combustion shall be used to establish the suitability. Subclause 4.1 of EN 450-1 requires maximum share of co-combustion of 40 % fuel-based and 25 % ash-based. Further, the allowed types of co-fired fuels are defined according to Table 1 of EN 450-1.

- Storage of coal and secondary fuels. Digging up the fuel from the storage to transport it to the fuel mills is normally also used to homogenise the fuel. This is also positive for a constant quality of the generated fly ash.

- Milling of the fuels results in a fine grain size distribution, which is necessary to obtain good burn-out of the fuel. This is also positive for the LOI of the generated fly ash.

- Combustion process. The combustion process is optimised to improve the efficiency of the boiler. This implies that a high burn-out is being aimed for, which results in a low LOI fly ash.

8.2 Quality control and conformity evaluation technical properties

With EN 450-1 requirements regarding uniformity, innocuity and effectiveness are defined to guarantee the minimum quality of the resulting fly ash for the use as concrete addition within European countries. The proof that these requirements are fulfilled is guaranteed by a quality control, which consists of a factory production control by the producer and a third party control by an accepted supervisory board.

The fly ash producer is responsible for the factory production control consisting of the internal quality control and the autocontrol testing of samples. A scheme for the production control in a power plant is given in Figure 5.

The internal quality control is based on test results gained from samples taken at the outlet of the electrostatic precipitator. At this point the fly ash samples have to be tested on loss on ignition and fineness and – based on the results – conveyed to a silo for fly ash meeting the requirements of EN 450-1 (Quality QI) or to a silo for off-specification fly ash (Quality QII).

The autocontrol tests, i. e. chemical and physical tests are performed on fly ash samples taken from the silo by the producer as well as those to be performed by the certification body (TPC).

An important part of the provisions defined in EN 450-1 is the documentation of procedures for the production control in a works quality manual. The manual should contain all quality aims, responsibilities and powers of the responsible staff with regard to product quality, production and quality control techniques as well as inspections and tests during and after production. Responsible for the manual is the producer of fly ash, who is owner of the certificate of conformity.

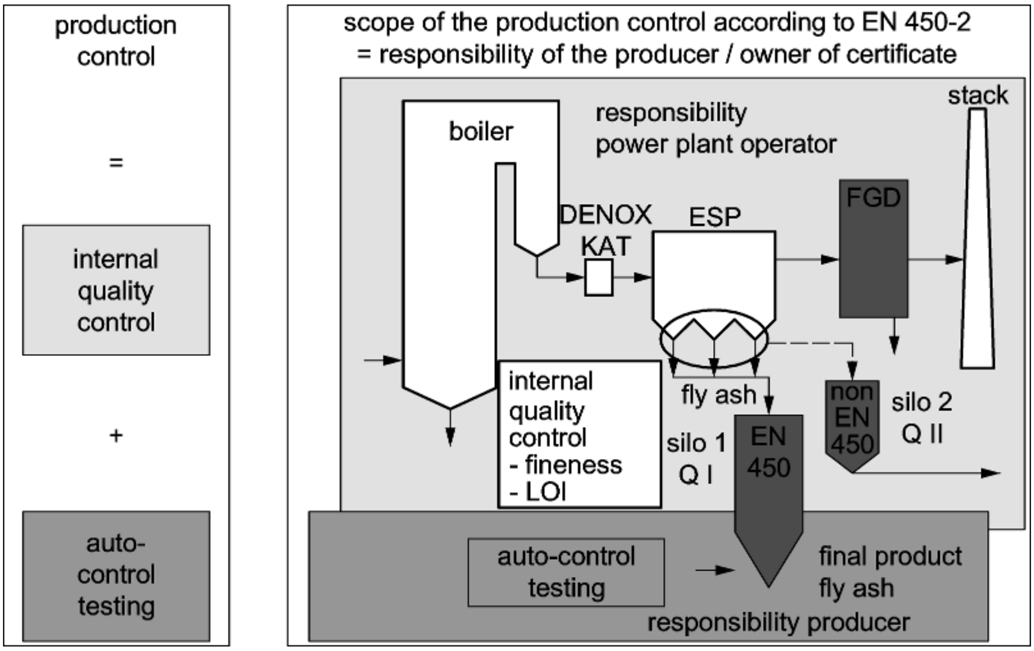


Figure 6 — Scheme of the production control according to EN 450-1 (Feuerborn, 2006)

8.3 Conformity evaluation toxicological and environmental aspects

Toxicological and hazardous properties of generated fly ashes are being monitored according to respectively REACH (from end 2010) and to the European Waste Catalogue.

The suitability and environmental compatibility (4.2 and 4.3) of fly ash obtained from co-combustion has to be demonstrated in each case (i.e. for each co-combustion material at maximum amount) by a testing procedure according to national regulations of the country, where the material is to be used. Conformity to the relevant regulations is required to be evaluated before the production. This procedure is observed by the product certification body before drawing up the certificate of conformity as described for the system of attestation of conformity 1+ (i. e. the certificate of conformity, CE-mark).

9 Impact of co-combustion on the release of regulated dangerous substances

9.1 General

In this clause, the additional information for fly ash from higher shares of co-combustion of biomass will be compiled and an update on the regulations for environmental aspects will be given (REACH, EWC, CLP).

Fly ash contains inorganic compounds like Si, Fe and Al but also very small concentrations of heavy metals. Further, it contains a small amount of relicts of organic fuel, which is measured as Loss on Ignition. Power plants obtain almost complete combustion of the fuels at very high temperature. Concentrations of relicts of incomplete combustion like dioxins (PCDD), furans (PCDF) and polycyclic hydrocarbons (PAH) are therefore very low and mostly below the detection limit. There is no indication that due to high percentages of co-combustion these concentrations are increased (Winkel, 2010).

9.2 Overruling regulation regarding toxicological and environmental aspects

9.2.1 General

The use of co-combustion material in power plants requires a specific permission regarding emissions to air, soil and water for the operation of the power plant. Fly ash from coal fired power plants has to follow regulations regarding waste. By this, the requirements of the European Waste Catalogue as well as specific regulations for waste utilisation have to be considered.

Fly ash for use in concrete has to meet the REACH regulations as they are placed on the market as products. The European power producers have registered the ashes from power production with the co-combustion materials as defined in EN 450-1:2012.

9.2.2 European Waste Catalogue

In January 2001, the European Commission has adopted a decision in order to come to a harmonised list of hazardous and non hazardous waste, the European Waste Catalogue (EWC). Ashes produced at 100 % coal-firing are defined as non-hazardous waste in the EWC, with EWC-codes 10 01 15 for bottom ash and 10 01 17 for coal fly ash. For ashes from co-combustion classification has to be assessed. The classification has to be established based on the chemical composition of the ashes and limit values for several classes of hazard properties. If the ashes contain hazardous compounds above one of the limit values, the EWC-codes are 10 01 14* and 10 01 16* for bottom ash and fly ash respectively. In that case the ashes are considered as "hazardous waste". If the concentrations are below the limit values, the ashes get the same EWC-code as ashes from 100 % coal-firing and are considered as "non-hazardous waste".

After extensive standardised assessments (Winkel and Cuperus, 2005) it was concluded that all tested co-combustion fly ash from Annex C are classified as non-hazardous waste.

For fly ash as a non hazardous material the SDS is prepared on voluntary basis.

9.2.3 REACH

REACH is a new European Community Regulation on chemicals and their safe use (EC 1907/2006). It deals with the Registration, Evaluation, Authorisation and Restriction of Chemicals. The new law entered into force on 1 June 2007. The two most important aims are to improve protection of human health and the environment from the risks of chemicals while enhancing the competitiveness of the EU chemicals industry.

Existing substances with more than 1 000 ton/year production like fly ash, has to be registered before December 1st 2010. The registration is based on a dossier containing data about physico-chemical, ecotoxicological and toxicological information to be considered for use and exposures. Producers of substances with hazardous properties have the obligation to prepare Safety Data Sheets for the intended uses of their products, based on the Chemical Safety Report, which is a part of the dossier for the registration. If the material is used as prescribed in the Safety Data Sheet no harmful exposure of the environment and humans will occur, with exception of incidents.

Fly ash from co-combustion of secondary fuels as described in EN 450-1 are included in the REACH registration of coal ash.

9.2.4 Directive on Dangerous Substances

In 1967, the Directive on Dangerous Substances was introduced to protect public health, in particular the health of workers handling dangerous substances. The law introduced EU-wide provisions on the classification, packaging and labelling of dangerous substances. One tool to inform about dangerous properties is the Health and Safety Data Sheet (HSDS), which for fly ash is produced on a voluntary basis as fly ash, do not possess hazardous properties.

The Directive has regularly been updated to take into account the latest scientific and technical progress so as to ensure the highest level of protection for individuals and the environment. The current classification and labelling system is in the process of being replaced by a new law known as the Regulation on the Classification, Labelling and Packaging of Substances and Mixtures (CLP Directive), which takes effect from 20 January. 2009 and has to be considered together with the REACH registration of ash.

The CLP Regulation incorporates the classification criteria and labelling rules agreed at UN level, the so-called Globally Harmonised System of Classification and Labelling of Chemicals (GHS).

9.3 Environmental regulations (Leaching)

The use of fly ash according EN 450-1 requires environmental compatibility with national laws, regulations and administrative provisions in the place of use (4.3).

At least in the Netherlands and in Germany additional requirements have to be met for fly ash from co-combustion. Already for the last revision of EN 450-1 a CEN report was prepared based on an enquiry of CEN/TC 104/WG 4 in 1998 on “Fly ash obtained from co-combustion – A report on the situation in Europe” which was published in May 2008 as CEN/TR 15677.

A systematic assessment of leaching has been performed on Dutch co-combustion fly ashes during the last 15 years as part of the conformity procedure. Up to July 2008, leaching behaviour has to meet the requirements of the Dutch Building Materials Decree (and from July 2008 on, it has to meet the limit values of the Decree on Soil Quality). Leaching tests have been performed on concrete in which 30 % of cement is replaced by co-combustion fly ash. The tests were performed on concrete by the so-called diffusion test (NEN 7375) according to the Dutch guideline BRL 2505. Tests have been performed for many different co-combustion fly ashes in high co-combustion percentages. The principal of these test method is meeting that of the harmonised test procedure for bound material prepared in CEN/TC 351/WG 1.

In Table 6 maximum measured leaching values are given next to the most stringent limit values of the Building Materials Decree (expressed as immission values). Hg, Pb, Sn and V were not measured as these are not potentially critical, based on the leaching during the maximum availability test, which is the worst case situation for leaching. The results show that leaching of all concrete tests are well below the limit values of the Building Materials Decree, with exception of Se. However, selenium is mainly derived from coal instead of co-combustion fuel. This means that co-combustion fly ashes can be used in concrete without any restriction. This low leaching values can be explained by the facts that most allowed secondary fuels are not contaminated and that in the case of contaminated fuels (PET-cokes and sewage sludge), maximum co-combustion is limited by other parameters and environmental regulations.

Table 6 — Measured leaching of concrete with co-combustion fly ash as pozzolanic filler (KEMA, 2007)

Compound	Limit mg/m^2 [a]	Range mg/m^2 [a]
As	435	< 14 –180
Ba	6 300	160 – 1300
Cd	12	< 1,1 – 3,5
Co	300	< 11 – 35
Cu	540	11 – 39
Mo	150	5,5 – 18
Ni	525	11 – 35
Sb	39	4,4 – 14
Se	15	1,1 – 14
Zn	2 100	44 – 180
F	14 000	220 – 700
Br	90	18 – 56
Cl	30 000	29 – 92
SO_4	45 000	400 – 1900

[a] Expressed as immission value to soil.

Annex A
(informative)

List of abbreviations

CCSEM	Computer Controlled Scanning Electron Microscope
CUAP	Common Understanding of Assessment Procedure
CUR	Civieltechnisch Centrum Oitvoering (Civil Engineering Centrum for Execution of Research and Regulation (CUR))
ETA	European Technical Approval
ICP	Inductively Coupled Plasma – Atomic Emission Spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

Annex B
(informative)

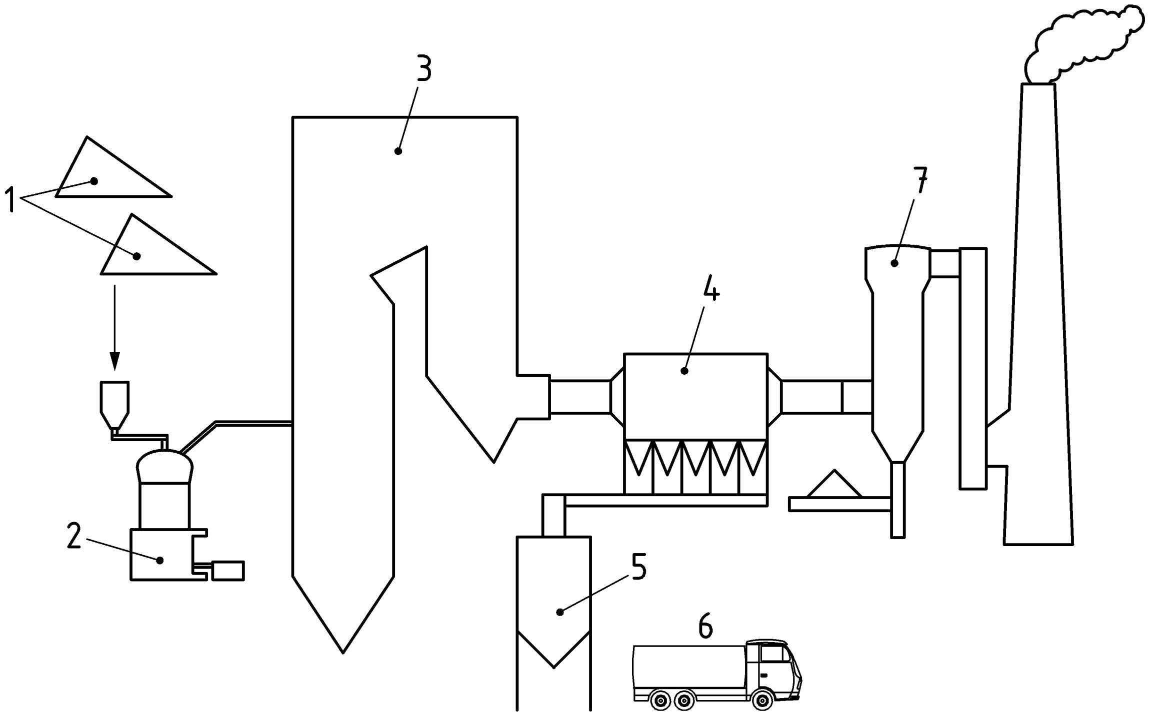
Generation of fly ash

B.1 The chain from fuel to fly ash, ready for use in concrete

Fly ash is derived from the burning of pulverised coal with or without co-combustion materials. This means that fly ash is generated in special boilers, based on the principle of cloud combustion. This type of combustion need fuels that are suitable for firing in the boiler and have to meet specific requirements to get an efficient and working combustion, as the residence time is only a few seconds. Main requirements are fineness (100 % < 100 μm; 70 %– 95 % < 75 μm), minimum caloric value and chemical composition in relation to corrosion (Cl), slagging and fouling (Cl, K, S).

The following steps can be distinguished in the chain from fuel to fly ash, ready for use in concrete (see Figure B.1):

- Storage of coal and secondary fuels. Coal is normally stored in open air. Secondary fuels can be stored outside, in silo's or in (half) open storages.
- Fuel milling to a grain size 100 % < 100 μm; 70 %– 95 % < 75 μm.
- Cloud combustion of fuel. From the fuel mills, the powdered fuel is pneumatically transported and injected into the boiler by jet or swirl burners. The pulverised coal is injected towards the tangent of a virtual circle in the core of the combustion chamber. Through this configuration a rotating fireball is created. Jet burners are generally situated in the corners of tangential-fired boilers. The temperature of this fireball is about 1 400 °C – 1 500 °C. The boiler has normally an end of furnace temperature of about 1 175 °C. The average residence time of an ash particle in the boiler is between 1 – 3 s.
- Capture of fly ash. About 87 % by mass of the ash that is produced during the combustion process, leaves the boiler with the flue gasses; the other 13 % by mass falls directly or indirectly (after slagging) to the bottom of the boiler (bottom ash). Before the flue gases are de-sulfurised, the ash particles are removed by electrostatic precipitators (ESP).
- Storage of fly ash in silo's.
- Transport to concrete producer's facility (after quality control).



Key

1 storage of coal and secondary fuels
2 fuel milling
3 cloud combustion of fuel at 1 300 – 1 500 °C
4 capture of fly ash (ESP)
5 storage of fly ash
6 transport to industry
7 FGD

Figure B.1 — Process scheme of power generation and fly ash generation

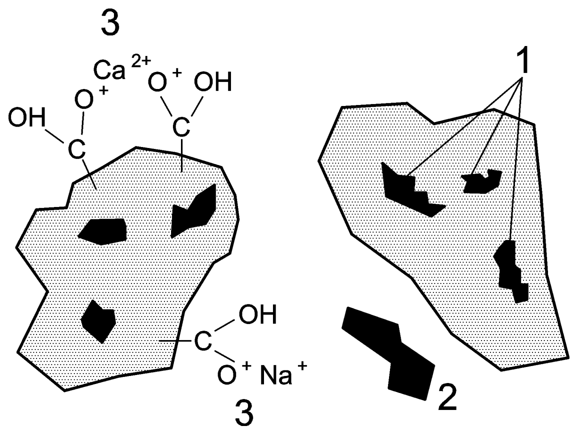
B.2 Ash formation during combustion

Coal can be defined as a combustible, sedimentary organic rock, which is composed mainly of carbon, hydrogen and oxygen. It is formed from vegetation, which has been consolidated between other rock strata and altered by the combined effects of pressure and heat over millions of years to form coal seams (definition used by the World Coal Institute). A coal layer is mostly a part of a regular succession of sediments (a so-called cyclothem) like limestone, sand, shale and shells. It can be imaged that coal also after processing, always contains a certain amount of these compounds. Such compounds are also present in the coal layers itself. In general the term mineral matter is used. Mineral matter can be defined as representing the sum of the minerals and inorganic matter in and associated with coal (Ward, 2002).

This mineral matter can be present (IEA Coal Research, 1996) (see also Figure B.2) in a number of forms:

- excluded mineral grains, which break free of the coal during milling or are added to the coal from an external source due to the mining process; these grains are relatively large;
- included mineral grains which are retained in the coal during milling and tend to be smaller;
- organically bound elements, which are distributed within the coal macerals; these elements are liberated during the combustion process;
- salts dissolved in pore water.

The latter two are more dominant in lower rank coals like lignite and sub-bituminous coals, but these are present in relatively low concentrations in bituminous coals (Ward, 2002).



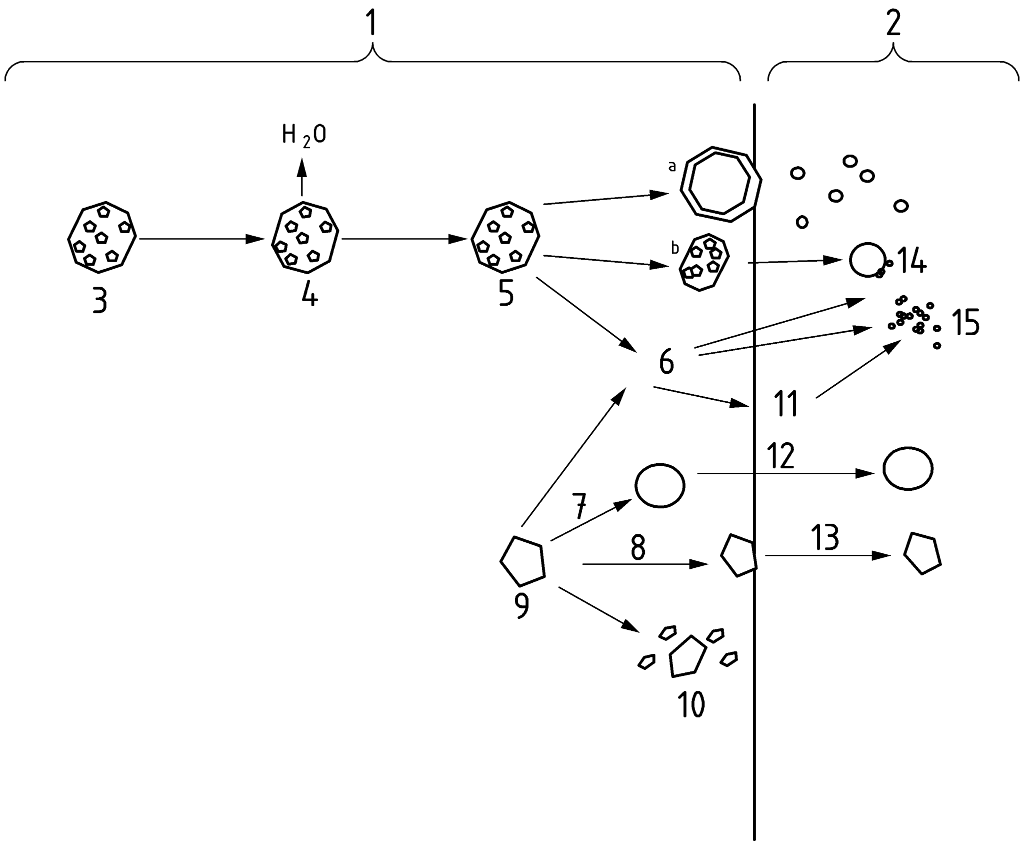
Key

1 included minerals
2 excluded mineral
3 organically associated elements

Figure B.2 — Distribution of ash-forming matter in coal [Hansen, 1998]
(format modified according to ISO 128 (all parts) and ISO 129 (all parts))

This mineral matter contains the basic compounds for ash formation during the combustion processes of coals and co-combustion materials. During this process many different ash-forming processes take place. The basic ash-forming processes are (see also Figure B.3):

- Coalescence of ash-forming grains in one coal particle.
- Vaporisation and condensation of organically bound elements.
- Fragmentation of excluded minerals due to the thermal shock during the combustion process.
- Conversion, melting, followed by solidification of minerals like illite.
- Conversion of minerals like calcite (decarbonation), quartz (crystal modification) and apatite.
- Vaporisation and condensation of inorganically bound elements.
- Oxidation, mainly of pyrite.



Key

1 heating
2 cooling
3 original coal particle with included mineral grains and organically bound elements
4 drying
5 devolatilisation
6 vaporisation
7 fusion
8 conversion
9 excluded mineral grain
10 framentation
11 reaction
12 solidfaction
13 conversion
14 condensation and adhesion to 22
15 condensation to submicron particles
a swelling ratio > 1,3
b swelling ratio > 0,9

Figure B.3 — Ash-forming mechanisms, based on (IEA, 2006)
(format modified acc. ISO 128 (all parts) and ISO 129 (all parts))

The main reaction products during coal firing, with and without co-combustion, are an amorphous phase consisting of alumino-silicate glass, which is about 50 % to 70 % by mass of the total fly ash. This phase is responsible for the pozzolanic behaviour. Further, other mineral phases are present, which are enlisted in Table B.1.

Table B.1 — Overview of common and less common mineral phases in fly ash, meeting the requirements of EN 450-1 (CUR, 2003)

Group	Classification	Phases
0	Non-crystalline and organic phases, always present [a]	Amorphous phases (alumino-silicate glass) Unburnt matter
1	Crystalline phases, nearly always present [b]	Anhydrite ($CaSO_4$) Free lime (CaO) Quartz (α-SiO_2) Hematite (α-Fe_2O_3) Mullite ($Al_6Si_2O_{13}$)
2	Crystalline phases, sometimes present [b]	Calcite ($CaCO_3$) Magnetite (Fe_3O_4)
3	Crystalline phases, incidentally present [b]	Periclase (MgO) Rutile (TiO_2) Corundum (Al_2O_3) Sillimanite (Al_2SiO_3) Feldspars

[a] To be identified using gravimetric and/or chemical methods.

[b] As identified with X-ray diffraction.

Annex C
(informative)

Overview of tested fly ashes obtained from co-combustion

Table C.1 gives an overview of fly ashes with maximum co-combustion percentages according CUAP 03.01-34[4].

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[4] Evaluation report for the assessment of ETA for Vliegasunie, October 2007, Evaluation report for the assessment of ETA for Electrabel, June 2007, Evaluation report for the assessment of ETA for E.ON, December 2007.

Table C.1 — Overview of fly ashes with maximum co-combustion percentages

Co-combustion material type	**Ash content in Co-combustion material** % by mass	**Co-combustion material proportion** % by mass	**Co-combustion ash in total ash** % by mass
Vegetable materials			
Cacao shells	9,4	21,1	18,6
Citrus shells	4,4	4,3	1,9
Coffee grounds	3,8	3,1	1,2
Demolition wood A	2,1	23,5	6,1
Demolition wood A/B	5,0	10,0	5,3
Grape kernels	3,5	4,2	1,3
Grass seed	27,3	1,4	3,7
Olive shells	11,9	10,0	11,7
Palm shells	6,0	19,6	12,8
Peanut shells	3,5	20,0	8,0
Poultry litter	9,9	2,5	2,5
Soya shells	4,2	19,0	9,0
Wheat husk	3,7	5,8	2,2
Wood pellets	1,5	35,4	5,0
Biomass pellets	18,7	8,3	14,5
Animal meal (meat and bone meal)			
Animal fat	0,0	3,4	0,0
Animal meal (meat and bone meal)	15,6	10,2	15,1
Municipal sewage sludge			
Municipal sewage sludge	45,0	7,0	27,7
Paper sludge			
Paper sludge	44,0	5,0	18,8
Virtually ash free liquid and gaseous fuels			
Industrial HC liquid	0,0	7,0	0,0
Other fuels, not meeting Table 1			
Carbon black	0,7	0,7	0,1
Industrial sewage sludge	7,6	0,9	0,7
Solid recovered fuels 1	11,0	3,0	3,0
Solid recovered fuels 2	34,0	3,3	10,4

Annex D
(informative)

Calculated maximum co-combustion amounts

D.1 Objective

The objective of this study is to assess the maximum co-combustion percentages of secondary fuels in coal-fired power plants (dry bottom) in relation to the chemical requirements of EN 450-1:2005 and CUAP 03.01/34. See further (KEMA, 2008).

D.2 Method

The KEMA TRACE MODEL® is an empirical and statistical model to predict the emissions and ash composition of coal fired power plants. It is developed on the basis of more than 20 years of experience with mass balance studies at coal-fired power plants (dry bottom boilers) in the Netherlands (with and without co-combustion. The KEMA TRACE MODEL® – variant Pulverised Fuel Combustion - is regularly used by KEMA to calculate the consequences of coal firing and co-firing with respect to ash quality and emissions. Results of model calculations are used in official documents in discussions with governmental authorities, in Environmental Impact Statements and in permit applications.

D.3 Data

The input of the model is based on a database that contains the composition of both coal and secondary fuels, as fired in Dutch power stations, and originating from all over the world. This database is up-to-date and most of its values are derived using the most advanced analysing techniques possible to date. The latest weighted average coal composition is from 2006. For some secondary fuels the data were obtained in 2007.

The composition of the residues and flue gases of a coal-fired power plant for 4 main components, 10 macro elements and 36 micro and trace elements is calculated. The composition of bottom ash and fly ash can be examined according to several Dutch and European regulations, for example the EWC (European Waste Catalogue) limits, EN 450-1 and BRL 2505. In case of co-firing, a judgment is made on whether the ash is hazardous or non-hazardous waste, according to the EWC.

D.4 Results

In Table IV-1 the results are presented of the model calculations. In column 2, for each fuel the criterion of EN 450-1 is given that limits the co-combustion share. In column 3 and 4 the accompanying maximum co-combustion percentage is given (ash-based and fuel-based).

Biomass pellets and green wood are limited by the definition that allows maximum co-combustion, which means that all other chemical requirements are being met. In other cases these requirements are met by directly limiting one of the chemical requirements like total P2O5 for palm kernels. An exception is PET-cokes which are not limited by the chemical requirements of EN 450-1, but by other national regulations regarding emissions, occupational health and safety and production of hazardous waste. See also Note 1 of Annex ZA of EN 450-1:2005+A1:2007.

Some illustrating results of the calculated chemical composition of co-combustion fly ashes at the maximum allowed co-combustion percentage are presented in Table D.2.

Table D.1 — Maximum proportion of fuel and ash derived from co-combustion materials (M) of fly ashes from co-combustion adjusted to the maximum amount for the most critical requirements concerning chemical properties of fly ash or to the definition of maximum co-combustion (KEMA, 2008)

secondary fuel	**Limiting criterion** **EN 450-1:2005+A1:2007**	**Ash based** % by mass	**Fuel based** % by mass
Vegetable materials			
green wood 1	Co-combustion fuel based	15	40
green wood 2	Co-combustion fuel based	3	40
green wood 3	Co-combustion fuel based	3	40
bark wood	reactive CaO	13	34
Cacao shells	Na_2O equivalent (K)	15	20
palm kernels	total P_2O_5	16	29
poultry dung	reactive CaO	15	10
biomass pellets	Co-combustion ash based	25	12
Animal meal			
meat & bone meal	total P_2O_5	12	6
Municipal sewage sludge			
municipal sewage sludge	total P_2O_5	21	8
Paper sludge			
Paper sludge [b]	Reactive CaO	16	5
Petroleum cokes			
PET-cokes	—	(2) [a]	(37) [a]
Virtually ash free liquid and gaseous fuels			
Industrial HC liquid [b]	Co-combustion fuel based	0	40

[a] Maximum co-combustion percentage avoiding classification of hazardous waste according to EW.

[b] Extra calculations performed.

Table D.2 — Calculated chemical composition of co-combustion fly ashes at the maximum allowed co-combustion percentage (KEMA, 2008)

	100% Coal % by mass	**Wood Bark** % by mass	**municipal sewage sludge** % by mass	**cacao residues** % by mass
Proportion of coal Combustion (Kc)	100	66	92	80
Proportion of ash derived from co-combustion materials (M)	0	13	21	15
Composition				
Al_2O_3	26,8	23,6	23,7	23,0
CaO	4,1	10,0	6,6	4,1
Cl	0,001	0,002	0,001	0,001
Fe_2O_3	6,5	6,7	9,2	5,7
K_2O	1,3	3,0	1,3	6,8
MgO	2,0	2,1	2,0	3,4
Na_2O	0,6	0,6	0,6	0,5
P_2O_5	0,8	1,1	5,0	3,0
SiO_2	52,4	46,7	46,7	47,0
SO_3	0,03	0,3	0,3	0,3
TiO_2	1,3	1,7	1,2	1,1

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