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The Materials and Energy Potential Method for the Quantitative Distinction Between Waste Valorization and Elimination in the Cement Industry

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Executive summary

This report proposes a quantitative method to distinguish between the valorization and elimination of waste in a cement kiln. Examples are presented to illustrate the consequences of the developed approach. These examples are related to the process conditions in the kiln in the dry- and the wet-cement process.

Valorization is defined as the processing of a waste in a cement kiln to substitute raw materials and/or fuels. In this case, the waste contributes, in a positive way, to the cement production process.

Waste combustion in a cement kiln without any substitution or process improvement and with the sole purpose of final waste processing is defined as elimination.

The differentiation between elimination and valorization is of importance as regulations distinguish between waste elimination and valorization. For instance, directives of the European Union allow the export of waste for the purpose of valorization.

A review of earlier proposed methods to define valorization shows that most approaches are based on the comparison of the waste with a fuel and that a clear appreciation of both the energy and the raw material value of a waste does not exist.

The method which is presented in this report is based on the recognition that a specific waste can contribute to the cement-making process as an alternative raw material and, at the same time, as a source of energy. This is a specific advantage of waste processing in the cement process which is expressed in the assessment method: the Materials and Energy Potential (MEP) method.

Essential steps in the development of the proposed method are:

- division of the waste in a raw materials fraction and the rest or energy fraction which is separately evaluated as a source of energy;
- quantitative measures for the raw materials content and the value of the energy fraction are developed;
- based on these measures, an assessment of waste processing as valorization or elimination is proposed.

Below, the decision scheme is shown to decide upon valorization or elimination of a waste in a cement kiln following the MEP method.

Another essential aspect of the proposed method is the interpretation of the term “source of energy”. In this study, a “source of energy” is distinguished from a “fuel” with calorific values of 15 MJ/kg up to 40 MJ/kg (wood, coal, oil). The starting point chosen is that any energy contribution (to the cement process) is sufficient for the classification “energy source”.

First, the raw materials part is established. This fraction contains the components that are useful to (functional in) the cement process: CaO ($CaCO_3$), SiO_2, Al_2O_3, Fe_2O_3 and SO_3. The other inorganic components (including water) in the waste are allocated to the raw materials fraction up to maximum values, mwaf and maif, by which the fraction functional components is allowed to contain an equivalent amount of water and non-functional components as occur in natural raw materials. If Ca occurs as $CaCO_3$, the $CaCO_3$ quantity is allocated to the raw materials fraction. The following expression is used to calculate the measure **M** for the raw materials value of the waste:

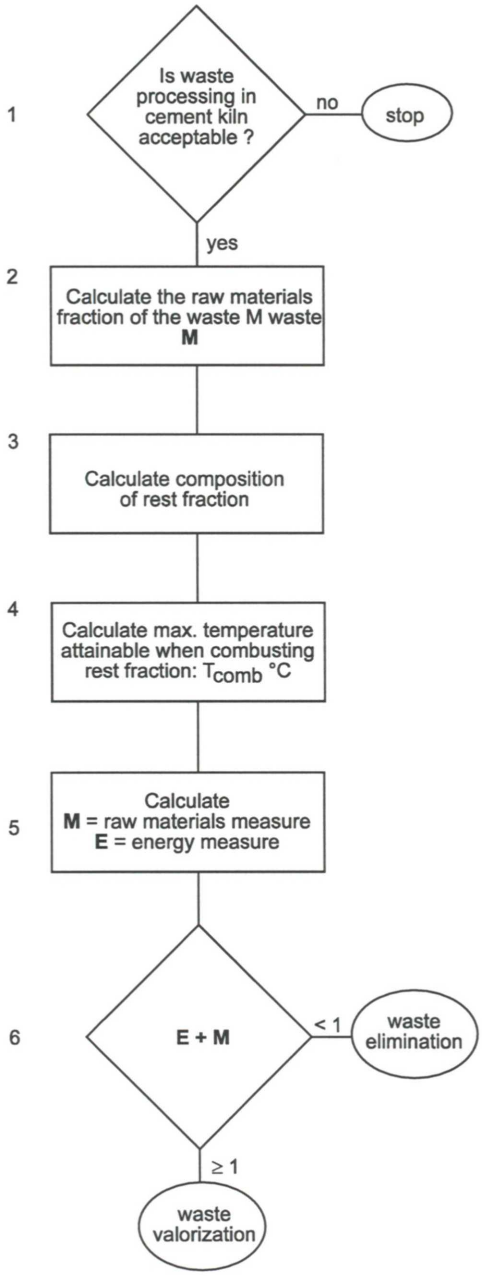
$$M = usmf / (1 - minw) (1 - mini)$$

wherein:
usmf = fraction of useful materials in waste as such
waf = water fraction in waste as such
inf = fraction of inert, non-functional components in the waste
mwaf = maximum water fraction allowed in raw materials fraction
maif = maximum inert fraction allowed in raw materials fraction
mini = minimum value of inf and maif
minw = minimum value of waf and mwaf.

Example 1: For the dry-cement process, the raw materials fraction can contain up to 15 % water. In this report, a maximum of 10% is used as an example for the non-functional part of the raw materials. So, for the dry-cement process mwaf = 0.15 and maif = 0.10.
Example 2: For the wet-cement process, up to 30 % water and the same percentage, 10, of non-functional (inert and trace) elements are allocated to the raw materials fraction, comparable to the natural raw materials. Again, as an example a maximum of 10% non-functional components is used for the non-functional part of the raw materials fraction. So, for the wet-cement process mwaf = 0.30 and maif = 0.10.

Secondly, the energy value of the rest or energy fraction (= waste minus raw materials fraction) is expressed in a measure **E**. It is proposed to consider the combustion of a material as energy valorization if the autothermal combustion temperature calculated for the actual condition, exceeds a reference temperature level, T_{ref}, essential for the process.

Decision scheme for waste valorization in a cement kiln.



Remarks:

Acceptable with regard to:
- health risks
- emissions
- technical product quality
- environmental product quality
- see Chapter 3.2

Raw materials fraction M:
- sum of CaO, $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and SO_3
- corrected for moisture content and non-functional components in natural raw material
- see Chapter 3.3

Calculate concentrations and heating value based on 100 % rest fraction

Process conditions in cement kiln:
- process temperature min. 1500 °C (= T_{ref})
- 75 % energy efficiency
- 3 % oxygen content
- air inlet 800 °C (= T_0)
- see Chapter 3.4

- **M** = raw materials fraction
- see Chapter 3.3

- **E** = $(T_{comb} - T_0)/(T_{ref} - T_o)$
- T_0 = initial temperature (e.g. air inlet)
- T_{ref} = reference temperature, required in process

For example, for the process of clinker formation in the cement kiln a temperature of 1450°C is minimally required

For the measure for the energetic value of a material in a process, E, the following expression is introduced:

$$E = (T_{comb} - T_o) / (T_{ref} - T_o)$$

wherein:

T_{ref} = an essential reference temperature level in the process to be reached (°C)

T_{comb} = the autothermal combustion temperature of the considered material under the prevailing process conditions (°C)

T_o = an initial temperature level in the process to be considered as the starting temperature for the heating process (°C).

E expresses relatively the extent to which the required temperature level, T_{ref}, is reached or exceeded by the combustion of the energy fraction. This being the case, the material is able to contribute to the energy needs of the process. T_o expresses a basic temperature to be used as the initial temperature for calculating T_{comb}. For example, T_o could be the combustion air temperature at the inlet of the kiln.

As a consequence of the above, a material with the composition of the energy fraction is valorized as a source of energy if:

$$\boldsymbol{E} \geq 1$$

*Example: For the dry- as well as for the wet-cement process T_{ref} is set at 1500 °C, exceeding the minimum required temperature of 1450 °C .The process conditions to calculate the combustion temperature are: an oxygen concentration of 3 %, an inlet temperature of the air of 800 °C (= T_o) and an energy efficiency of 75 %. Thus, the **E** measure is calculated as:*

$$\boldsymbol{E} = (T_{comb} - 800)/(1500 - 800)$$

For the general assesment of processing a waste with a raw materials and an energy part, the Materials and Energy Potential of the waste, defined as the sum of **M** and **E**, is proposed as a measure. It follows from the starting points referred to above that processing a waste with **E**≥1 or **M**=1 in the cement kiln is a case of valorization.
It is proposed generally to consider processing of a waste in a cement kiln as valorization when

$$\boldsymbol{E} + \boldsymbol{M} \geq 1$$

This relation is the basis for the Materials and Energy Potential method presented in this study. E is calculated from the energy fraction, M from the raw materials fraction. Examples are presented to show the consequences of this method that enables a quantitative distinction between valorization and elimination. For wastes with an **M** value of nearly 1, the formulated condition may be too strict.

The result of the appreciation of the raw materials aspect is that TNO's MEP method favours processing of wastes with a raw materials component in the cement kiln. The allocation of (part of the) water in the waste to the raw material fraction is favours the processing of wet wastes in the wet-cement process. Generally, however, from the results of the calculations for actually applied as well as for artificially composed wastes, it is concluded. that in many cases the conclusion is the same for the wet process as for the dry process.

In the following table, some calculations are presented as example.

↓ → **waste** **characteristics**	**Organic solvent**	**Filtration earth**	**Artificial waste**	**Filter cake**	**LD slag**
LHV * (MJ/kg)	25	12.5	3.4	6	0
water (%)	20	20	50	50	5
ash (%)	–	50	20	20	95
Dry-cement process					
T_{comb} (excl. raw materials fraction) (°C)	1873	1912	1151	1400	–
M (–)	0	0.59	0.24	0.24	1.0
E (-)	1.53	1.75	0.50	0.86	–
E + M (-)	1.53	2.45	0.74	1.09	1.0
Valorization	YES	YES	NO	YES	YES
Wet-cement process					
T_{comb} (excl. raw materials fraction) (°C)	1873	2023	1212	1476	–
M (–)	0	0.70	0.29	0.29	1.0
E (-)	1.53	1.75	0.59	0.96	0
E + M (-)	1.53	2.45	0.88	1.25	1.00
Valorization	YES	YES	NO	YES	YES

* Lower Heating Value of waste as such

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Appendix 1	The cement manufacturing process
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Appendix 3	More examples of MEP calculations and comparison with Eurits method

1. Introduction

1.1 Valorization or elimination

In the classical cement manufacturing process, the raw materials and fuels used (such as limestone, clay components and coals, fuel oil or natural gas) are of predominantly natural origin [4a]. By making controlled use of the known and proven process technology of the cement manufacturing process, these can be replaced by so-called secondary materials: waste materials from industrial production processes or from waste collection. Research and development in the cement industry have resulted in new sludge and solids handling systems to make the handling of these new secondary materials possible [7].

Secondary raw materials are therefore residues which can be used as alternatives to primary raw materials. Secondary fuels are combustible residues which represent alternatives to primary fuels. Some secondary materials can be classified as composed of an alternative raw material and of a fuel part.

In this report, the processing of a waste in a cement kiln to substitute raw materials and/or fuels is defined as waste valorization. In this case, the waste contributes, in a positive way, to the cement production process.

Next to valorization of waste in a cement kiln, waste can be incinerated in a cement kiln as an alternative to waste combustion in a specialized waste combustion plant; the goal is the final treatment of the waste and there is no (or no significant) contribution to the cement production process. The high temperatures in the cement kiln, the alkaline environment, and the potential immobilization of ashes in the cement can make combustion in a cement kiln an attractive process for final treatment of a waste.

Waste combustion in a cement kiln with the sole purpose of final waste processing is defined here as elimination.

The differentiation between elimination and valorization is of importance as regulations distinguish between waste elimination and valorization. For instance, directives of the European Union allow the export of waste for the purpose of valorization.

The attraction of a cement kiln for the valorization or elimination of wastes and the importance of the difference has resulted in extensive literature and many proposals by authorities that often deal with the subject from different viewpoints emphasizing different aspects. Competition between cement kilns and the existing infrastructure of waste incinerators has led to discussions and proposals on the preference and admission of final waste treatment, either in cement kilns or in waste incinerators.

1.2 Goal and subject of the study

The goal of the study is to formulate criteria for the discrimination between valorization and elimination of waste in a cement kiln. If possible, these criteria should be quantifiable.

The criteria should be the result of technological considerations. Commercial and safety aspects are not considered in this study. Legal questions and contents of regulations are discussed only briefly.

1.3 Working method

In addition to views from literature, discussions with experts and authorities have been held to set up an overview of factors that are considered to determine the difference between valorization and elimination, and of the (variation in) positions that can be taken.

A quantitative method has been developed to distinguish between waste valorization and elimination for the wet- and the dry-cement process. The method has been demonstrated by calculating of the consequences for a number of illustrative wastes. Originally, this method has been developed for the wet-cement process. Febelcem, the Federation of the Belgian Cement Industry, has members producing cement by either the dry cement or the wet-cement process. Therefore, by order of Febelcem, the method has been extended to include dry-cement processes.

The Belgian cement industry has a great deal of experience in using solid and liquid wastes in its cement process. Appendix 2 presents an overview of raw materials, fuels, wastes and energetic and environmental aspects illustrate the potentials of waste usage as well as the related environmental conditions.

2. Proposals to distinguish between valorization and elimination

2.1 Overview

A technological answer to the question 'valorization or elimination?' should be decided by conditions on thermal value and raw materials content. In recent papers, a number of proposals are encountered for criteria mainly based on calorific value and, sometimes, on raw materials content. The choices made are not all clearly founded and not always based on waste application specifically in the cement industry. Arguments, other than direct technological or ecological ones, are often considered, such as protection of an existing waste incineration infrastructure, maintainability and simplicity of regulations.

Examples of conditions on calorific value or raw materials content are:

- In Germany, according to the "Kreislaufgesetz", the energy content has to be larger than 11 MJ/kg and the fuel efficiency must be at least 75 %. Conditions on raw materials content have not been published [19].

- The Ministry of the Environment (VROM) in the Netherlands sets a calorific value limit of 15 MJ/kg and states that only liquids can be processed (valorized) properly in a cement kiln (i.e. no sludges and no solids). In a former paper, a limit had been proposed of 18 MJ/kg or a useful ash content exceeding 50%.

- In France, based on EC Directive 94/67, energy recovery for the cement industry is recognized from 5 MJ/kg.

- In a proposition to BUWAL and in an OVAM paper, it is proposition that processing of a waste can only be regarded as valorization if the calorific value exceeds 25 MJ/kg and the contaminants in the waste do not exceed the given concentration limits <u>or</u> the calorific value exceeds 15 MJ/kg and the concentration of the contaminants in the waste does not exceed the limits, and the total concentration of Ca, Si, Al and Fe is larger than 10 % [18, 20].

- Eurits (an organization formed by the specialized waste incinerators) proposes calorific limits of 11.5 MJ/kg and 15 MJ/kg, depending on the chlorine content of the waste being smaller or higher than 1 %, respectively [21]. Eurits promotes the application of its calculations for all co-combustion processes.

With the exception of the limits proposed in the Eurits paper, the calorific limits are based on values from fuels applied in cement kilns or in other applications. The calorific values proposed by Eurits have a more technological base [21]. They are derived from EC conditions on incineration of hazardous waste in installations specialized in waste incineration (EC Directive 94/67/EG). These conditions are 850 °C at 6 % O_2 excess when the waste contains less than 1 % Cl and 1100 °C at 6 % O_2 excess when the Cl content exceeds 1 % (these conditions, however, are not valid for co-incineration in a cement kiln).

As a general criterion for co-incineration, the Eurits paper formulates that the waste considered should be able to reach these temperatures autonomously. From this starting point, the calorific values mentioned above have been derived, assuming a waste with 25 % water and 35 % ash and 10 % energy loss during waste incineration.

2.2 Discussion

Considering the proposals mentioned above, the following aspects deserve attention.

- The emphasis in the discussion on valorization is on the value of the waste as a substitute for fuel;
- Limits for the energetic value of the waste are often proposed based on comparison with calorific values of fuels. The energy contribution of the waste to the cement process is not evaluated directly, though the EC Directive mentions the use of the waste as “a source of energy”;
- Criteria for the raw materials content are mostly lacking or a limit value is arbitrarily set;
- The possible synergy in the cement process that a waste can contribute to the energy need as well as to the raw materials need is only appreciated to some extent in the OVAM proposal;
- In its EURITS paper, the waste industry has proposed criteria derived from combustion properties and process conditions in a waste incinerator; not from the positive value as a raw material or a source of energy.

Most criteria are not specific to the use and functionality of the waste in the cement process. In this respect, the proposal in this study differs from others. As a consequence of the definition for valorization as stated in Chapter 1.1, the waste value for the cement process is chosen as the major criterion to distinguish waste valorization from elimination in the cement process.

3. Valorization or elimination

3.1 General

In this chapter, a method to distinguish between valorization and elimination is developed. The method is based on the recognition that a specific waste can contribute to the cement-making process as an alternative raw material and at the same time as a source of energy. This is a specific advantage of waste processing in the cement process that should be expressed by the assessment method.

Essential steps in the method developed are:

- division of the waste in to two fractions: a raw materials fraction and the rest fraction, also called the energy fraction, which is separately evaluated as a source of energy;
- quantitative measures for the raw materials content and the energetic value of the energy fraction are proposed;
- based on these measures, an assessment method for waste processing as valorization or elimination is presented.

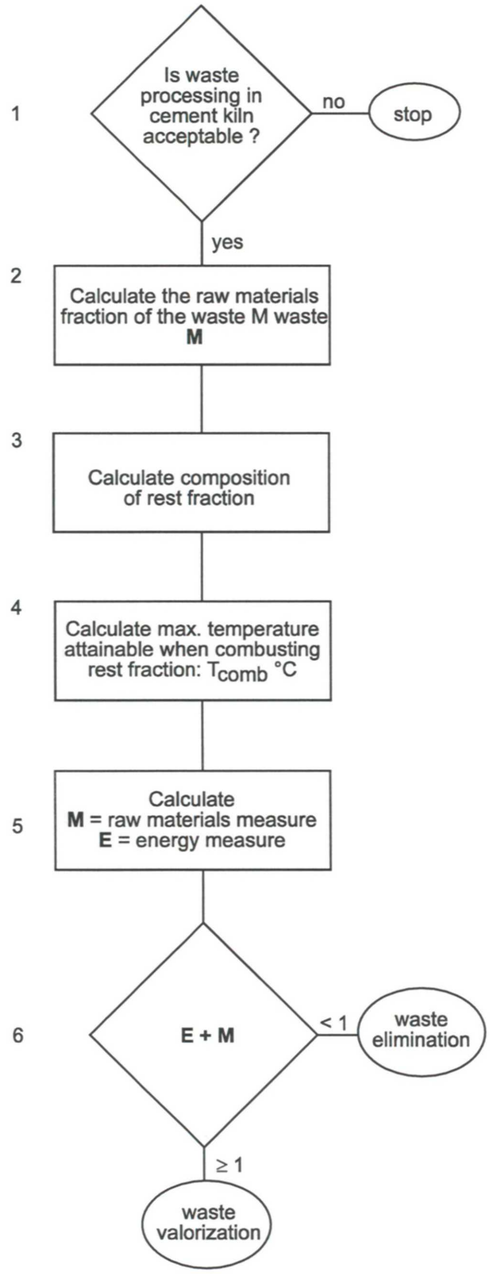
The expression “source of energy” is used in the EC Directive 75/442/EC. An essential aspect in the proposed method is the interpretation of the term “source of energy”. In this study, a “source of energy” is distinguished from a “fuel” with calorific values of 15 MJ/kg up to 40 MJ/kg (wood, coal, oil). The starting point chosen is that any positive energy contribution (to the cement process) is sufficient for the classification “energy source”.

To evaluate the energy content, the combustion behaviour at the process conditions in the kiln is used as a starting point. More specifically, the combustion temperature that can be reached autothermally is used to define a measure for the energetic value of the waste or a waste fraction.

The definition of the raw materials fraction is derived from the composition of natural raw materials. Raw materials for the wet process differ from those for the dry-cement process, mainly in water content. As a consequence, the definition of the raw materials fraction for the wet-cement process differs from that for the dry-cement process.

Figure 3.1 summarizes the decision scheme, elaborated in this chapter, to decide upon valorization or elimination of a waste in a cement kiln.

Figure 3.1 Decision scheme for waste valorization in a cement kiln.



Remarks:

Acceptable with regard to:
- health risks
- emissions
- technical product quality
- environmental product quality
- see Chapter 3.2

Raw materials fraction M:
- sum of CaO, $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and SO_3
- corrected for moisture content and non-functional components in natural raw material
- see Chapter 3.3

Calculate concentrations and heating value based on 100 % rest fraction

Process conditions in cement kiln:
- process temperature min. 1500 °C (= T_{ref})
- 75 % energy efficiency
- 3 % oxygen content
- air inlet 800 °C (= T_0)
- see Chapter 3.4

- **M** = raw materials fraction
- see Chapter 3.3

- **E** = $(T_{comb} - T_0)/(T_{ref} - T_o)$
- T_0 = initial temperature (e.g. air inlet)
- T_{ref} = reference temperature, required in process

In the following parts of this chapter, the raw materials fraction is defined and a method is described to assess the energetic value of the energy fraction. Next, a decision parameter to distinguish between valorization and elimination of the total waste is proposed. First, however, a summary is given of general conditions that waste processing must fulfil.

3.2 General conditions for waste processing

In order to have an acceptable treatment of waste in a cement kiln, some general conditions have to be met:

- permit conditions and emission standards must be met;
- the quality of the cement must fulfil limits with respect to its structural capabilities and its environmental compatibility;
- the production process must not be impaired and the safety of the workplace must be ensured;
- an environmental assessment should show that the cement process must be the best way of handling the waste materials. In this assessment, the cement option should be compared with alternatives such as reuse, recycling, incineration in specialized waste combustion facilities or other facilities;
- the waste materials should not be mixed in order to reach the maximum allowable limits of contaminants in the waste.

These requirements result in criteria which limit the quantity of secondary materials used or can exclude specific wastes entirely. Several criteria have been formulated in the literature [4a, 4b, 4c, 4d, 12, 14, 19, 20, 21, 22] and are related to gaseous emissions, cement quality, health standards, and reactor maintenance.

These criteria are necessary conditions for the application of waste in general, but do not determine the difference between elimination of waste or valorization. When these conditions are not met, the waste considered cannot be treated in a cement kiln: processing is not acceptable.

3.3 Definition of raw materials fraction

The first step in the MEP-method is to define the raw materials fraction. This fraction is subtracted from the waste as such. The next step is to evaluate the value of the rest or energy fraction as a source of energy.

Generally, for the cement process, a waste can be described by the following fractions (see Figure 3.2):
- the organic fraction constituting the energy source of the waste;
- an inorganic fraction consisting of the useful, functional components;
- water;
- an inorganic fraction with the harmful compounds such as heavy metals (trace elements mostly);

- an inorganic fraction consisting of neutral compounds without a clearly positive or negative contribution to cement production such as Mg, P, Na, K oxides.

Most of the water and the last two inorganic fractions mentioned are not functional for the cement production.

To assess the contribution of the waste to the raw materials, a raw materials fraction is defined . The value of this weight fraction is proposed as the measure **M** for the raw materials valuet of the waste.
This raw materials fraction consists of:

- the fraction useful compounds CaO or $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and SO_3 in the waste. If the Ca-content occur as $CaCO_3$, this $CaCO_3$ quantity is allocated to the raw materials fraction (see example 4 below).
- other inorganic components (including water) in the waste up to maximum values, mwaf and maif. These maximum values are introduced to allow for the same amounts of water, non-functional compounds and impurities in the materials fraction that are also present in natural materials.

Generally, CaO, SiO_2, Al_2O_3 and Fe_2O_3 are mentioned as the functional, constituting compounds for the cement clinker. However, as gypsum is added to and ground with the cooled clinker to produce cement, SO_3 is considered useful as well. $CaCO_3$ is introduced because in this form CaO occurs in natural raw materials.

M can be expressed by:

$$M = usmf / (1 - minw) (1 - mini)$$

wherein:
usmf = fraction of useful materials in waste as such
waf = water fraction in waste as such
inf = fraction of inert, non-functional components in the waste
mwaf = maximum water fraction allowed in raw materials fraction
maif = maximum inert fraction allowed in raw materials fraction
mini = minimum value of inf and maif
minw = minimum value of waf and mwaf.

The values of maif and mwaf have to be established for the process under consideration and the quality of the natural raw materials used therein. For example, for the wet-cement process the mwaf will be higher than for the dry-cement process as the water content of the natural raw materials is higher. For both processes, an indication for the values of mwaf and maif is elaborated below.

Example1: the wet-cement process. For the wet process, the raw material fraction is assumed to contain 30 weight % water (or as a maximum the amount of water that is present in the waste material) in conformity with the natural raw material (see Appendix 1 and 2). In a similar way, percentages of the inert and trace elements of inorganic fractions are allocated to the raw materials fraction. These percentages should be based on the percentages occurring in natural raw materials. This aspect is discussed below in example 3. Schematically, the partitioning is depicted in Figure 3.2.

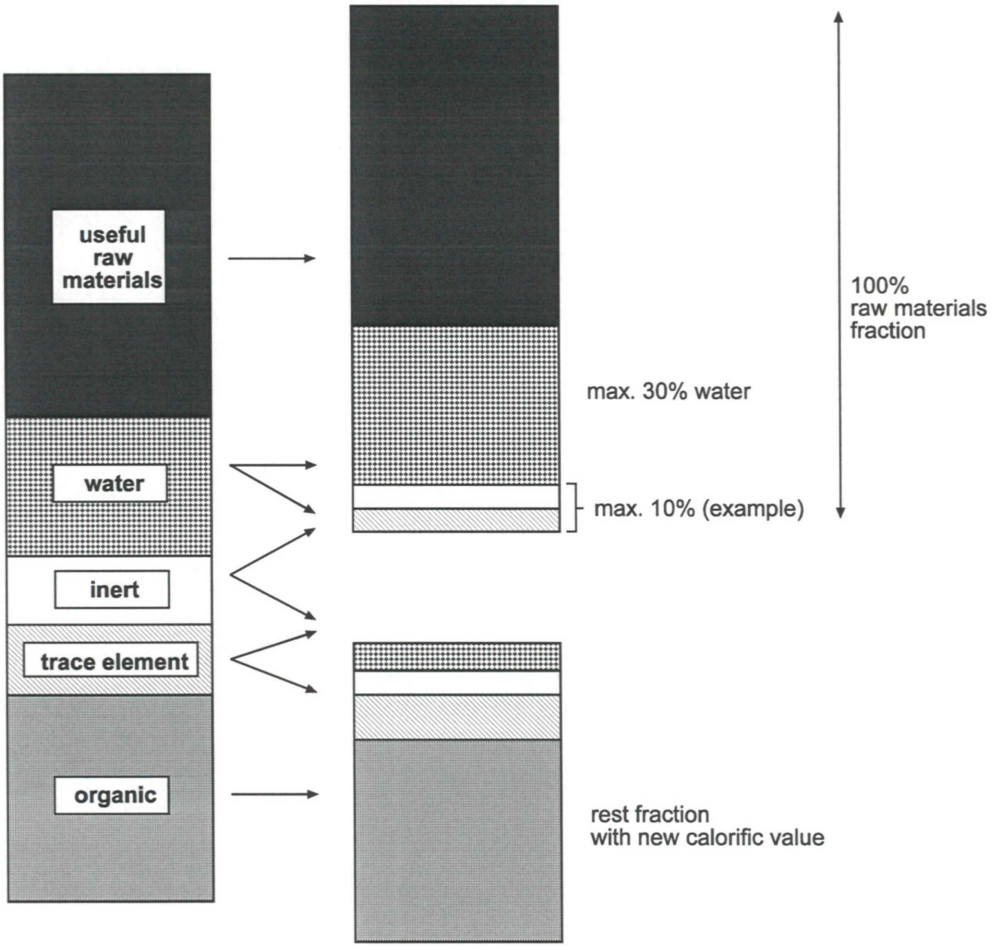


Figure 3.2 Wet-cement process: partitioning of the waste in a raw materials fraction and an energy fraction

Example 2: the dry-cement process. For the dry-cement process, the water content of the raw materials fraction is set at a maximum value of 15 %. Normally, the raw materials are dried before being fed into the cement kiln. Again, as for the wet-cement process, percentages of the inert and trace elements of inorganic fractions are allocated to the raw material fraction. These percentages should be based on the percentages occurring in natural raw materials. This aspect is discussed below in example .3. Schematically, the partitioning is depicted in Figure 3.3

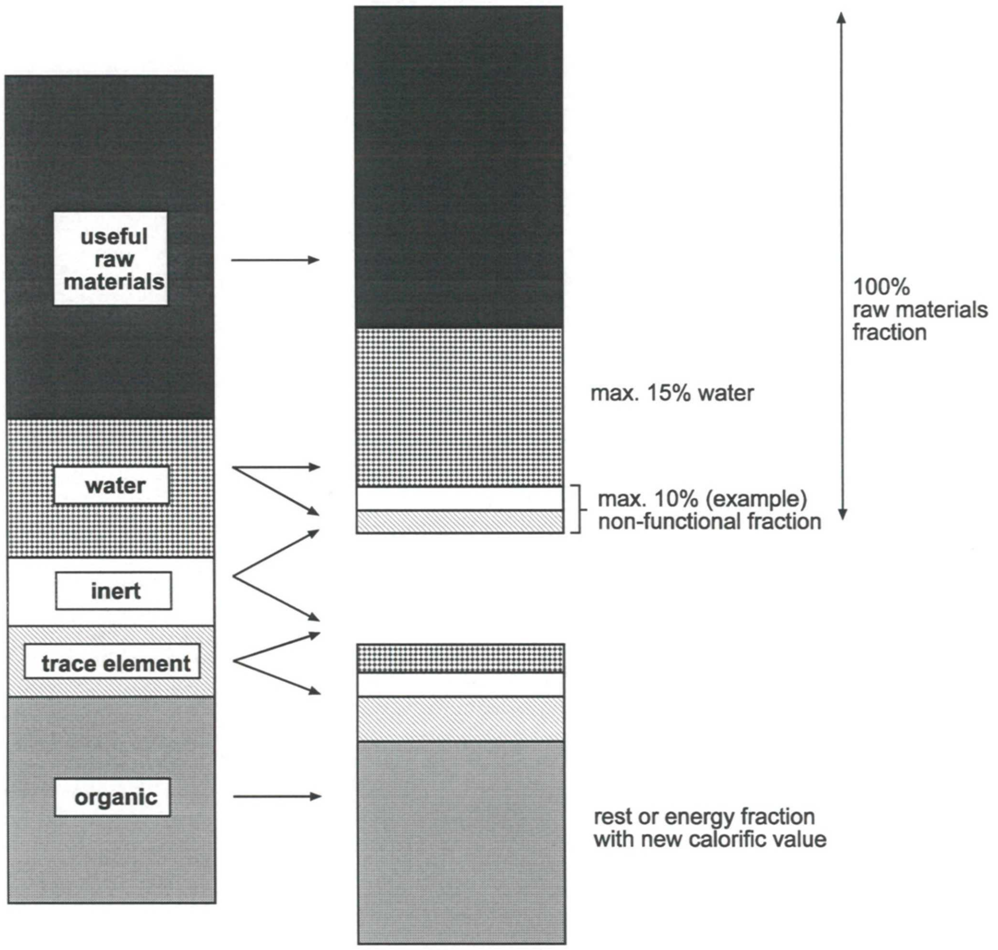


Figure 3.3 Dry-cement process: partitioning of the waste in a raw materials fraction and an energy fraction

Example 3: the inert fraction. As an example of the amounts of non-functional components in a natural raw material, see the data in Table A.2.3: the raw material described here contains (in elemental form) approximately 5 % inert natural and 0.2 % trace elements.
An overview of concentrations occurring in natural Dutch clays [16] reveals approximately 3 % inerts, mainly Na_2O and K_2O, and 0.1 % trace elements, mainly heavy metals.
Lime ($CaCO_3$) can contain 0.2 % inert material and 0.05 % heavy metals [17].

LD slag, a commonly used raw material, contains approximately up to 10 % inert inorganic compounds, mainly as magnesium oxide and phosphorous oxide (see Table 4.1).

Example 4: in the wet-cement process, a raw material is applied, consisting of 30% water and 70% $CaCO_3$*. Using* $CaCO_3$ *instead of CaO, to express its Ca-content, results in a material that is 100% useful. This is important in the assessment method presented in Chapter 3.5. For the dry-cement process analogue examples can be presented.*

Therefore, based on the examples above, the raw materials fraction for the cement process can contain up to 15 or 30 % water respectively for the dry and wet cement process, and up to 10 % inert components. If the waste itself does contain less than this quantity of water or components, the actual quantity in the waste is allocated to the raw materials fraction. These values are preliminary values; a better justification based on an inventory of the natural raw materials applied by the cement industry is recommended.

For the presented formulae to calculate the M measure for the raw materials value of a waste, this means that:
mwaf = 0.3 for the wet-cement process;
mwaf = 0.15 for the dry-cement process;
maif = 0.1 for both cement processes.

The total Ca-content of the waste could be expressed as $CaCO_3$, the form in which Ca occurs in natural raw materials. As a consequence, for a waste mainly consisting of CaO the calculated raw materials content would exceed 100%. This could be justified by the fact that CaO as a feed material has the advantage over $CaCO_3$ that the calcination step in the cement kiln is superfluous. Calcination is a major energy consuming reaction. However, if the CaO would also contain water, this advantage woud decrease by the presence of $Ca(OH)_2$. Furthermore, chosing $CaCO_3$ to express the Ca-content would introduce an unreal aspect in the definition of the raw materials fraction and is, also for this reason, rejected.

3.4 Assessment of waste as a source of energy

It is proposed here to consider a material as a source of energy when, at the prevailing process conditions in the kiln, this material produces at least some surplus of energy. In many thermal processes an essential temperature level can be identified that should be reached to enable the process. For example, for the process of clinker formation in the cement kiln a minimum temperature of 1450 °C is required. It is proposed to consider the combustion of a material as energy valorization if the autothermal combustion temperature, calculated for the actual process conditions, exceeds this reference temperature, essential for the process.

As a measure for the energetic value of a material in a process, **E**, the following expression is introduced:

$$E = (T_{comb} - T_o) / (T_{ref} - T_o)$$

wherein:

T_{ref} = an essential reference temperature level in the process to be reached (°C)
T_{comb} = the autothermal combustion temperature of the considered material under the prevailing process conditions (°C)
T_o = an initial temperature level in the process to be considered as the starting temperature for the heating process (°C).

E expresses relatively the extent to which the required temperature level, T_{ref}, is reached or exceeded. As a consequence of the above, a material with the composition of the energy fraction is valorized if:

$$E \geq 1$$

This being the case, the material is able to contribute to the energy needs of the process.
T_o expresses a basic temperature to be used as the initial temperature for calculating T_{comb}. For example, T_o could be the combustion air temperature at the inlet of the kiln. Below, as an example, the choice of the temperatures T_{ref} and T_o and of the process conditions to calculate T_{comb}, is illustrated for the cement kiln.

Example: the cement kiln. (See Appendix A.1 for the cement process conditions). The reaction temperature to be considered may depend on the feeding system options that are available. As an example, the mid-kiln feeding system that has been developed in the United States can be mentioned Ciments d'Obourg will implement this system. It allows the feeding of material into the middle of the kiln where typically the decarbonization of calcium carbonates occurs, a major energy-demanding step in the process. Typical reactor temperatures at this point are 1100°C in the gas phase and 800°C for the solids (see Figure A.2). In the dry process, applied by CBR and CCB in Belgium, waste processing is possible in the precalciner. Process temperatures here are typically between 800 and 1000°C. However, maximum temperatures in the kiln are 2000 °C in the gas phase and 1450 °C for the solids.
What situation should now be used to calculate the energy potential of the waste?

This study is restricted to the actual cement kiln. Therefor, it is postulated that a substance is a source of energy when it is able to reach autothermally a combustion temperature of 1500 °C, exceeding the minimum required temperature of 1450 °C.
With respect to the process conditions to calculate this temperature, it is assumed that there is 3 % oxygen (approximately 16 % air surplus) and that the energy losses in the kiln amount to 25 %.

The energy of the hot solids leaving the kiln is used to preheat the inlet air up to more than approximately 800 °C. Therefore, a further premise for the calculation of the autothermal combustion temperature is an air inlet temperature of 800 °C. This choice takes into account the effect of heat recovery in the process.

These conditions ensure that a material contributes, in a positive way, to the energy demand of the cement process. In the next Section 3.5, a generalized evaluation is presented to distinguish between valorization and elimination. This generalized approach is based on the evaluation of the raw materials fraction and the rest or energy fraction. This energy fraction is assessed as a possible source of energy.

3.5 Generalized assessment of a waste as a source of raw materials and energy

A generalized method to decide between valorization and elimination is proposed, based on two measures that express the energy and the materials value of the waste, respectively.

The measures are:

- the raw materials fraction, expressed as a weight fraction of the waste. This fraction **M**, is smaller than or equal to 1 and defined in Section 3.3 by:

  $$\boldsymbol{M} = usmf / (1 - minw)(1 - mini)$$

- the energy value, calculated from the autothermal combustion temperature T_{comb} of the rest or energy fraction, the desired reference temperature T_{ref} and the air inlet temperature T_o as defined in Section 3.4 by:

  $$\mathbf{E} = (T_{comb} - T_o) / (T_{ref} - T_o)$$

For a natural (almost) purely inorganic raw material **E** = 0 and **M** = 1.

According to the statement in 3.1, the waste processing should be classified as valorization, when there is a raw materials fraction (**M** > 0) and **E** is larger than 1. In this case, the waste consists of two fractions that both contribute to the cement production process in a positive way. In conformity with the definition of valorization in Chapter 1.1, waste processing should be seen as valorization.

When **E** < 1, there is not sufficient energy in the waste to produce some energy surplus at T_{ref}. For a classification as valorization, this should be compensated by the importance of the raw materials factor **M.**

It is proposed to classify waste processing in the cement kiln as valorization, as opposed to elimination, when:

$$\boldsymbol{E} + \boldsymbol{M} \geq 1$$

This relation is the basis for the Materials and Energy Potential method presented in this study. The choice for the linear relationship is arbitrarily: it is the most simple formulation.
The intention of the MEP method is to give an indicative judgement about valorization or elimination for high-temperature processes, such as the cement manufacturing process in the cement kiln. Therefor, one of the premises for application of the **E** formulae is that the temperature difference (T_{ref} - T_o) is significant.

The defined measures will be calculated for a number of wastes (see Chapter 4 and 5) to illustrate the consequences of this assessment method, summarized in the decision scheme in Figure 3.1. Some features of the developed method will be discussed in Chapter 6.

4. Calculations with the MEP method for the wet cement process

4.1 Calculations

The MEP method developed in Chapter 3 to distinguish between valorization and elimination is illustrated by calculations on four wastes and on medium-quality coal, all actually applied in a cement process. The compositions of these wastes and the coal are presented in Table 4.1.

In Table 4.2, some artificial wastes have been defined, mostly low calorific variants of the actually applied wastes from Table 4.1 (the organic fraction is supposed to be cellulose and the lower heating values are calculated by the Michel formulae).

The Tables 4.3 and 4.4, respectively, present the calculated **M** and **E** measures, based on the following premises:

- oxygen concentration for incineration: 3 % oxygen on dry air;
- energy efficiency 75 %; 25 % loss by radiation and other causes;
- raw materials fraction: raw materials including up to 30 % water.
- Ca is present as CaO.

Allocation of part of the inert fraction and/or the hazardous fraction to the raw materials fraction has been disregarded.

To calculate the combustion temperature, it is necessary to estimate the composition of the organic fraction of the waste since no data is available. The organic fraction of the low calorific waste examples is supposed to be cellulose.

Table 4.1 Composition of waste examples HPC, FE, FC, DSS and medium coal.

	Unit	HPC solvents	FE filtration earth	FC filter cake	DSS dry sewage sludge	PC poor coal	LDS LD-slag
LHV (*)	MJ/kg	25	12.5	6.0	11.1	16.2	–
H_2O	%	20	20	50	22	7	5
Ash	%	0	50	20	44	46	95
S	%	1	1	1	1	1.5	0.2
CaO	% ash	0	25	25	11	7	46
SiO_2	% ash	0	45	5	51	46	12
Al_2O_3	% ash	0	15	15	16	26	2.5
Fe_2O_3	% ash	0	5	45	9	8	32
SO_3	% ash	0	10	10	3	7	0.5

* LHV = Lower Heating Value

Table 4.2 Composition of artificial waste examples LPC, LFE, LFC, and LSS and wet sewage sludge WSS for theoretical calculations.

	Unit	LPC	LFE	LFC	LSS	WSS
LHV (*)	MJ/kg	11.7	6.2	3.4	4.7	2.9
H_2O	%	20	20	50	22	70
Ash	%	0	50	20	44	11.2
S	%	1	1	1	1	1
CaO	% ash	0	25	25	11	11
SiO_2	% ash	0	45	5	51	51
Al_2O_3	% ash	0	15	15	16	16
Fe_2O_3	% ash	0	5	45	9	9
SO_3	% ash	0	10	10	3	3

* LHV = Lower Heating Value

Table 4.3 Results of calculations of Materials and Energy measures for air inlet temperatures of 25 and 800 °C (raw mat.=sum of useful oxides), T comb = combustion temperature. Wet-cement process with up to 30% water in raw materials fraction.

Air inlet temperature 25 °C

	Unit	HPC solvents (a)	FE filtration earth	FC filter cake	DSS dry sewage sludge	PC poor coal	LDS LD-slag
T_{comb} waste as such	°C	1451	1311	993	1300	1477	–
Useful[*] oxides	(-)	0	50	20	40	46	93
T_{comb} rest fraction	°C	1451	1584	1107	1544	1612	–
Calorific value	MJ/kg	20.3	12.5	6.0	11.0	16.2	–
calculated[**]	MJ/kg	20.3	43.4	8.7	31.0	35.2	–

Air inlet temperature 800 °C

	Unit	HPC solvents	FE filtration earth	FC filter cake	DSS dry sewage sludge	PC poor coal	LDS LD-slag
T_{comb} waste as such	°C	1873	1702	1311	1688	1932	–
Useful oxides[*]	(-)	0	50	20	40	46	93
M measure	(-)	0	0.70	0.29	0.63	0.53	1.00
T_{comb} excl. raw materials fraction	°C	1873	2023	1476	2015	2128	–
E measure	(-)	1.53	1.75	0.96	1.74	1.90	–
E + M	(-)	1.53	2.45	1.25	2.37	2.43	1.00

[*] only raw materials as such: CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO3

[**] upper value: for waste as such; lower value: for rest fraction = waste minus raw materials fraction

Table 4.4 *Results of theoretical calculations of Materials and Energy measures for artificial waste examples for air inlet temperatures of 25 and 800 °C (raw mat. = sum of useful oxides). Wet-cement process.*

Air inlet temperature 25 °C

	Unit	LPC	LFE	LFC	LSS	WSS
T_{comb} waste as such	°C	1376	1141	781	1042	635
T_{comb} rest fraction	°C	1378	1445	918	1477	696
Calorific value[**]	MJ/kg	11.7	6.2	3.4	4.7	2.9
calculated	MJ/kg	11.7	22.3	5.1	13.8	3.6

Air inlet temperature 800 °C

	Unit	LPC	LFE	LFC	LSS	WSS
T_{comb} waste as such	°C	1752	1472	1049	1338	905
Useful[*] oxides	(-)	0	50	20	40	11
M measure	(-)	0	0.70	0.29	0.63	0.16
T_{comb} excluding raw materials fraction	°C	1752	2003	1212	1875	979
E measure	(-)	1.36	1.72	0.59	1.54	0.26
E + M	(-)	1.36	2.42	0.88	2.17	0.42

[*] only raw materials as such: CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3

[**] upper value: for waste as such; lower value: for rest fraction = waste minus raw materials fraction

4.2 The Materials and Energy Potential scheme

For the wet-cement process, the Materials and Energy measures are plotted in Figure 4.1, with the line

$$M + E = 1$$

Combustion of actually processed wastes as filtration earth, poor coal, dry sewage sludge, HPC and filter cake should be valued as valorization.

From the artificial wastes, WSS (very clearly) and LFC are examples of waste elimination. LPC, LFE and LSS are shown to be wastes that can be valorized in a wet-cement kiln.

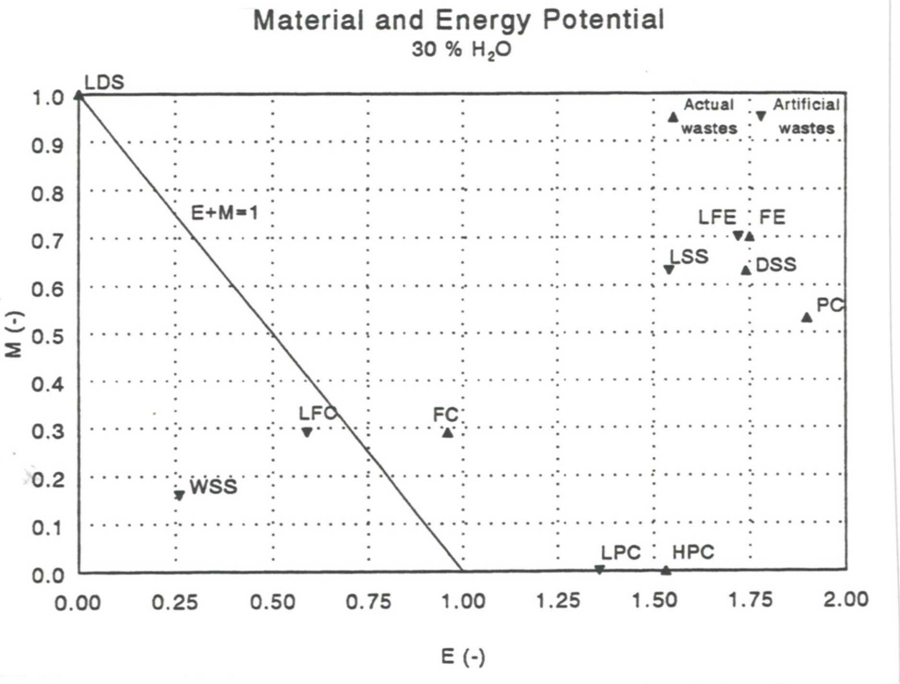


Figure 4.1 *MEP scheme: Materials and Energy Potential scheme for the wet-cement process. Values from Tables 4.3 and 4.4 are used*

4.3 Theoretical wastes and MEP values

For a number of theoretical waste compositions, MEP values are calculated to show some relations and sensitivities. For simplicity, the waste is composed of an ash fraction, water and an organic fraction. The ash fraction is supposed to consist entirely of useful components. The organic fraction constitutes the energetic value of the waste. A complete review of the results is shown in Appendix 3.

The following cases have been calculated:

- with an organic fraction with a low High Heating Value (HHV=25 MJ/kg) and with a high HHV (40 MJ/kg);
- with a raw materials fraction with up to 30 % water for the wet-cement process;
- for a raw materials fraction without water;
- for Eurits conditions (see below), combustion temperatures are calculated.

In Figure 4.2, the resulting conclusions from the MEP method are illustrated in graphs showing areas of waste compositions that are valorized or eliminated, respectively.

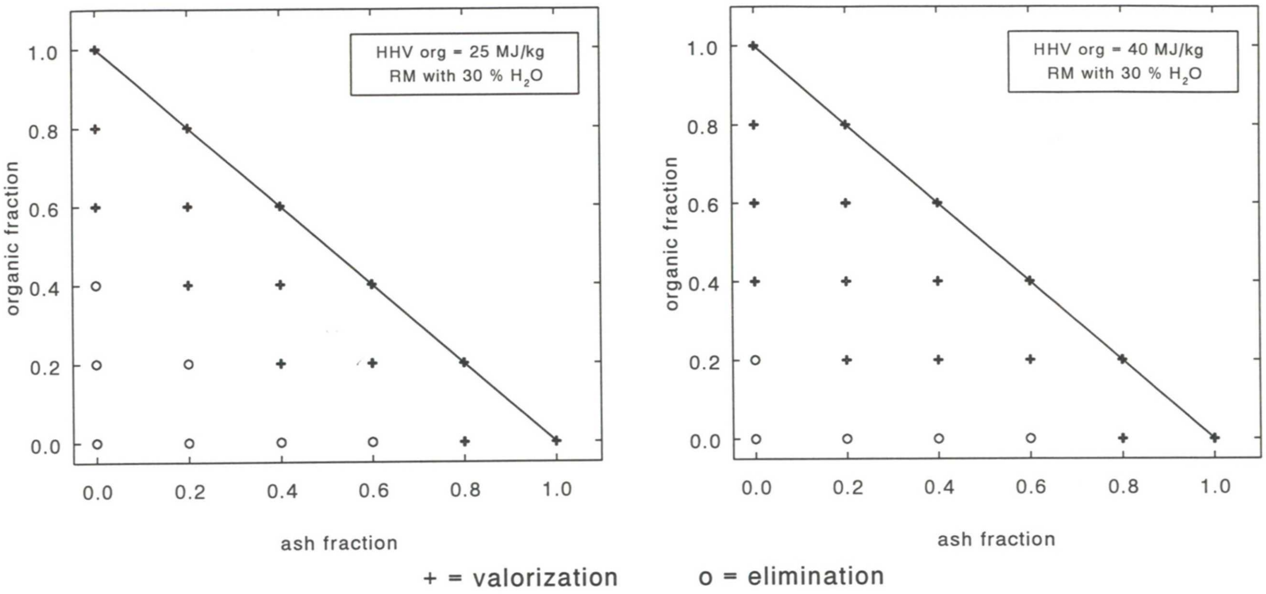


Figure 4.2 *Results of MEP method for theoretical waste compositions containing ash, water and an organic fraction (RM = 30% for the wet cement process). The HHV of the organic fraction is indicated.*

5. Calculations with the MEP method for the dry cement process

5.1 Calculations

In this section 5.1 results are presented of calculations with the MEP method when applied to the dry-cement process. The compositions of these wastes (of liquid or sludge character) and the coal, all actually applied in the cement industry, are presented in Table 5.1. In addition in Table 5.3, some dry wastes are defined that are mostly considered to be "alternative fuels".

In Table 5.5, some artificial wastes have been defined, mostly low calorific variants of the actually applied wastes from Table 5.1 (the organic fraction is supposed to be cellulose and the lower heating values are calculated by the Michel formulae).

Tables 5.2, 5.4 and 5.6, respectively, present the calculated **M** and **E** measures, based on the following premises:

- oxygen concentration for incineration: 3 % oxygen on dry air;
- energy efficiency 75 %; 25 % loss;
- raw materials fraction: raw materials including up to 15 % water (see 3.3),
- Ca occurs as CaO.

Allocation of part of the inert fraction and/or the hazardous fraction to the raw materials fraction has been disregarded.

To calculate the combustion temperature, it is necessary to estimate the composition of the organic fraction of the waste since no data is available. The organic fraction of the low calorific waste examples is supposed to be cellulose.

Table 5.1 *Composition of waste examples HPC, FE, FC, DSS and medium quality coal.*

	Unit	HPC solvents	FE filtration earth	FC filter cake	DSS dry sewage sludge	PC poor coal	LDS LD-slag
LHV (*)	MJ/kg	25	12.5	6.0	11.1	16.2	–
H_2O	%	20	20	50	22	7	5
Ash	%	0	50	20	44	46	95
CaO	% ash	0	25	25	11	7	46
SiO_2	% ash	0	45	5	51	46	12
Al_2O_3	% ash	0	15	15	16	26	2.5
Fe_2O_3	% ash	0	5	45	9	8	32
SO_3	% ash	0	10	10	3	7	0.5

* LHV = Lower Heating Value

Table 5.2 *Results of calculations of Materials and Energy measures for air inlet temperatures of 25 and 800 °C (raw mat.=sum of useful oxides), T_{comb} = combustion temperature. Dry-cement process with up to 15 % water in raw materials fraction.*

Air inlet temperature 25 °C

	Unit	HPC)	FE	FC	DSS	PC	LDS
T_{comb} waste as such	°C	1451	1311	993	1300	1477	–
T_{comb} rest fraction	°C	1451	1467	1065	1453	1612	–
Calorific value** calculated	MJ/kg	20.3	12.5	6.0	11.0	16.2	–
	MJ/kg	20.3	29.0	8.0	23.3	35.2	–

Air inlet temperature 800 °C

	Unit	HPC solvents	FE filtration earth	FC filter cake	DSS dry sewage sludge	PC poor coal	LDS LD-slag
T_{comb} waste as such	°C	1873	1702	1311	1688	1932	–
Useful oxides*	(-)	0	50	20	44	46	93
M measure	(-)	0	0.59	0.24	0.52	0.53	1.00
T_{comb} excl. raw materials fraction	°C	1873	1912	1400	1892	2128	–
E measure	(-)	1.53	1.59	0.86	1.56	1.90	–
E + M	(-)	1.53	2.18	1.09	2.08	2.43	1.00

* only raw materials as such: CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO3

** upper value: for waste as such; lower value: for rest fraction = waste minus raw materials fraction

Table 5.3 *Composition of dry alternative fuels. The ash fraction is considered to consist of useful components.*

	Unit	TYR	PAP	SHW	RDF
		Car tyres	Waste paper	Shredder waste**	Fuel from waste
LHV (*)	MJ/kg	31.7	16.8	28.8	18.3
H_2O	%	3	10	1	11.2
Ash	%	15.4	12.3	24	15.4

* LHV = Lower Heating Value

** SHW = heavy fraction of shredder waste

Table 5.4 *Results of calculations of Materials and Energy measures for air inlet temperatures of 25 and 800 °C (raw mat.=sum of useful oxides), T_{comb} = combustion temperature. Dry-cement process with up to 15 % water in raw materials fraction.*

Air inlet temperature 25 °C

	Unit	TYR	PAP	SHW	RDF
		Car tyres	Waste paper	Shredder waste	Fuel from waste
T_{comb} waste as such	°C	1572	1475	1542	1451
T_{comb} rest fraction	°C	1597	1508	1581	1497
Calorific value**	MJ/kg	31.7	16.8	21.2	14.9
calculated	MJ/kg	38.8	19.7	28.8	18.3

Air inlet temperature 800 °C

	Unit	TYR	PAP	SHW	RDF
		Car tyres	Waste paper	Shredder waste	Fuel from waste
T_{comb} waste as such	°C	2068	1902	2007	1866
Useful oxides*	(-)	0.15	0.12	0.24	0.15
M measure	(-)	0.18	0.14	0.25	0.18
T_{comb} excl. raw materials fraction	°C	2106	1948	2065	1929
E measure	(-)	1.87	1.64	1.81	1.61
E + **M**	(-)	2.05	1.78	2.05	1.79

* only raw materials as such: CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO3

** upper value: for waste as such; lower value: for rest fraction = waste minus raw materials fraction

Table 5.5 *Composition of artificial waste examples LPC, LFE, LFC, and LSS and wet sewage sludge WSS for theoretical calculations.*

	Unit	LPC	LFE	LFC	LSS	WSS
LHV (*)	MJ/kg	11.7	6.2	3.4	4.7	2.9
H_2O	%	20	20	50	22	70
Ash	%	0	50	20	44	11.2
S	%	1	1	1	1	1
CaO	% ash	0	25	25	11	11
SiO_2	% ash	0	45	5	51	51
Al_2O_3	% ash	0	15	15	16	16
Fe_2O_3	% ash	0	5	45	9	9
SO_3	% ash	0	10	10	3	3

- LHV = Lower Heating Value

Table 5.6 *Results of theoretical calculations of Materials and Energy measures for artificial waste examples for air inlet temperatures of 25 and 800 °C (raw mat. = sum of useful oxides). Dry-cement process with up to 15 % water in raw materials fraction.*

Air inlet temperature 25 °C

	Unit	LPC	LFE	LFC	LSS	WSS
T_{comb} waste as such	°C	1376	1141	781	1042	635
T_{comb} rest fraction	°C	1378	1401	865	1301	672
Calorific value **	MJ/kg	11.7	6.2	3.4	4.7	2.9
calculated	MJ/kg	11.7	15.6	4.6	10.1	3.4

Air inlet temperature 800 °C

	Unit	LPC	LFE	LFC	LSS	WSS
T_{comb} waste as such	°C	1752	1472	1049	1338	905
Useful* oxides	(-)	0	50	20	44	11
M measure	(-)	0	0.59	0.24	0.52	0.13
T_{comb} excluding raw materials fraction	°C	1752	1803	1151	1657	952
E measure	(-)	1.36	1.43	0.50	1.22	0.22
E + M	(-)	1.36	2.02	0.74	1.74	0.35

* only raw materials as such: CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3

** upper value: for waste as such; lower value: for rest fraction = waste minus raw materials fraction

5.2 The Materials and Energy Potential scheme

For the dry-cement process, the Materials and Energy measures are plotted in Figure 5.1, with the line

$$M + E = 1$$

From the data, it is concluded that combustion of actually processed wastes as filtration earth, poor coal, dry sewage sludge, HPC and filter cake (just) should be valued as valorization.

Obviously, the same conclusion holds for the alternative fuels: waste paper, car tyres, heavy shredder waste and refuse derived fuel RDF. (For waste paper, the question may be asked whether reuse as a raw material for the paper industry is not the more sustainable, environmentally better solution. According to the general conditions formulated in Chapter 3.2, processing in the paper industry should than be prefered.)

From the artificial wastes, WSS (very clearly) and LFC are examples of waste elimination. LPC, LFE and LSS are shown to be wastes that can be valorized in a dry-cement kiln.

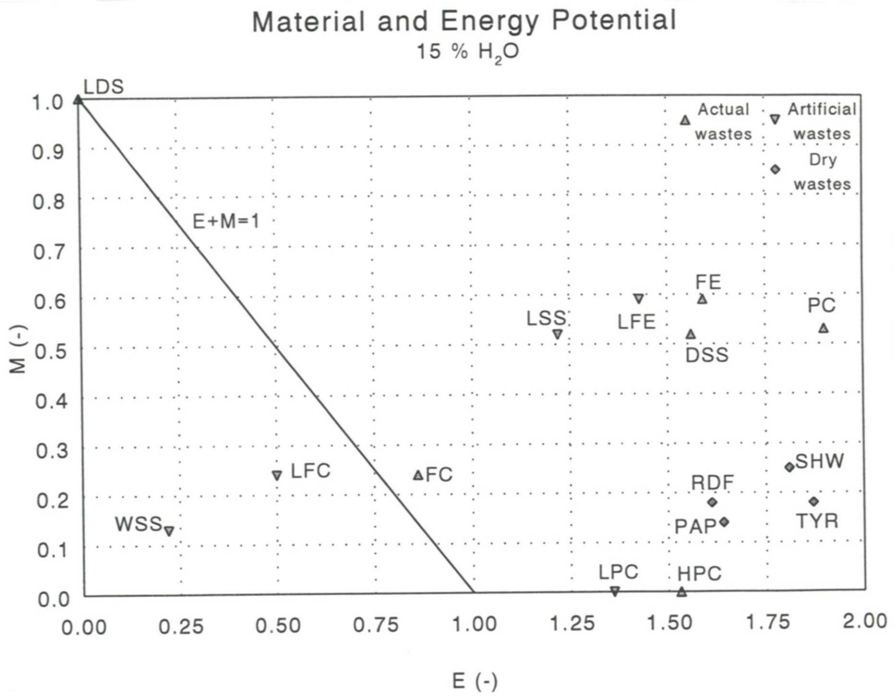


Figure 5.1 MEP scheme: Materials and Energy Potential scheme for the dry-cement process. Values from Tables 5.3 and 5.4 are used

5.3 Theoretical wastes and MEP values

For a number of theoretical waste compositions, MEP values are calculated to show some relations and sensitivities. For simplicity, the waste is composed of an ash fraction, water and an organic fraction. The ash fraction is supposed to consist entirely of useful components. The organic fraction constitutes the energetic value of the waste. A complete review of the results is shown in Appendix 3.

The following cases have been calculated:

- with an organic fraction with a low High Heating Value (HHV=25 MJ/kg) and with a high HHV (40 MJ/kg);
- with a raw materials fraction with up to 15 % water for the dry cement process;
- for a raw materials fraction without water;
- for Eurits conditions (see below), combustion temperatures are calculated.

In Figure 5.2, the resulting conclusions from the MEP method are illustrated in graphs showing areas of waste compositions that are valorized or eliminated, respectively.

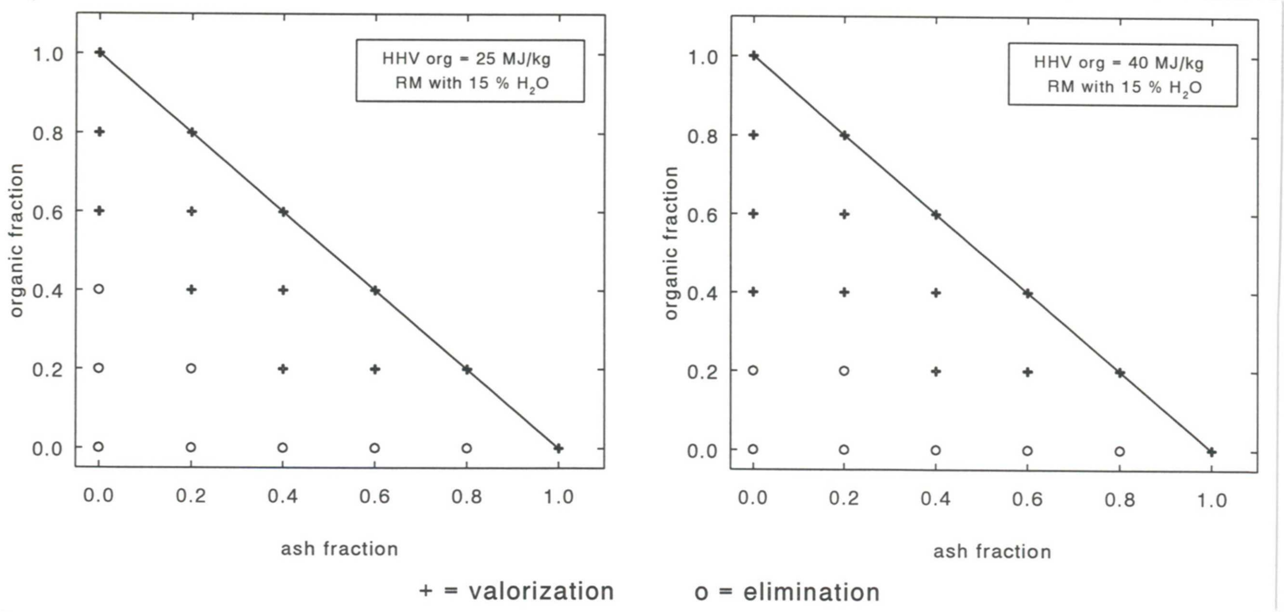


Figure 5.2 Results of MEP method for theoretical waste compositions containing ash, water and an organic fraction (RM = 15 % for the dry cement process). The HHV of the organic fraction is indicated.

6. Discussion of the method and the results

6.1 General aspects of the MEP method

M is defined in a way that it indicates, per tonne of waste, the saving in tonnes of raw materials. The water and other components introduced in the cement kiln with the natural primary raw materials are included in the definition of the raw materials fraction.
For a dry-cement process, this water fraction is smaller than for the wet-cement process; as a consequence, the wet-cement process has an advantage for wet wastes in this approach.
Allocation of (part of) the water fraction to the raw materials fraction promotes a judgement in favour of valorization. First, the measure **M** increases and, second, the combustion temperature rises because the rest fraction contains less water. This effect is most clearly seen for wastes with a high ash content.

Despite of the differences in allocation of water to the raw material fraction, the resulting judgements; valorization or elimination, are equal in the many cases calculated as examples

The MEP method allows up to 10 % (as a preliminary value) of non-functional inorganics in the raw materials fraction. One might think that, as a result, a very high concentration of heavy metals is allowed in the waste. Therefore, it is emphasized that the general conditions, mentioned in Chapter 3.2, should be fulfilled: emission, product quality, health aspects, etc. should be within the existing limits. As a consequence, there will be limits to the amounts of heavy metals.

E is an indicator of the energy contribution (or requirement) of the non-raw materials fraction, the energy fraction, of the waste.
If **E** ≥ 1, the rest fraction can produce an energy surplus at the process conditions in the kiln. If this is the case, the waste can be regarded as the sum of two fractions, both contributing to the cement process: one fraction is a substitute for natural raw materials, the other produces energy. In this case, the waste as such can be processed in the kiln with a positive contribution to the cement-making process and it is proposed to see this as a clear case of waste valorization.

In case **E** < 1, **E** indicates to what extent the energy fraction is self-supporting with respect to the energy demands of the cement process. In this situation, the raw materials fraction should be so important that it compensates for the energy shortage of the rest fraction. Weighing of these energy and mass aspects against each other may be possible in specific cases by a Life Cycle Analysis approach. Here, as a general arbitrary starting point for discussion, the condition is formulated that for valorization: $\mathbf{E} + \mathbf{M} \geq 1$.

With **M** approximately 0 and **E** equal to 1 or slightly higher (the LPC waste is almost an example), the contribution to the cement production is small and it may seem questionable that this is valorization. However, the waste can be processed without energy demand and the conditions are formulated in such a way that there must be at least some energy surplus. Therefore, there seems to be no clear objection against defining such a case as valorization, realizing that it is a bottom limit. Possibly, however, there are more attractive ways for co-incineration or processing these wastes.

For wastes with an **M** value of nearly 1 and no organic fraction (E approx. 0), the condition $\mathbf{M + E \geq 1}$ can be too strict. For instance, a waste material containing, as the useful component only 70% of $CaCO_3$ (or even 70% CaO) and 15% water would be excluded. This could be too restrictive from an environmental point of view.

The condition $\mathbf{M + E \geq 1}$ can be distinctive as is shown by the following.
The calculated examples show that wastes with a substantial raw materials fraction have an advantage above wastes without this fraction. Compare for example LPC and LSS in Table 4.4. LPC is barely a valorization case (**E** = 1.36, **M** = 0), despite the heating value of 11.7 MJ/kg, that would make it a fuel according to German law. LSS with a much lower heating value of 4.7 MJ/kg is even more clearly valorized (**E** = 1.43, **M** = 0.57). The latter is due to the raw materials. An additional reason for this strong effect is that part of the water fraction is allocated to the raw materials fraction (both wastes have a water fraction of approximately 20 %.)

The actually applied wastes and the coal (filtration earth, dry sewage sludge and the poor coal) score relatively high too, because of their raw materials fraction.

These examples further show that the proposed MEP method to distinguish between valorization and elimination favours the strong point of waste processing in a cement kiln, that is, the energy as well as the ash content of a waste can be used.

6.2 Waste pre-treatment and valorization

In Sections 4.1 and 5.1, the Materials and Energy Potentials (MEP values) for dry sewage sludge (DSS) and wet sewage sludge (WSS) are calculated to illustrate the MEP method. It is concluded that DSS processing is definitely valorization and WSS processing should definitely be classified as elimination.

What effect does pre-treatment, drying in this case, have on the MEP method?

Three aspects are of interest:
- generally, sewage sludge has to be dried to 50% dry solids or higher to make it acceptable for disposal or incineration in a waste combustion facility. There-

fore, it is acceptable to consider the dried sewage sludge to calculate the MEP value;

- it could be reasoned that it is efficient to feed the wet sewage sludge directly into the kiln to integrate drying and combustion in the cement kiln. Efficiency of processing wet sewage sludge may improve from an economic point of view but also energetically (and thus environmentally). In other words, it may be more favourable to process WSS in the cement kiln than processing WSS via an external drying followed by processing inn a cement kiln;
- to assess the environmental consequences of this approach is not within the scope of the MEP method. It requires an in-depth environmental analysis (for example an approach by Life Cycle Analysis methods) to evaluate this working method.

The MEP method quantifies whether waste pre-treatment results in a waste that can be valorized in the cement process. Whether the waste should be evaluated before or after pre-treatment should be based on other considerations.

6.3 Comparison of results

In Appendix 3, results are included of combustion temperature calculations based on the Eurits approach (see Chapter 2 and [21]) for hazardous waste. According to this approach, waste co-incineration is acceptable if the waste as such can reach a combustion temperature of 1100 °C at 6 % O_2 and 10 % energy loss. It is shown in Appendix 3 that the results of the *thermal* analysis of the MEP method largely coincide with those of the Eurits method, the differences being caused by the fact that the MEP method first sets apart the raw materials fraction. In Table 6.1 the waste compositions are summarized that result in different conclusions for both methods. It can be seen that these differences occur for waste compositions with a high ash content.

Table 6.1 Waste compositions resulting in different conclusions between MEP method on valorization and Eurits approach on co-incineration (HHV = High Heating Value of organic fraction)

ORGANIC FRACTION	HHV MJ/kg	WATER	ASH	MEP METHOD	EURITS on co-incineration	NUMBER (see appendix 3)
0.20	25	0.40	0.40	valorization	no	13
0.20	25	0.20	0.60	valorization	no	16
0.00 *	–	0.20	0.80	valorization*	no	19
0.20	40	0.60	0.20	valorization	no	28
0.20	40	0.40	0.40	valorization	no	32
0.00 *	–	0.20	0.80	valorization	no	38

* for wet-cement process only.

7. Conclusions

- The main types of criteria for waste treatment in a cement process discussed in literature are conditions for emission standards, limits on concentrations of contaminants in the waste and limits with respect to cement quality. These aspects do not distinguish between valorization and elimination; cement processes in which wastes are used have to respect these limits whether valorization or elimination is at stake.

- Generally, it can be concluded that in Germany, Belgium and The Netherlands, the issue of valorization and elimination has not been worked out on process technological considerations only, which explains the widely different ranges of criteria.
  Proposed conditions are mainly based on limits to heating values. Raw material aspects are hardly discussed.
  The approach developed by Eurits (the specialized waste incineration organization) to assess co-incineration is based on process conditions during waste combustion in hazardous waste incinerator processes and is therefore not applicable to waste processing in a cement kiln.

- A Materials and Energy Potential (MEP) method is proposed that can distinguish quantitatively between valorization and elimination in case of waste processing in a cement kiln.

- The MEP method is based on the recognition that a specific waste can contribute to the cement-making process at the same time as an alternative raw material and as a source of energy. This is a specific advantage of waste processing in the cement process.

- Essential steps in the developed method are:
  - division of the waste in a raw materials fraction and the rest or energy fraction
  - quantitative measures for the raw materials content (**M**)and the energy value of the rest or energy fraction (**E**) are calculated
  - the measures are combined to a criterion that decides between valorization and elimination.

- It has been a starting point that the energy fraction of the waste can be classified as a source of energy if this fraction produces some energy surplus at the process conditions in the cement kiln. In this approach, comparisons to the heating values of fossil fuels are superfluous.

- The measures **E** and **M** are defined in the following way:

- **M** is the raw materials fraction, expressed as a weight fraction of the waste. This fraction contains the components that are useful to (functional in) the cement process: CaO, $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and SO_3. The other inorganic components (including water) in the waste are allocated to the raw materials fraction up to maximum values. By this correction, the fraction functional components is allowed to contain an equivalent amount of water and non-functional components as occur in natural raw materials;
- the energy value **E** is defined as the quotient of the maximum combustion temperature, T_{comb}, achievable by the rest fraction, and an essential reference temperature, T_{ref} , required in the process.
  T_o being the initial temperature level, for example the air temperature at the inlet, the following expression is proposed for **E:**

$$E = (T_{comb} - T_o) / (T_{ref} - T_o)$$

- Based on these measures, a general condition is formulated for the assessment of waste processing as valorization

$$E + M \geq 1$$

  In this study, the method is elaborated and demonstrated for the main process conditions in the cement kiln.

- The defined reference process conditions for waste combustion in a cement kiln are:
  - a maximum solids temperature of 1500 °C ($T_{ref)}$;
  - an air inlet temperature of 800 °C (T_o;
  - an oxygen concentration of 3 % and an energy efficiency of 75 % to calculate the combustion temperature.

  These conditions are more strict than actual conditions (oxygen 2.5 %, 1450 °C max. solids temperature) in a cement kiln.

- The MEP method favours processing of wastes with a raw materials component in the cement kiln.

- Non-functional compounds (Mg, P, Na-, K components and trace elements) are allowed in the raw materials fraction up to a preliminary maximum of 10 %. A better justified value should result from a study of quantities occurring in natural raw materials.

- It is shown that the thermal analysis and limits proposed by TNO result in approximately the same judgement as the Eurits approach. The difference is the result of the appreciation of the raw materials aspect in TNO's MEP method.

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9. List of Abbreviations

Buwal	Swiss Bundesumweltamt
CCB	Compagnie des Ciments Belges
CBR	Cimenteries et Briqueteries Réunies
E	Measure of energy value
Eurits	European Union for Responsible Incineration and Treatment of Special Waste
HHV	High heating value
LHV	Lower (net) heating value
LUA NRW	Landesumweltamt Nordrhein-Westfalen
M	Measure of raw materials content
MEP	Materials and Energy potential
OVAM	Openbare Vlaamse Afvalstoffen Maatschappij (Flemish Waste Authority)
RM	Raw materials fraction
T_{comb}	Combustion temperature
VROM	Netherlands Ministry for Housing, Spatial Planning and the Environment

10. Authentication

Name and address of the sponsor

FEBELCEM

Federatie van de Belgische Cementnijverheid
Federation de l'industrie cimentiere Belge
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Name and function of the contributing personnel

Dr. J.A. Zeevalkink	Project Manager

Names of establishments to which parts of this research were sub-contracted

–

Period in which the research took place

December 1996 - mei 1997

Signatures

Dr. J.A. Zeevalkink
Project Manager

Date: 23-5-'97

Approved by

J. de Koning, M.Sc.
Head Department of Thermal
Conversion Technology
Date: 23/5/97

Appendix 1 The cement manufacturing process

The cement production can be divided into two major parts: (1) heating of raw materials to form clinker which is cooled and (2) grinding of the clinker and mixing with a small amount of gypsum, fly ashes and other materials to produce cement [8,23].

Essential components for the clinker are CaO, SiO_2, Al_2O_3 and Fe_2O_3. SO_3 is added as gypsum to the clinker after cooling. Blended and ground raw materials (such as limestone, clay, sand and iron ore) are fed into the cement kiln and burnt under controlled high-temperature conditions. Typically, the cement kiln is a long rotating cylinder. The raw materials are fed at the elevated end and, through the rotations of the kiln, move slowly down towards the firing end where heat is applied with coal, gas or oil flame. A solids temperature of approximately 1450 °C is necessary to produce a melt, required for clinker formation

Two types of cement processes are dealt with in this study; the dry and the wet cement process.

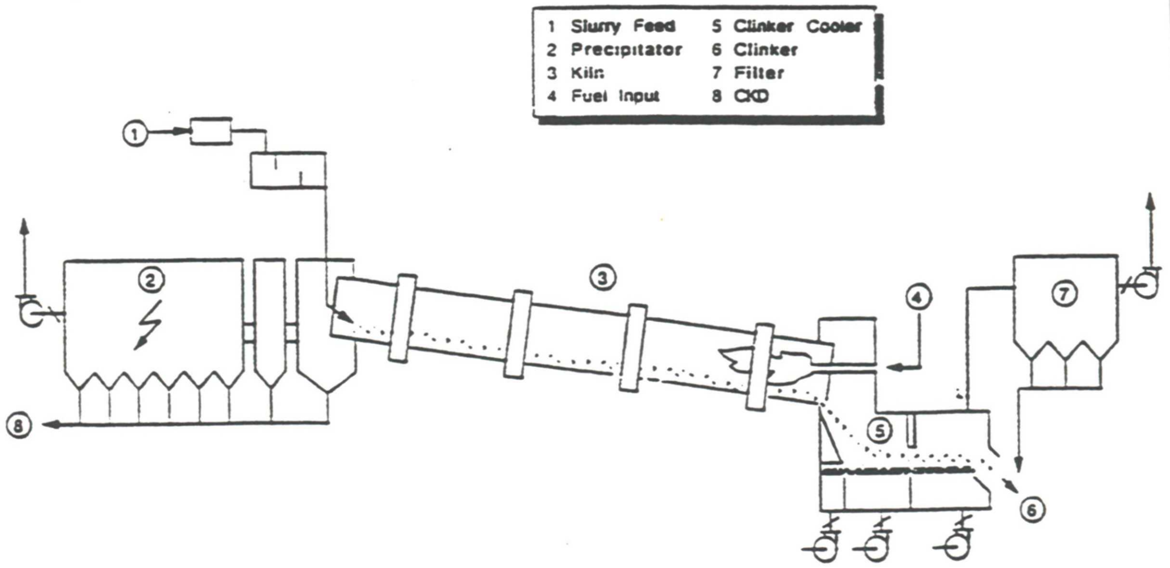

Figure A.1 Typical Wet Process Cement Kiln.

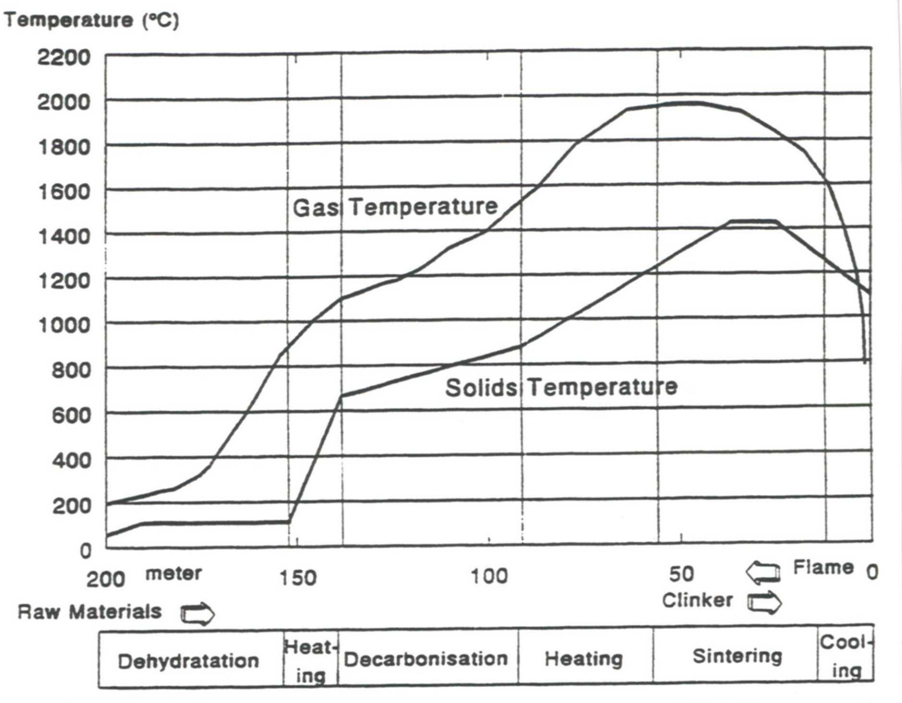

Figure A.2 Temperature profiles in cement kiln

The wet cement process

In Belgium, the wet-cement process is applied by Cimenteries CBR at Lixhe and Harmignies and by Ciments d'Obourg. The wet plant at Lixhe produces 540 ktons/year clinker; the plant at Harmignies 180 ktons/year white cement.
At Ciments d'Obourg, two kilns are used (length 202 and 227 m, respectively, and diameters of 6.75 and 7.16 m, respectively) to produce about 1,555 ktons of clinker per year. At the Obourg plant, a wet process is applied, since the limestone near Obourg contains about 30% water.
In the wet process, the slurry is fed directly into the inclined end of the kiln. The water promotes homogenization of the mixture. Evaporation of water from the kiln requires both a cement kiln with a long dry and preheating zone and a substantial energy requirement.
The rotating cylinders are lined with heat-resistant bricks. The residence time of the raw materials in the kiln is about two hours and 45 minutes. Figure A.1 gives a process scheme.

Ciments d'Obourg is currently introducing a mid-kiln feeding device making waste feeding in batches in the middle of the kiln possible.

The temperature profile of the cement kiln is depicted in Figure A.2. Waste materials can be fed at the low temperature end or the high temperature end of the kiln. Wastes containing volatile organics are fed with the fuel replacing wastes at the high temperature zone.

The dry-cement process

The dry process for cement manufacture utilizes a dry kiln feed rather than a slurry. Apart from the need for evaporation of water, its operation can be similar to that of a long wet kiln.

In a modern dry-process kiln a suspension preheater system is added. The dry, pulverized material passes through a series of cyclones where it is preheated several times. The partially calcined feed leaves the preheater at about 800-900^{0}C. The kiln length required for completion of the process is shorter than that of a conventional kiln, and the heat exchange is very good.

The dry raw materials contain 4-15% water.

The success of preheater kiln systems has led to precalciner systems. Second burners are used to carry out calcination in a separate vessel attached to the preheater. This precalciner system permits the use of smaller kilns because only actual clinkering is performed in the rotary kiln.
It is desirable to cool the clinker rapidly as it leaves the burning zone in the kiln. Heat recovery, preheating of combustion air and clinker cooling are achieved by clinker coolers. The air is preheated up to 800^{0}C. The principle is shown in Figure A.3

In Belgium, cement manufacturers applying the dry process are:
- Cimenteries CBR at Antoing, producing 950 ktons/year clinker (with preclacinator);
- Cimenteries CBR at Lixhe, producing 1100 ktons/year clinker and grey cement (no precalcinator);
- Compagnies des Ciments Belges, CCB, at Gaurain-Ramecroix, producing 1710 ktons/year grey cement in a process with precalcinator.

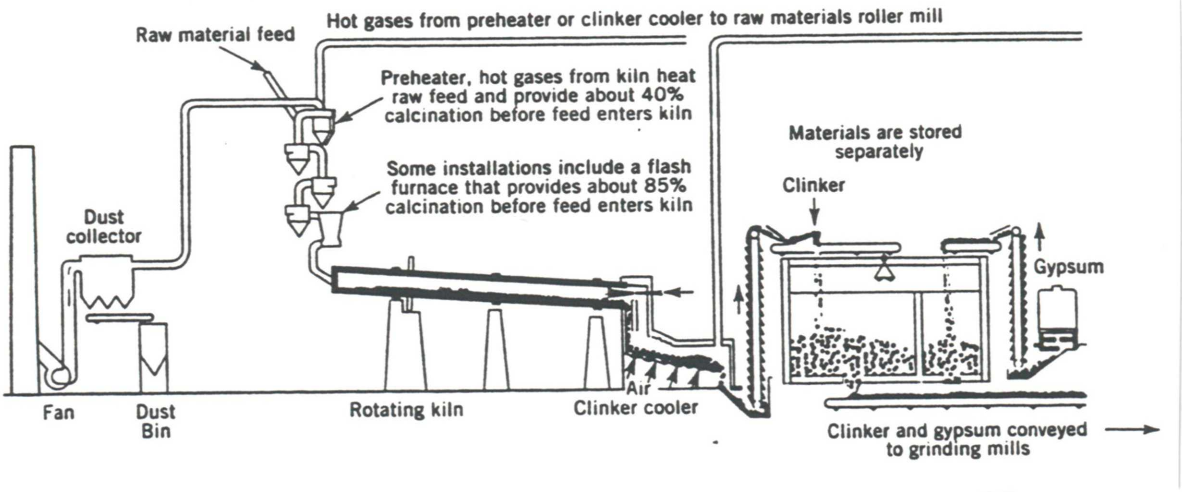

Figure A.3 Principle of dry-cement process with preheater.

Appendix 2 Raw materials and wastes for the cement industry

La productoin annuelle des cimentaries Belges (actuellement 6 Mio tonnes clinker et 7.5 Mio tonnes de ciment) nécessite des vollumes importants de:

- *matières premières*: de l'ordre de 10 Mio tonnes; essentiellement carbonate de calcium (calcaire dur et craie) et argile et, accessoirement, scories, suies, fluidifiants, bauxites pour leur apport en silice, alumine, oxyde de fer.
- *matières secondaires ou ajouts* (= déchets): de l'ordre de 2.8 Mio tonnes; les principaux ajouts sont:
  - le laitier de haut fourneau et les cendres volantes pour leur contribution au pouvoir de liant hydraulique du ciment;
  - les sulfates naturels ou résiduels (gypse et anhydride) pour leur propriétés de retardeur de prise.

Diverses qualités de ciment peuvent êtres obtenues en ayant recours à l'addition d'ajouts. C'est ainsi que l'industrie cimentière a diversifié la production de ses ciments en réduisant la production de ciments Portland au profit, essentiellement, des ciments à la pouzzolane et, dans une moindre mesure, des ciments métallurgiques.

Les ajouts contribuent à la préservation des ressources naturelles en diminuant le besoin en clinker pour le ciment; résidus de procédés industriels, ils trouvent en cimenteries une valorisation car ils représentent un apport en constituants esentiels du ciment par leur teneur en matières hydrauliques et ou pouzzolaniques. Ils contribuent donc également à économiser l'energie de frabrication relative au clinker remplacé.

A titre d'exemple:

Apports en constituant principaux du ciment (% poids de l'ajout)		
Eléments apportés	**par le laitier**	**par les cendres volantes**
chaux	36	2
silice	38	53
alumine	10	28
oxyde de fer	1	7
autres éléments	15	10

- combustibles: (de l'ordre de 26.000 T Joules) tels que
    - les combustibles fossiles classiques (C.F.C.): les charbons (à diverses teneurs en cendres), les fiouls, le gaz naturel, ….
    - les combustibles fossiles secondaires (C.F.S.) et de récupération (C.F.R.): les cokes de pétrole (résidu final provenant de la distillation des pétroles), les schistes de terrilgissus des anciennes exploitations charbonnières, les schlamms provenant du lavage des charbons, les boues d'épuration enriches au charbon, …
    - les combustibles de substition liguides (C.S.L.) et solides (C.S.S.): les solvants organiques usés, les sciures de bois imprégnées de résidus organiques, les pneus, les bois, papiers, cartons, plastiques, textiles, …

      En 1995, les combustibles de substitution, ç-à-d les déchets combustibles, ont couvert 20% de l'ensemble des besoins thermiques.

Appendix 3 More examples of MEP calculations and comparison with Eurits method

A number of theoretical waste compositions have been calculated to show some sensitivities and to compare the conclusions on valorization with the conditions formulated by Eurits for co-incineration. For simplicity, the waste is composed of an ash fraction, water and an organic fraction. The ash fraction is supposed to consist entively of useful components. The organic fraction constitutes the energetic value of the waste.
The results are shown in Table A.3.1.

The following cases have been calculated:

- with an organic fraction with a low High Heating Value (HHV=25 MJ/kg) and a high HHV (40 MJ/kg);
- with a raw materials fraction with up to 30 % water as defined in the standard approach for the wet-cement process;
- with a raw materials fraction containing 15 % water as defined for the dry-cement process;
- with a raw materials fraction containing no water to illustrate the effect of the water allocated to the raw materials fraction..

The tables contain the following information:

- the mass fractions organics, water and ash of these wastes
- combustion temperature (based on 3% oxygen, air inlet temperature of 800 °C) and LHV for the waste as such;
- combustion temperature, LHV for the energy fraction, and **E** and **M** values of the waste, corresponding with the indicated water content in the raw materials fraction
- the combustion temperature of the waste as such under the conditions defined in the Eurits approach for co-incineration of hazardous waste and the heating value of the waste as such. The Eurits condition for co-incineration is that this temperature is above 1100 °C;

From the calculation examples 3, 4 and 23, it can be seen that the thermal limits of the two methods almost coincide. Apparently, the thermal MEP limit of 1500 °C (at 3 % O_2, air temperature of 800 °C, 25 % energy loss) gives approximately the same result as the Eurits limit for co-incineration of hazardous waste (1100 °C at 6 % O_2, air temperature of 25 °C, 10 % energy loss). Therefore, the difference between the two methods is mainly the result of the appreciation of the raw materials contribution of a waste in the MEP methodology. This is illustrated by the examples 13, 16 and 19.

This result is confirmed by other calculations such as the waste example in the Eurits paper to illustrate the 1100 °C limit. Under the standard conditions of the MEP method, the autothermal combustion temperature of this waste just exceeds 1500 °C.

Allocation of (part of) the water fraction to the raw materials fraction promotes a judgement in favour of valorization. First, the measure **M** increases and, second, the combustion temperature rises because the rest fraction contains less water. Again, this difference is most clearly seen in wastes with a high ash content.

Table A1 Results of MEP calculations for artificially composed wastes.

HHV Organ fractie 25.00 MJ/ton

15 % water in raw materials fraction

30 % water in raw materials fraction

				WASTE AS SUCH		MATERIALS FRACTION with		0 % water			DRY CEMENT					WET CEMENT					EURITS
	ORG.FR	WATER	ASH	T comb	LHV	LHV rest	T comb	E	M	E+M	LHV rest	Tcomb(rest)	E	M	E+M	LHV rest	Tcomb(rest)	E	M	E+M	T comb
1	1.00	0.00	0.00	1975	22.9	22.9	1975	1.68	0.00	**1.68**	22.9	1975	1.68	0.00	**1.68**	22.9	1975	1.68	0.00	**1.68**	1513
2	0.80	0.20	0.00	1843	17.8	17.8	1843	1.49	0.00	**1.49**	17.8	1843	1.49	0.00	**1.49**	17.8	1843	1.49	0.00	**1.49**	1422
3	0.60	0.40	0.00	1660	12.8	12.8	1660	1.23	0.00	**1.23**	12.8	1660	1.23	0.00	**1.23**	12.8	1660	1.23	0.00	**1.23**	1287
4	0.40	0.60	0.00	1376	7.7	7.7	1376	0.82	0.00	**0.82**	7.7	1376	0.82	0.00	**0.82**	7.7	1376	0.82	0.00	**0.82**	1061
5	0.20	0.80	0.00	828	2.6	2.6	828	0.04	0.00	**0.04**	2.6	828	0.04	0.00	**0.04**	2.6	828	0.04	0.00	**0.04**	588
6	0.80	0.00	0.20	1928	18.3	22.9	1975	1.68	0.20	**1.88**	22.9	1975	1.68	0.20	**1.88**	22.9	1975	1.68	0.20	**1.88**	1480
7	0.60	0.20	0.20	1753	13.3	16.6	1803	1.43	0.20	**1.63**	17.4	1831	1.47	0.24	**1.71**	18.8	1873	1.53	0.29	**1.82**	1356
8	0.40	0.40	0.20	1481	8.2	10.2	1536	1.05	0.20	**1.25**	10.8	1567	1.10	0.24	**1.33**	11.8	1614	1.16	0.29	**1.45**	1147
9	0.20	0.60	0.20	957	3.1	3.9	1011	0.30	0.20	**0.50**	4.2	1048	0.35	0.24	**0.59**	4.6	1102	0.43	0.29	**0.72**	707
10	0.00	0.80	0.20	-	-	-	-	-	0.20	**0.20**	-	-	-	0.24	**0.24**	-	-	-	0.29	**0.29**	-
11	0.60	0.00	0.40	1855	13.7	22.9	1975	1.68	0.40	**2.08**	22.9	1975	1.68	0.40	**2.08**	22.9	1975	1.68	0.40	**2.08**	1429
12	0.40	0.20	0.40	1598	8.7	14.5	1729	1.33	0.40	**1.73**	16.7	1808	1.44	0.47	**1.91**	21.2	1935	1.62	0.57	**2.19**	1238
13	0.20	0.40	0.40	1099	3.6	6.0	1238	0.63	0.40	**1.03**	6.7	1297	0.71	0.47	**1.18**	9.4	1487	0.98	0.57	**1.55**	833
14	0.00	0.60	0.40	-	-	-	-	-	0.40	**0.40**	-	-	-	0.47	**0.47**	-	-	-	0.57	**0.57**	-
15	0.40	0.00	0.60	1729	9.2	22.9	1975	1.68	0.60	**2.28**	22.9	1975	1.68	0.60	**2.28**	22.9	1975	1.68	0.60	**2.28**	1336
16	0.20	0.20	0.60	1258	4.1	10.2	1536	1.05	0.60	**1.65**	14.8	1742	1.35	0.71	**2.05**	22.9	1975	1.68	0.80	**2.48**	969
17	0.00	0.40	0.60	-	-	-	-	-	0.60	**0.60**	-	-	-	0.71	**0.71**	-	-	-	0.86	**0.86**	-
18	0.20	0.00	0.80	1443	4.6	22.9	1975	1.68	0.80	**2.48**	22.9	1975	1.68	0.80	**2.48**	22.9	1975	1.68	0.80	**2.48**	1118
19	0.00	0.20	0.80	-	-	-	-	-	0.80	**0.80**	-	-	-	0.94	**0.94**	-	-	-	1.00	**1.00**	-

HHV Organ fractie 40.00 MJ/ton

15% water in raw materials fraction

30 % water in raw materials fraction

				WASTE AS SUCH		MATERIALS FRACTION with		0 % water			DRY CEMENT					WET CEMENT					EURITS
	ORG.FR	WATER	ASH	T comb	LHV	LHV rest	T comb	E	M	E+M	LHV rest	Tcomb(rest)	E	M	E+M	LHV rest	Tcomb(rest)	E	M	E+M	T comb
20	1.00	0.00	0.00	2046	37.2	37.2	2046	1.78	0.00	**1.78**	37.2	2046	1.78	0.00	**1.78**	37.2	2046	1.78	0.00	**1.78**	2109
21	0.80	0.20	0.00	1955	29.3	29.3	1955	1.65	0.00	**1.65**	29.3	1955	1.65	0.00	**1.65**	29.3	1955	1.65	0.00	**1.65**	1467
22	0.60	0.40	0.00	1822	21.4	21.4	1822	1.46	0.00	**1.46**	21.4	1822	1.46	0.00	**1.46**	21.4	1822	1.46	0.00	**1.46**	1385
23	0.40	0.60	0.00	1605	13.4	13.4	1605	1.15	0.00	**1.15**	13.4	1605	1.15	0.00	**1.15**	13.4	1605	1.15	0.00	**1.15**	1225
24	0.20	0.80	0.00	1153	5.5	5.5	1153	0.50	0.00	**0.50**	5.5	1153	0.50	0.00	**0.50**	5.5	1153	0.50	0.00	**0.50**	859
25	0.80	0.00	0.20	2013	29.3	37.2	2046	1.78	0.20	**1.98**	37.2	2046	1.78	0.20	**1.98**	37.2	2046	1.78	0.20	**1.98**	1514
26	0.60	0.20	0.20	1890	21.9	27.3	1926	1.61	0.20	**1.81**	28.7	1946	1.64	0.24	**1.87**	30.9	1975	1.68	0.29	**1.96**	1431
27	0.40	0.40	0.20	1686	13.9	17.4	1729	1.33	0.20	**1.53**	18.3	1753	1.36	0.24	**1.60**	19.8	1788	1.41	0.29	**1.70**	1286
28	0.20	0.60	0.20	1259	6.0	7.5	1310	0.73	0.20	**0.93**	7.9	1340	0.77	0.24	**1.01**	8.7	1385	0.84	0.29	**1.12**	950
29	0.00	0.80	0.20	-	-	-	-	-	0.20	**0.20**	-	-	-	0.24	**0.24**	-	-	-	0.29	**0.29**	-
30	0.60	0.00	0.40	1962	22.3	37.2	2046	1.78	0.40	**2.18**	37.2	2046	1.78	0.40	**2.18**	37.2	2046	1.78	0.40	**2.18**	1286
31	0.40	0.20	0.40	1774	14.4	24.0	1873	1.53	0.40	**1.93**	27.5	1930	1.61	0.47	**2.08**	34.6	2019	1.74	0.57	**2.31**	1350
32	0.20	0.40	0.40	1374	6.5	10.8	1496	0.99	0.40	**1.39**	12.5	1572	1.10	0.47	**1.57**	16.1	1692	1.27	0.57	**1.85**	1045
33	0.00	0.60	0.40	-	-	-	-	-	0.40	**0.40**	-	-	-	0.47	**0.47**	-	-	-	0.57	**0.57**	-
34	0.40	0.00	0.60	1870	14.9	37.2	2046	1.78	0.60	**2.38**	37.2	2046	1.78	0.60	**2.38**	37.2	2046	1.78	0.60	**2.38**	1417
35	0.20	0.20	0.60	1503	7.0	17.4	1729	1.33	0.60	**1.93**	24.5	1882	1.55	0.71	**2.25**	37.2	2046	1.78	0.80	**2.58**	1147
36	0.00	0.40	0.60	-	-	-	-	-	0.60	**0.60**	-	-	-	0.71	**0.71**	-	-	-	0.86	**0.86**	-
37	0.20	0.00	0.80	1648	7.5	37.2	2046	1.78	0.80	**2.58**	37.2	2046	1.78	0.80	**2.58**	37.2	2046	1.78	0.80	**2.58**	1257
38	0.00	0.20	0.80	-	-	-	-	-	0.80	**0.80**	-	-	-	0.94	**0.94**	-	-	-	1.00	**1.00**	-