Uncertainty Analysis of CO_2 Emissions from Cement Production

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Abstract: - This study is focused to the uncertainty analysis of the CO_2 emitted from the cement clinker production. The algorithms developed utilize the mass and energy balances describing the combustion and process emissions and apply the error propagation technique to evaluate the uncertainty estimate of each dependent variable. An example of application of the proposed model is demonstrated and a parametric analysis of some main factors influencing the CO_2 uncertainty as well as the specific CO_2 emissions follows.

Key-Words: - Uncertainty, cement, clinker, emission, model, simulation

1 Introduction

Uncertainty estimates are an important element of the CO_2 emissions inventory. Information of this kind shall be counted as a tool facilitating the efforts to improve the accuracy of inventories in the future. An uncertainty analysis of the CO_2 quantities emitted from installations of cement clinker production is developed taking into account specific tiers according the guidance presented in the Official Journal of European Union (26.2.2004) [1]. The analysis is subjected to some limitations due to the fact the three types of uncertainty exist [2]: (1) scientific uncertainty, (2) statistical uncertainty and (3) bias. The first one appears when the energy and mass balances do not represent adequately the process. It is assumed that the reported equations perfectly describe the emission processes. The bias is difficult to be quantified and for this reason the mentioned guidance as well as the IPCC Good Practice Guidance [3], aim to eliminate any intentional systematic error. As a result the analysis is restricted to the statistical uncertainty generated from several natural variations. The statistical analysis is derived as well by taking into account several guidance as reference [4, 5, 6, 7].

2 Model Formulation

The CO_2 emitted in the clinker production is produced from the fuel consumption and the limestone decarbonation during the burning process. For each source the corresponding energy and mass balances are formulated. Using these equations the combined uncertainty of each output variable is calculated using the error propagation technique [8].The method is applied if the following two assumptions are fulfilled: (1) The estimated value is the mean value of the population, (2) The parameters are normally distributed.

2.1 Mass and Energy Balances

The emissions related with the general combustion activities are estimated using the formula:

$$CO_2\_Em = Ac\_D \cdot E\_F \cdot F \tag{1}$$

Where:
CO_2_Em = CO_2 emissions, Ac_D = activity data, E_F = emission factor, F = oxidation factor.
The activity data is expressed as the net energy content of the fuel consumed (TJ) during the reporting period that is one year, calculated from the formula (2):

$$E\_C = F\_C \cdot NCV \tag{2}$$

Where:
E_C = energy content of the fuel consumption (TJ), F_C = fuel consumption (t), NCV = net calorific value (TJ/t).
As concerns the variables included in the equation (2), the following tiers are considered according to the guidance presented in the Official Journal of European Union [1].
Fuel consumed: Tier 4b
Net calorific value: Tier 3
Emission factor: Tier 2a or 3.
These tiers are taken only as a reference. Any other tier or case described with a balance can be incorporated in the model.

To calculate the fuel consumed according to the tier 4b, the following mass balance was considered:

$$Fuel\_C = Fuel\_P + Fuel\_S - Fuel\_E \quad (3)$$

Where: Fuel C = Fuel combusted, Fuel P = Fuel purchased, Fuel S = Fuel stock at the beginning of the reporting period, Fuel E = Fuel stock at the beginning of the reporting period. No fuel used for other purposes is considered. The average NCV of each fuel, consumed during the reporting period is considered. The oxidation factor is equal to one.

The CO_2 emitted from the clinker production process, because of the limestone calcination, is calculated with the same formula (1), where as F the conversion factor is considered that is equal to one. The following tiers are selected according the mentioned guidance [1].

Calculation method B: Clinker production
Activity data: Tier 2b
Emission factor: Tier 2

The activity data is the amount of clinker produced in the reporting period. This variable is estimated by applying the following mass balances:

$$Cement\_Produced_i = Cement\_Sold_i + Final\_Stock_i - Initial\_Stock_i \quad (4)$$

$$Clinker\_Consumed = \sum_{i=1}^{M} Cement\_Produced_i \cdot Clinker/Cement_i \quad (5)$$

Where i=1 2, … M the different cement types. All the quantities are given in tons.

$$Clinker\_Produced = Clinker\_Consumed - Clinker\_Supplied + Clinker\_Dispatched - Initial\_Clinker\_Stock + Final\_Clinker\_Stock \quad (6)$$

All the quantities are given in tons. The emission factor, E_F, in tons of CO_2 per ton of clinker is calculated using the average oxides analysis by the expression:

$$E\_F = 0.785\frac{\%CaO}{100} + 1.092\frac{\%MgO}{100} \quad (7)$$

The cement kiln dust, CKD, as well as not carbonated CaO, MgO in the raw materials are not taken into account.

The total CO_2 emitted is the sum of the emissions from the two sources:

$$CO_{2\_Total} = CO_{2\_Fuel} + CO_{2\_Clinker} \quad (8)$$

The specific emissions can be considered as performance indicators. Two indicators of this kind are presented:

$$ton\_CO_2/ton\_Clinker = \frac{CO_{2\_Total}}{Clinker\_Produced} \quad (9)$$

$$ton\_CO_2/ton\_Cementitious\_Products = \frac{CO_{2\_Total}}{Cement\_Produced + Clinker\_Dispatched} \quad (10)$$

2.2 Uncertainty Estimates

It shall be elucidated that the uncertainty estimation is only one step towards ensuring high inventory quality [7]. The uncertainty estimate of each variable included in the equations (1)-(10) is a tool to detect the week points and initiate improvement actions. According the previously mentioned guidance [1], the permissible uncertainty, U, shall be expressed as the 95% confidence interval around the measured value. The above means that [7]:

$$U = t(0.95, n-1)\frac{s}{\sqrt{n}},\ for \quad n \to \infty \ , \quad t = 1.96 \quad (11)$$

To calculate the variance of the depended variable of each balance, the following general formula given in the norm ENV 13005 [8] is utilized:

For: $Y = f(x_1, x_2, \ldots x_N)$ (12)

$$s_Y^2 = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 s_i^2 + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j} r_{ij}\, s_i s_j \quad (13)$$

If between two parameters x_i, x_j there is not covariance, e.g. $r_{ij}=0$, then the equation (10) is simplified accordingly. The existence of covariance can be evaluated using actual data, taken during the reporting period. Each variable x_i, has degrees of freedom ν_i. The effective freedom degrees, ν_{eff} of the function Y are given by the equation:

$$\frac{s_y^4}{\nu_{eff}} = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^4 \frac{s_i^4}{\nu_i} \quad (14)$$

The coefficient of variation of the uncertainty U, of a variable x, with average value x_{Aver}, is given by the expression:

$$CV\_U = \frac{U}{x_{Aver}} \cdot 100 \quad (15)$$

The general form of the equations (3), (4), (6), (7), (8) is:

$$Y = \sum_{i=1}^{N} c_i \cdot X_i \quad (16)$$

In the case that the parameters X_i are uncorrelated, then the variance of the depended variable Y, is given by the equation:

$$s_Y^2 = \sum_{i=1}^{N} c_i^2 \cdot s_{Xi}^2 \quad (17)$$

In the case that the analysis of the actual data shows correlation between the variables, then the covariance has to be taken into account. Such case is possible to exist between, initial stocks, final stocks, purchased materials and sold products. The processing of actual data shows that between the clinker production and the consumption of energy contained in the fuel there is a very strong positive correlation with a regression coefficient around 1. The above strong covariance exists independently if one or a mix of fuels is utilized. Then in this case the standard deviation of the total quantity of CO_2 emitted is given by the simple expression:

$$s_{CO2\_Total} = s_{CO2\_Fuel} + s_{CO2\_Clinker} \quad (18)$$

Correspondingly the general form the equations (1), (2) is:

$$Y = X_1 X_2 \quad (19)$$

If no covariance exists, the variance of the variable Y is equal to:

$$s_Y^2 = Y^2 \left(\left(\frac{s_{X1}}{X_1} \right)^2 + \left(\frac{s_{X2}}{X_2} \right)^2 \right) \quad (20)$$

The equation (5) is a combination of the forms (16) and (19) and the variance of the output variable is the combined effect of the equations (17) and (20). The equation (9) has the form:

$$Y = \frac{X_1}{X_2} \quad (21)$$

In this case the simplified expression of the variance is:

$$s_Y^2 = X_1^2 \left(\left(\frac{s_{X1}}{X_1} \right)^2 + \left(\frac{s_{X2}}{X_2} \right)^2 \right) \quad (22)$$

Finally the equation (10) is a combination of the equations (16) and (21) and the variance is estimated respectively.

The uncertainties of the input variables shall be estimated using existing experimental data, standard methods uncertainties, certified laboratories uncertainties or the maximum standard values given in the guidance presented in the Official Journal of European Union [1] according the tiers selected.

3 Results and Discussion

To test the ability of the model to evaluate the uncertainty not only of the of the CO_2 emissions but of all the variables involved, a simulation of an actual cement process is performed. After the demonstration of the results a parametric analysis follows.

3.1 Simulation Results

The simulation is performed by assuming three types of fuel, one type of clinker produced and three cement types with different cement to clinker ratios. The results are shown in the tables 1, 2, 3.

The simulation provides exact results as regards the specific CO_2 emissions, representative of a dry process kiln line. For the selected level of production, stocks and number of measurements, the total uncertainty is found in a very acceptable level. The advantage of the analysis is that provides uncertainty results in each step of the cement and clinker production for the tiers selected.

The results in bar chart format are demonstrated in the figures 1 and 2. Obviously the higher uncertainty of the CO_2 emitted from the fuels in comparison to that liberated from the decarbonation, becomes from the higher uncertainty of the energy consumption. The specific emission per ton of cement is considerably lower than the corresponding per ton of clinker. The reason is that only composite CEM II cements are utilized in the simulation. The fact that in Europe the composite cements have substituted the high clinker consuming CEM I [9] appears to be a procedure environmentally friendly, because for the same cement volumes, the specific CO_2 emission is lower.

Table 1. Fuel mass and energy balances, CO_2 emissions and uncertainty

	Unit	Total	Uncert. 95%	CV_U 95%
Fuel 1 consumption	t	103967	530	0.51
Energy of fuel 1	TJ	3246.5	27.7	0.85
Fuel 2 consumption	t	873	1.4	0.16
Energy of fuel 2	TJ	29.6	1.16	3.92
Fuel 3 consumption	t	1109	23.3	2.1
Energy of fuel 3	TJ	44.5	1.98	4.45
Total energy consumption	TJ	3276	27.7	0.85
CO_2 emission fuels	t	326604	2679	0.82

Table 2. Material and process balances, CO_2 emissions and uncertainty

	Unit	Total	Uncert. 95%	CV_U 95%
CEM X1	t	573573	3068	0.53
CEM X2	t	641837	839	0.13
CEM X3	t	9353	165	1.76
Total cement production	t	1224762	3185	0.26
Clinker/Cement ratios				
CEM X1		0.82	$2.86 \cdot 10^{-3}$	0.35
CEM X2		0.66	$2.56 \cdot 10^{-3}$	0.39
CEM X3		0.71	$3.92 \cdot 10^{-3}$	0.55
Total clinker production	t	927184	4214	0.45
Oxides content of the clinker				
CaO	%	65.15	0.076	0.12
MgO	%	2.19	0.039	1.77
CO_2 emissions from the clinker	t	459911	2323	0.47
Total CO_2 emissions	t	822515	5010	0.61

Table 3. Specific CO_2 emissions and uncertainties

	Unit	Fraction	Uncert. 95%	CV_U 95%
t CO_{2_Fuels} / t Clinker	t/t	0.35	$3.3 \cdot 10^{-3}$	0.95
t $CO_{2\_Clinker}$ / t Clinker	t/t	0.53	$3.5 \cdot 10^{-3}$	0.65
t CO_{2_Total} / t Clinker	t/t	0.89	$6.7 \cdot 10^{-3}$	0.76
t CO_{2_Total} / t Cem. Products	t/t	0.66	$8.1 \cdot 10^{-3}$	1.22

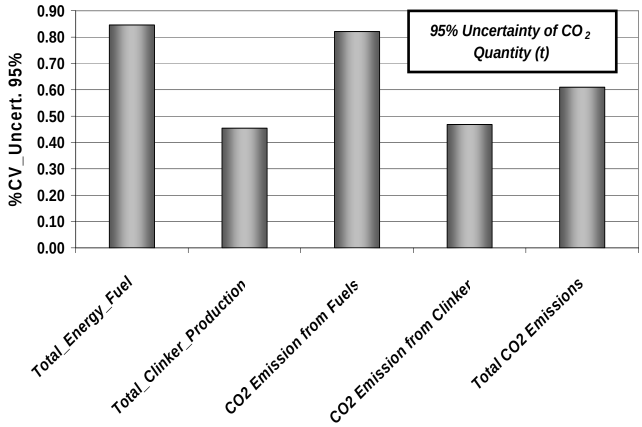

Fig.1. Coefficient of variation of uncertainty for fuel, clinker and CO_2

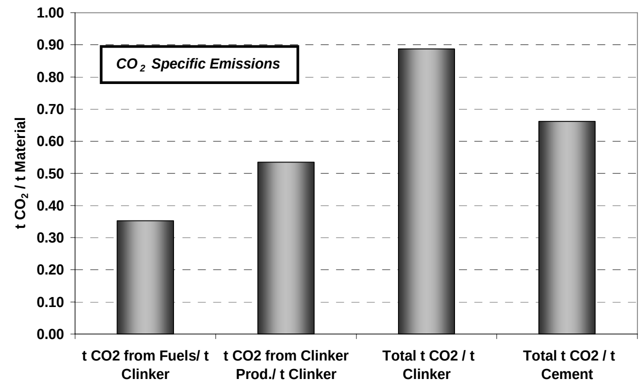

Fig.2. Specific emissions of CO_2

3.2 Parametric Analysis

The uncertainty analysis model developed is applied to study the impact of different factors on the uncertainty level as well as on the specific emission. The following factors were examined:

(1) The solid fuel stock quantity.
(2) The number of clinker oxides analysis during the reporting period
(3) The average clinker to cement ratio

3.2.1 Solid Fuel Stock Quantity

Because of the higher uncertainty as regards the stocks of solid raw materials – the maximum permitted is 10% - the stock amount it is expected to have a strong effect on the CO_2 emitted from the fuel as well as on the total uncertainty of the CO_2. The main solid fuel used in the model is pet coke. The simulation was applied for the same stock at the beginning and the end of the reporting period, but varying from 0 to 30% as percentage of the pet coke consumed during the reporting period that is supposed to be one year. The results are depicted in the figure 3. From this figure the following conclusion can be drawn

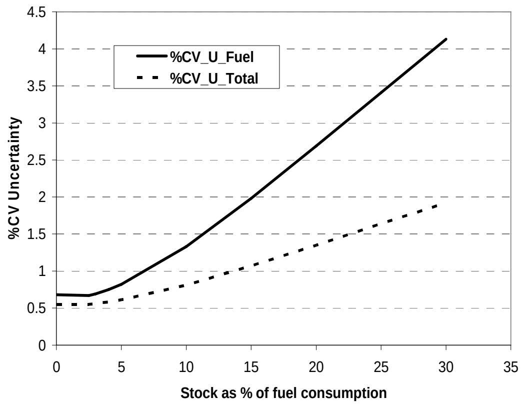

Fig.3. Coefficient of variation of uncertainty as function of the fuel stock level.

For a stock percentage up to 5% of the consumption, both uncertainties remain low. It must be noticed that in the initial application of the simulation, presented in the subsection 3.1, the stock level was kept to 5% of the consumption amount. As the stock percentage increases, the uncertainty increases and specially the uncertainty of CO_2 emitted from the fuels augments enormously. The above means that in the case that a plant has high stock volumes, has to take measures to have as much as possible low uncertainty of this stock, enough less than 10% that is the permitted. Otherwise it suffers from high uncertainties. In the case that the reporting period in one month instead of one year, then the a higher uncertainty is expected, because the consumption is around 12 times less and the percentage of the stock shall be increased by increase around an order of magnitude.

3.2.2 Number of Clinker Oxides Analysis

Depending on the clinker production level and the raw materials quality and stability, each plant has a different frequency to perform a full clinker analysis. The influence of the number of the clinker oxides analysis on the CO_2 emissions uncertainty is studied, by assuming the same level of standard deviation for each oxide, independently of the analysis number. The results of the simulation application appear in the figure 4. As it is obvious from this figure the uncertainty level strongly depends on the number of analysis, especially if this number is low. As the number clinker analysis N_{cl} increases, the uncertainty decreases. In the case that $N_{cl} > 100$, then any additional increase of the number of analysis, causes a very small improvement of the uncertainty. For values of N_{cl} between 300 and 1000, the level of uncertainty is practically the same. The above means that in the case of one clinker type, a daily analysis of the average clinker ($N_{cl} \approx 300$) provides the optimum level of uncertainty, with the minimum number of analysis.

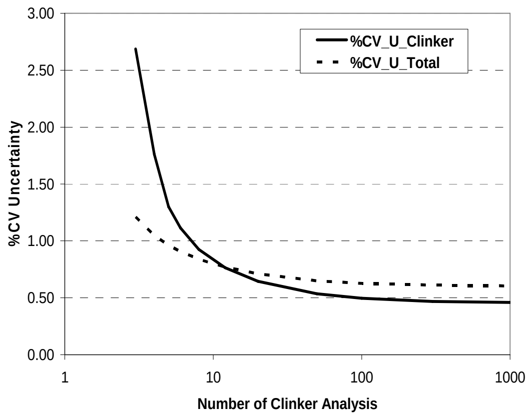

Fig.4. Coefficient of variation of uncertainty as function of the number of clinker analysis.

3.2.3 Average Clinker to Cement Ratio

The simulation is applied for different Clinker/Cement ratios for the same volumes of the cement produced. The specific emission expressed as t CO2/ t Cement is then calculated. The results are presented in the figure 5.

In the case that the cement produced is only CEM I, then the specific emission is ~ 0.85. On the contrary if the cement is CEM II B according the norm EN 197-1 [10], then the specific emission is found in the area of 0.60. As a result, the application of the simulation quantifies the very positive effect of the production of composite cements on the specific CO_2 emission factor.

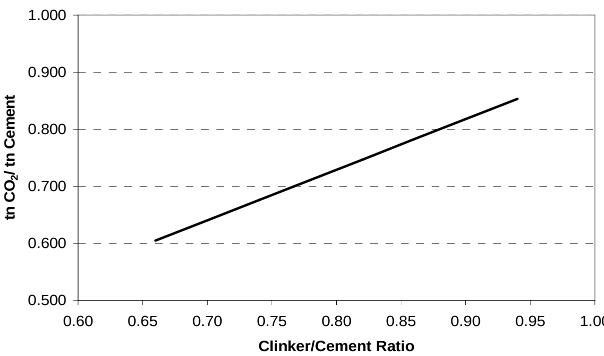

Fig.5. t CO_2 / t Cement as function of Clinker/Cement ratio.

4 Conclusion

The statistical uncertainty of the CO_2 emissions from the clinker production is analyzed, taking into account some specific tiers as regards the CO_2 emitted from the fuel and from the raw materials decarbonation. A similar analysis can be performed for any other tier. The uncertainty of each output variable is calculated using the error propagation method. The techniques applied here can help in the estimating and reporting of the CO_2 uncertainties.

A parametric analysis is also performed, to study the sensitivity of the uncertainty, when some important factors vary. As the stocks increase as fraction of the materials consumption, the uncertainty increases as well. The increase of the number of analysis has a positive effect to the uncertainty reduction, but an optimum level of number of analysis exists. After this level the cost of analysis increases, without to achieve an actually better uncertainty.

For the same cement volumes, the production of composite cements, instead of pure CEM I, permits a considerable reduction of the CO_2 emitted per ton of cement.

References:

[1] Commission Decision of 29 January 2004, Establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council, *Official Journal of the European Union*, 2004.

[2] ICF Consulting, *Estimating statistical uncertainties in the Greenhouse gas emissions measurement and reporting protocols for the UK trading scheme*, ICF Consulting, 2002.

[3] Intergovernmental Panel on Climate Change, *Good Practice Guidance and Uncertainty Measurement in National Greenhouse Gas Inventories*, IPCC National Greenhouse Inventories Program, 2000.

[4] J.Ranganathan, L. Corbier, P. Bhatia, S.Smitz, P.Gage, K. Oren, *A Corporate Accounting and Reporting Standard,* The Greenhouse Gas Protocol, 2001.

[5] Environmental Resources Trust, Inc., *Corporate Greenhouse Gas Verification Guideline,* Environmental Resources Trust, Inc., 2005.

[6] World Business Council for Sustainable Development, *Cement Sustainability Initiative*, *CO_2 Accounting and Reporting Standard for the Cement Industry,* World Business Council for Sustainable Development, 2005.

[7] World Business Council for Sustainable Development, *GHG Protocol guidance on uncertainty assessment in GHG inventories and calculating statistical parameter uncertainty,* http://www.ghgprotocol.org/templates/GHG5/layout.asp?type=p&MenuId=OTAx&doOpen=1&ClickMenu=No,

[8] UNI CEI ENV 13005:2000, *Guide to the expression of uncertainty in measurement,* UNI – CEI, 2000.

[9] H. Ludwig, Influence of process technology on the manufacture of market-oriented cements, *Proceedings of VDZ Congress, Process Technology of Cement Manufacturing*, 2002, pp 2 - 24.

[10] ELOT EN 197-1, *Cement- Part 1: Composition, specifications and conformity criteria for common cements,* ELOT, 2000.

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