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Adaptation of IPCC Guidelines and Software to Ukraine's Cement Sector

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SUMMARY

The cement industry in Ukraine makes a significant contribution to greenhouse gas emissions (GHG). The main emission sources in this industry are the calcination processes and fuel combustion to provide high-temperature conditions for the calcination processes.

Adaptation of the IPCC Inventory Guidelines for Ukraine's cement industry increases the accuracy of the estimated GHG emissions and reduction potential, and inspires confidence in the reliability of these estimates.

This report provides a:

- description of the technologies for cement production;
- description of the statistical sources that underlie the GHG inventory;
- description of the GHG inventory guidelines for Ukraine's cement industry;
- methodology and results for estimating GHG emissions from cement production;
- specification of GHG emission factors for calcination processes;
- set of Excel spreadsheets for automated calculation of GHG emissions;
- set of instructions for filling out the worksheets to estimate GHG emissions.

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Introduction

The Intergovernmental Panel on Climate Change (IPCC) estimates that the cement sector produces approximately 2.4% of the total global emissions from industrial sources. In the technical process of cement production (calcination), raw materials are heated and CO_2 is emitted as a by-product. The calcination process decomposes carbonate ($CaCO_3$) at a temperature of 820-907 ^{0}C to produce CaO the basis for cement and CO_2. In addition, CO_2 and other greenhouse gasses are emitted from the fuel combusted to provide the high temperatures needed for the calcination process. Thus, it is necessary to account for both sources of CO_2 and GHG emissions to obtain full information on emissions in the cement production sector and the reduction potential.

The objective of this document is to prepare a methodology for estimating GHG emissions and present the results in a format consistent with the inventories performed by different countries and regions of the world. Depending on the available statistical information in [1], it is proposed to make estimations based on cement or clinker production data. It is also possible to specify CO_2 emissions under the IPCC Guidelines using available data. The methodology conforms to the requirements of the IPCC guidelines [1] for estimating national inventories, and draws upon other sources:

- Best Practice [2], which distinguishes estimation approaches based on clinker and cement production data and provides recommendations for specifying estimation factors that take into consideration a correction factor for cement lost to kiln dust;
- Methodologies proposed by the GHG Protocol Initiative recognize constrained data availability and propose two methodologies based on the IPCC Good Practice Guidelines [2]. One is a clinker-based GHG emission estimation methodology presented in WBCSD "Cement CO_2 Protocol" [10]. This estimation tool is written for cement companies to control and report on direct and indirect greenhouse gas emissions resulting from cement production at their facility. The second methodology was developed under the U.S. EPA's Climate Wise Program [11]. This approach proposes an estimation tool for plant mangers to facilitate the measurement and reporting of CO_2 emissions from cement production. These methodologies are aimed at developing estimates of GHG inventories for the cement sector that are consistent with the IPCC guidelines.

The methodology presented in this report for estimating the inventory of GHG emissions in Ukraine's cement sector is based on estimated emissions from the calcination process plus the emissions from fuel combustion needed to provide the high temperatures needed for the calcination process.

This report contains the following results:

- identification of GHG emissions sources in Ukraine's cement sector;
- selection of guidelines for estimating GHG emissions in Ukraine's cement sector;
- selection of estimation factors for GHG emissions in Ukraine's cement sector;
- development of instructions for filling out spreadsheets to estimate GHG emissions in Ukraine's cement sector.

1. Ukraine cement sector

1.1. General information

Cement (from Latin Caementum – crushed stone) is contained in a group of artificial inorganic powder-like binding materials [4]. It is one of the most important building materials used for the production of concrete, mortar, plaster, hydro-insulation, and other building materials. Binding materials are produced as a result of calcination, which heats a ground mixture that contains lime carbonate (CaO), sand (SiO_2), aluminum oxide (Al_2O_3), and ferrous oxide (FeO). Proportions of

these components determine the main properties of the different types of cement. After calcination and grinding, the powder is mixed with water and other materials to produce aplastic and viscous dough that may harden to a stone like substance, depending on its physical and chemical properties, and preserve its strength in the air and water.

The following types of cements produced in Ukraine are:

1) Cements for common construction purposes used [9] for monolithic concrete for civil and industrial buildings, built-up ferro-concrete construction such as bridges, road-building, external parts of water treatment facilities, and mortars – are shared among [5]:

- Portland cement;
- Blended Portland cement that contains:
  - Slag;
  - Pozzolan;
  - Ash ejection;
  - Limestone;
  - Composite cement ;
- Asbestos-cement products;
- Slag Portland cement;
- Fast-hardening cement;
- Road cement;
- Pozzolan cement;
- Composite cement;
- Cement types that do not require forming.

2) Sulfate and frost-resistant cements [6] are used [9] for construction periodically subject to conditions of sulfate aggression, freezing and defrosting, and damping and drying:

- Sulfate-resistant Portland cement;
- Sulfate-resistant blended Portland cement;
- Sulfate-resistant slag Portland cement;
- Pozzolan Portland cement.

3) Oil-well Portland cements are used [9] for plugging petroleum and gas-bores, and are characterized by fast bondability and slow hardening [8]:

- Oil-well Portland cement without additives;
- Oil-well Portland cement with normal requirements at water cement ratio[1];
- Oil-well blended Portland cement with mineral additives;
- Oil-well Portland cement with special additives that control cement dough density.

4) Alumina cements are used where fast hardening is needed in extreme environments [17, 18]:

- Alumina cement is used [9] for urgent and emergency repair, rehabilitation, or buildings being exposed to mineralized water or sulfur trioxide, and for heat-resistant concretes and mortars. Alumina cement is not used in high-temperature or humid conditions. This cement is characterized fast hardening at normal and low temperatures, and is resistant to mineralized water;
- Gypsum and alumina expanding cement is used [9] for waterproof concretes and mortars, sealing, repairing, and plugging petroleum and gas bores. This cement expands when setting, hardens fast, has high density, and is waterproof and sulfate-resistant.

In order to estimate the inventory CO_2 emissions from the calcination process, it is necessary to have the information on the types of cement, their composition, and the amount and composition of the clinker (CaO) component

[1] Water cement ratio – is a ratio water to the molecular weights of lime (CaO), sand (SiO_2), alumina (Al_2O_3), and ferrous oxide (FeO).

1.2. Technology of cement production

The modern cement production process covers the extraction of raw material and/or the use of some industrial wastes (metallurgic slams, CHP ashes, stripping rock, etc.), crushing and fine grinding of the material, forming a homogeneous mixture with certain properties, and calcifying the mixture. The cement clinker is obtained as a result of this process, which is then crushed with additives in order to obtain cement with relevant properties as a final product.

We will briefly review the mechanism of chemical reactions for producing the Portland cement clinker [3]. A mixture of the raw material, which undergoes special treatment, is placed in a kiln under conditions of increasing temperature. The raw materials are dried first and then dehydrated at temperatures of 550-800° to form aluminosilicate. This phase produces particles with a loose structure with increased internal energy and reactivity.

At 820 ^{0}C the reaction that decomposes chalk ($CaCO_3$) into CaO and CO_2 occurs, and ends at 907 ^{0}C. Simultaneously the reaction between the calcium oxides (CaO) and products of clay dehydration, which contain mainly aluminum oxides and silicon oxides, begins. Single lime aluminate ($CaO \cdot Al_2O_3$) and single lime silicates are formed ($CaO \cdot SiO_2$) from the CaO in lime and the SiO_2 and AI_2O_3 in clay at temperatures of about 800^{0}C. Subsequently, at 900^{0}C, $CaO \cdot SiO_2$ is enriched with the lime and gradually transforms into two-lime silicate ($2CaO \cdot SiO_2$), and finally at 1,150^{0}C lime (CaO) cease to exist as a reacting substance. Simultaneously, $CaO \cdot AI_2O_3$ is transformed into two lime silicates ($2CaO \cdot AI_2O_3$).

Reactivity increases at temperatures of 1,200-1,250 ^{0}C and two-lime ferrite $2CaO \cdot Fe_2O_3$, is formed, which induces a liquid phase that is a solution of particles of charged materials that have not reacted. These processes lead to supersaturation and crystallization of three lime silicates ($3CaO \cdot SiO_2$), which is the main artificial mineral of cement clinkers, which is a compact mass consisting of particles 4-20 mm in size.

The clinker mass is quenched in a special refrigerator to prevent formation of large crystals and preserve the material in a non-crystalline glass-like state, which maintains the internal energy of cement. Cement produced from non-quenched clinkers will have reduced reactivity with water.

At the next stage the clinker is finely ground and mixed with gypsum and active mineral additives or other materials to produce cements having specific properties.

The cement industry was one of the first to deal with dust (Cement Kiln Dust – CKD) removal techniques that have grown in number to include:

- Reduce the velocity of dusty air so that the dust particles settle out of the airstream;
- Filter the dust from the airstream;
- Apply centrifugal force to the airstream to 'trap' the heavier dust particles.
- Subject the airstream to electrostatic precipitation that removes 98-99% of the dust particles by applying an electric charge to the dust particles, causing them to be attracted to an opposite charge and precipitated out of the airstream.

Depending on the mixture and preparation of the raw materials, the calcination process may use a dry technology in rotary kiln, a wet technology in rotary kilns, or a rarely used combined technology. The selection of the calcination technology is based on a mix of technical and economic indicators that include the concentrations of the raw materials, the consumption of fuel and electricity, and labor. Irrespective of the technology it is always necessary to provide a finely ground and homogenous mix of raw materials, which influences the clinker quality, because as the density of the clinker becomes higher, the reactions between the raw materials become more intensive.

In the dry technology process [7], the raw materials are dried and then transformed into dry flour by crushing and grinding. The flour is then placed in the kiln for calcination. The dry technology

process consumes more electricity, which is explained by the requirement to crush the raw materials components.

The wet technology utilizes water in the crushing and grinding process to produce a slurry that contains 32-45% water and is the consistency of cream. The water reduces the energy consumption at this stage by reducing the hardness of the inputs and improving the grind-ability of the constituents, but requires more energy at the kiln stage as it must be evaporated away.

Advantages of the wet process [3] include:

- A more homogenous mixture that provides a more consistent and constant higher quality final product;
- Improvement in more hygienic working conditions because preparation and transportation of slurry is not accompanied with dust release;
- Lower capital costs because the production equipment is less sophisticated and costly.

On the other hand, the wet process requires higher energy consumption for the calcination process.

According to the data of the State Committee of Ukraine of Statistics in 2001, the dry production process was used only in the Dnipropetrovsk region and all other administrative units used the wet process. The fuel consumption per tonne of the cement using the dry process accounted for 98.8 kg c. e., whereas the fuel consumption for the wet process varied by the operation practices at specific enterprises from a low of 156.10 kg c.e./t (in Mykolayiv region) to a high of 259.4 kg.c.e./t (in Kharkiv region). The average fuel consumption for cement production in Ukraine is 186.265 kg.c.e./t, accounting for combustion of 1,077,786 t.c.e. It is evident that shifting to the dry technology is an effective energy saving measure that will provide for reductions in fossil fuel consumption and GHG emissions.

2. GHG inventory methodology for cement production

2.1.General information

GHG emissions are generated by the calcination process, which is the chemical transformation of input materials into cement, and the combustion of fuels to generate the heat necessary for calcinations to occur. GHG emissions from the calcination process and from fuel consumption will provide an estimate of total emissions from cement production and the reduction potential in Ukraine.

As background, CO_2 is produced during clinker production, an intermediate product from which cement is made. In the temperature range of 820-907^{0}C $CaCO_3$ from lime decomposes into CaO and CO_2, the latter being a byproduct of the reaction. Silica, aluminum, and iron oxides react with CaO to mineralize the clinker and form calcium silicate. The clinker, the end product of the baking process, is a system of artificial minerals [3]: $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot AI_2O_3$ and $2CaO \cdot Fe_2O_3$, which contains intermediate products from the unfinished reactions, as well as various admixtures of inactive ballast compounds. Each of the chemical compounds in a clinker contains oxygen oxides and, in practice, high-quality cement is based on the quantity of the most important oxides it contains follows: [3]: CaO – 62-68%, SiO_2 – 18-26%, AI_2O_3 – 4-9%, and Fe_2O_3 – 0.3-6%.

The clinker also contains an amorphous substance in the form of uncrystallized glass (6–10%) and it may also contain a small quantity of magnum oxide (not exceeding 5%). These additions are unavoidable since carbonate rock is used as a main raw component, the most important component, calcium carbonate, contains some magnesium carbonate. Clinkers do not contain free lime as it should be fully bounded during the high-temperature process, but available free calcium oxide (CaO) means that the burning process has not been accomplished.

Thus, CO_2 emissions from the calcination process are estimated under the assumption that the entire CaO content of the raw materials is transformed. The additional emission of CO_2 and other GHGs from fuel consumption provides an estimate of total GHG emissions from cement production in Ukraine and the reduction potential.

2.2. Methodology for inventory of GHG emissions from cement production

There are several methodologies for inventory of GHG emission from cement production:

- IPCC Guidelines [1];
- IPCC Good Practice Guidance [2];
- The methodology proposed by GHG Protocol Initiative based on clinker [10] and cement [11] production data.

Characteristics of these three methodologies are provided below:

Depending on the inventory objective and specification of the available statistics, the inventory of estimated GHG emissions from cement production might be performed for three specification levels:

1) GHG emissions based on total cement production – all factors are derived from IPCC Guidelines;
2) GHG emissions based on the production technology and volume of clinker production. It is possible to specify the relevant emission factors, provided that the statistical information is available, otherwise IPCC factors are used. Since the State Committee of Statistics of Ukraine does not provide information on the lost CKD, the IPCC CKD correction factor 1.05 was used to estimate CO_2 emissions from production of clinker, which is lost as CKD.
3) GHG emissions based on clinker production data from the separate enterprises – all IPCC factors are specified given the specific technological characteristics of the separate enterprises.

Based on the principals presented in the IPCC methodology [1] more detailed methodologies for estimating GHG emissions were developed [2, 10, 11]:

- Good Practice [2], specifies clinker and cement-based GHG emission estimation methodologies and recommends how to specify factors given the available statistics and the default CKD correction factor;
- The GHG Protocol Initiative proposes two methodologies based on the IPCC Good Practice Guidelines that recognize data availability constraints [2]. One is a clinker-based methodology presented in WBCSD "Cement CO_2 Protocol" [10]. This estimation tool is written for cement companies to control and report on direct and indirect greenhouse gas emissions resulting from cement production at their facility. The second methodology, developed under the U.S. EPA's Climate Wise program [11] (it is cement based), enables plant mangers to facilitate the measurement and reporting of CO_2 emissions from cement production. The objective of the latter methodology is to ensure consistency of GHG inventories for cement production according to the IPCC Guidelines.

IPCC Guidelines [1] define requirements to estimate national inventories of GHGs. The main objective of the Guidelines is to clearly define the consequence of estimation, record results to adhere to a common inventory format in various countries and regions, to facilitate comparison of their conclusions and reliability. Given the available statistics it is proposed to perform estimation based on the clinker or cement production, with specification of associated CO_2 emission factors.

2.3. GHG inventory methodology for cement industry of Ukraine

2.3.1. Conception of GHG inventory methodology for cement industry of Ukraine

The methodology for estimating Ukraine's GHG inventory in the cement industry is based on the experience of [1; 2]. The inventory methodology is based on CO_2 emission factors for the calcination process and on a broader range of GHG emissions produced by the fuel combusted for high-temperature calcination.

In addition to specifying CO_2 emission factors for the calcination process, the report proposes to determine the clinker content for all types of cement produced in Ukraine. It is assumed that all CaO is released from raw carbonate (i.e. lime $CaCO_3$) in the calcination process and that the associated CO_2 emissions are directly correlated with the CaO content in the clinker. CO_2 emissions may then be estimated based on the CaO content in clinkers and, using operating standards, the clinker content in cement, as well as molecular weight of each of the clinker compounds.

2.3.2. CO_2 inventory methodology for calcination process in the cement industry of Ukraine

The estimate of cement industry CO_2 emissions is based on the production of each cement type by determining CaO content in clinker and clinker content in cement, as well as molecular weight of each clinker compound. The estimates of CO_2 emissions for each cement type utilize the following information:

- determine cement production by administrative units of Ukrainian (Autonomous Republic of Crimea, Kyiv and Oblasts);
- determine clinker content in each type of cement;
- calculate CaO content in clinker for each cement type;
- calculate CO_2 emission factor;
- consider CO_2 emissions from production of clinkers lost as CKD – as available statistics of Ukraine doesn't give the information about quantity of CKD in the cement sector, it is necessary to use the correction factor from IPCC [2] – 1.05;
- calculate CO_2 emissions.

The calculation of the CO_2 emissions is expressed in the following formula:

$$V^*_{ri} = M_{ri}\ k_{cli}\ K^{cl}_{CO_2} k_{CKD}, \qquad (1)$$

where,
V^*_{ri} – CO_2 emissions, Gg[2];
r – index of administrative unit;
i – type of cement;
M_{ri} - each type of cement produced in Ukraine (tonne);
k_{cli}–fraction of clinker in each cement;
$K^{cl}_{CO_2}$ – CO_2 inventory factors for calcination process, t CO_2/t clinker[3];
k_{CKD} – default correction factor CKD correction factor for CO_2 emissions, relative units.

[2] Instruction for filling the worksheets on CO_2 emissions from calcinations process in the cement sector of Ukraine is contained in section 4.1.
[3] Methodology for this factor estimation is contained in section 3.2.

2.3.3. Inventory methodology for GHGs emitted from fuel combusted during high-temperature calcination process in the cement industry of Ukraine.

An inventory of emissions of CO_2, CH_4, and N_2O are estimated from the fuel combusted during the high-temperature calcination process are presented in this section based on the IPCC methodology [1].

This methodology for estimating CO_2 emissions from fuel combustion utilizes the following information and steps:

- estimate of apparent fuel combustion in terms of coal-equivalent;
- convert into a common energy units;
- multiply by emission factor to compute the carbon content;
- compute stored carbon;
- correct for unoxidised carbon;
- convert oxidized carbon to CO_2 emissions.

In general CO_2 emissions from fuel combustion are calculated based on the following formula:

$$V_{ri} = E_i \, Kc_i \, L_i, \tag{2}$$

where,

V – CO_2 emissions Gg[4];
r – index of administrative unit;
i – fuel type;
E_i – combusted i-type fossil fuel, t.c.e.;
Kc_i – CO_2 emission factor for i-type fossil fuel tC/TJ[5];
L_i – oxidized carbon fraction for i-type of fossil fuel, relative units[5].

Methane (CH_4) and nitrous oxide (N_2O) and other GHG emissions are also released during fuel combustion. The quantity of these emissions depends on fuel type, technology of fuel combustion, operation, and service life of equipment. The IPCC methodology [1] separates these emissions by four fuel types to facilitate estimation of these GHG emissions:

- coal;
- natural gas;
- oil, including transport gasoline, transport diesel oil, other oil products;
- biomass, including wood and wood waste, charcoal, other biomass and wastes.

The methodology [1] estimates CH_4 and N_2O emissions from fuel combustion in the following steps:

- estimate quantities of fuel, by type, combusted to provide high temperature calcination administrative units;
- estimate emission factors for each fuel;
- estimate emissions.

In general CH_4 and N_2O emission are calculated based on the following formula:

$$V_{ij} = E_i \, K_{ij}, \tag{3}$$

where,

V_{ij} – GHG emissions, Gg[6];

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[4] Instruction for filling the worksheets on CO_2 emissions from fuel combustion for providing high-temperature conditions of calcinations process in the cement sector of Ukraine is contained in section 4.2.1.
[5]Methodology for this factor estimation is contained in section 3.3.
[6] Instruction for filling the worksheets on methane and nitrous oxide emissions from fuel combustion for providing high-temperature conditions of calcinations process in the cement sector of Ukraine is contained in section 4.2.2.

j – index of GHG (methane or nitrous oxide);
i – fuel type;
E_i – consumed fossil fuel, TJ;
K_{ij} – GHG emission factor[5].

3. Initial data and GHG emission estimation factors for cement industry of Ukraine

3.1. Information sources for GHG inventory in cement industry of Ukraine

As already mentioned, GHG emissions in the cement sector of Ukraine are determined by the calcination process and fuel combustion to provide the necessary high temperature conditions for calcination. That is why it is necessary to possess the following data:

- amount of cement production, by type;
- content of cement clinker , by type of clinker;
- content of CaO in clinker;
- amount of fuel combusted to provide high temperature conditions of calcination.

The sources of information for preparation of this data are:

- Form 1-p "Enterprise's report on production" [12] – cement production data at the oblast and national levels;
- Form 11-MTP "Report on the results of fuel, heat and electricity consumption" [13] – energy consumption data in the cement sector at the oblast and national levels;
- State standards of Ukraine (DSTU);
- Technological regulations.

Form 1-p contains data on total cement production in natural units (net weight of production without packing) by administrative unit in Ukraine. A subsection of this form contains data on the total amount of cement production by type.

Form 11-MTP contains information on the total amount and specific fuel combustion (t.c.e.) for cement production by administrative units of Ukraine. This form also contains data on fuel combustion exclusively to provide the necessary high temperature conditions for calcination. Fuel combustion data by type of cement is not presented in form 11-MTP.

DSTU established the content of clinker in cement and content of CaO in clinker (Table 1). As one can see from the Table 1, the ranges in the values established by DSTU are wide, which introduces a high level of uncertainty in the inventories based on these values. Therefore, to improve the accuracy of CO_2 emissions from the technology process it is better to use the technological regulations of some enterprises.

The most universal source of primary data are the technological regulations that can provide all of the data at the enterprise level, but due to legal limitations for confidentiality reasons, the State Committee of Statistics of Ukraine does not provide this information at the enterprise level. However, study results show the content of clinker in cements and content of CaO in clinker as determined by the Ukrainian enterprises is within narrower limits. Further, clinker content in cement and CaO content in clinker is quite stable for each cement type and, for all practical purposes, doesn't depend on the enterprise where is the cement is produced. Thus, it is recommended to define clinker content in cement and CaO content in clinker based on the results of the analysis of technological regulations, which are performed periodically (once every several years) by experts in this field.

3.2. CO_2 inventory factors for the calcination process

A clinker consists of different artificial minerals and based on the fraction of each mineral in clinker, the CO_2 inventory factors for the calcination process might be specified by using the atomic mass of each chemical components of the minerals. In general, the CO_2 estimation factor for calcination is specified based on the information related to clinker production, using the following formula:

$$K_{CO_2}^{cl} = 0.785 \sum \delta_i \xi_i \quad (4)$$

where,

$K_{CO_2}^{cl}$ – CO_2 inventory factors for calcination process, t CO_2/t clinker;
0.785 – ratio of molecular weight of CO_2 and CaO, relative units;
i – index of artificial mineral, that contained in clinker;
δ_i – content of CaO in i-mineral, relative units;
ξ_i – content of each artificial mineral in clinker, relative units.

The CaO content in each artificial mineral contained in the clinker is estimated based on the molecular weight of each element contained in artificial mineral and the molecular weight of the whole artificial mineral.

$$\delta_i = \frac{N_i \mu_{CaO}}{\mu_i} \quad (5)$$

where,

δ_i – content of CaO in i-mineral, relative units;
N_i – number of CaO molecules in each artificial mineral, units;
μ_{CaO} – molecular weight of CaO, kg/mole;
μ_i – molecular weight of each artificial mineral, contained in a clinker, kg/mole.

Table 1 presents the CO_2 emission factors for each type of cement produced in Ukraine. The factors are expressed in ton of CO_2 per a ton of clinker, which is calculated using formula (4) using data from [5-9, 17, 18] and the atomic mass of chemical of clinker chemical components.

Table 1. CO_2 emission factor by cement types produced in Ukraine

Name of cement		Clinker content in cement, %	Artificial mineral in clinker	Mineralogical composition of clinker (% of weight)	CaO content in clinker, %	CO_2 emission factor, t CO_2/t clinker[7]	Sources
Sort	Sub-types						
	Portland cement	95-100	$3CaO \cdot SiO_2$	40-65	46.97-92.51	0.369-0.726	[5,9]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Portland cement with slag	65-94	$3CaO \cdot SiO_2$+ +$3CaO \cdot AI_2O_3$	0-65	43.87-16.87	0.344-0.132	[5,9]
			$2CaO \cdot SiO_2$+ +$4CaO \cdot AI_2O_3 \cdot Fe_2O_3$	33			
	Portland cement	80-94	$3CaO \cdot SiO_2$	40-65	46.97-	0.369-	[5,3]

[7] The factor for estimation of CO_2 emissions from the technology process at cement production (t CO_2/t clinker) takes into consideration a correction for ratio of molecular weight of CO_2 and CaO (0.785).

Name of cement		Clinker content in cement, %	Artificial mineral in clinker	Mineralogical composition of clinker (% of weight)	CaO content in clinker, %	CO_2 emission factor, t CO_2/t clinker[7]	Sources
Sort	Sub-types						
Cement for common construction purposes			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Portland cement with ash ejection	80-94	$3CaO \cdot SiO_2$	40-65	46.97-92.51	0.369-0.726	[5,3]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Portland cement limestone	80-94	$3CaO \cdot SiO_2$	40-65	46.97-92.51	0.369-0.726	[5,3]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Cement for asbestos cement products	80-94	$3CaO \cdot SiO_2$	40-65	46.97-9.51	0.369-0.726	[3,9]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Composite cement	65-94	$3CaO \cdot SiO_2$	40-65	46.97-92.51	0.369-0.726	[5,3]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Fast-hardening cement	90	$3CaO \cdot SiO_2 + 3CaO \cdot Al_2O_3$	0-65	60.74	0.477	[9]
			$2CaO \cdot SiO_2 + 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	35			
	Road cement	95-100	$3CaO \cdot SiO_2$	40-65	46.97-92.51	0.369-0.726	[5,3]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Slag Portland cement	20-64	$3CaO \cdot SiO_2$	40-65	46.97-92.51	0.369-0.726	[5,3,9]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Pozzolan cement	45-79	$3CaO \cdot SiO_2$	Not standard	45.74	0.359	[6,9]
			$3CaO \cdot AI_2O_3$	8			
			$3CaO \cdot AI_2O_3 + 4CaO \cdot AI_2O_3 \cdot Fe_2O_3$	Not standard			
			Al_2O_3	5			
			MgO	5			
	Composite cement	20-64	$3CaO \cdot SiO_2$	40-65	46.97-92.51	0.369-0.726	[3,5]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			

Name of cement		Clinker content in cement, %	Artificial mineral in clinker	Mineralogical composition of clinker (% of weight)	CaO content in clinker, %	CO_2 emission factor, t CO_2/t clinker[7]	Sources
Sort	Sub-types						
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
	Cement types for cementation without forming	20-64	$3CaO \cdot SiO_2$	40-65	46.97-92.51	0.369-0.726	[3,5]
			$2CaO \cdot SiO_2$	15-40			
			$3CaO \cdot Al_2O_3$	5-15			
			$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	10-20			
Sulfate-resistant cements	Sulfate-resistant Portland cement	100	$3CaO \cdot SiO_2$	0-50	51.37	0.403	[6, 9]
			$3CaO \cdot AI_2O_3$	0-5			
			$3CaO \cdot AI_2O_3$+ +$4CaO \cdot AI_2O_3 \cdot Fe_2O_3$	0-22			
			Al_2O_3	5			
			MgO	5			
	Sulfate-resistant blended Portland cement	80-90	$3CaO \cdot SiO_2$	Not standard	60.96	0.478	[6, 9]
			$3CaO \cdot AI_2O_3$	5			
			$3CaO \cdot AI_2O_3$+ +$4CaO \cdot AI_2O_3 \cdot Fe_2O_3$	22			
			Al_2O_3	5			
			MgO	5			
	Sulfate-resistant Slag Portland cement	20-50	$3CaO \cdot SiO_2$	Not standard	56.48	0.443	[6, 9]
			$3CaO \cdot AI_2O_3$	8			
			$3CaO \cdot AI_2O_3$+ +$4CaO \cdot AI_2O_3 \cdot Fe_2O_3$	Not standard			
			Al_2O_3	5			
			MgO	5			
	Pozzolan Portland cement	20-40	$3CaO \cdot SiO_2$	Not standard	56.48	0.443	[6]
			$3CaO \cdot AI_2O_3$	8			
			$3CaO \cdot AI_2O_3$+ +$4CaO \cdot AI_2O_3 \cdot Fe_2O_3$	Not standard			
			Al_2O_3	5			
			MgO	5			
Oil-well Portland cement	Oil-well Portland cement without additives	100	$3CaO \cdot SiO_2$	Not standard	68.32	0.536	[8, 9]
			$3CaO \cdot Al_2O_3$	3			
			$3CaO \cdot Al_2O_3$+ +$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	22			
	Oil-well Portland cement with normal requirements at water cement rati	100	$3CaO \cdot SiO_2$	48-65	49.69-65.33	0.390-0.513	[8]
			$3CaO \cdot Al_2O_3$	3-8			
			$3CaO \cdot Al_2O_3$+ +$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	24			
	Oil-well blended	80-94	$3CaO \cdot SiO_2$	Not standard	68.32	0.536	[8, 9]

Name of cement		Clinker content in cement, %	Artificial mineral in clinker	Mineralogical composition of clinker (% of weight)	CaO content in clinker, %	CO_2 emission factor, t CO_2/t clinker[7]	Sources
Sort	Sub-types						
			$3CaO \cdot Al_2O_3$	5			
			$3CaO \cdot Al_2O_3$+ +$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	22			
	Oil-well Portland cement with special additives that control cement dough density	30-89	$3CaO \cdot SiO_2$	Not standard	68.32	0.536	[8, 9]
			$3CaO \cdot Al_2O_3$	5			
			$3CaO \cdot Al_2O_3$+ +$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	22			
Alumina cement	Alumina cement	100	$CaO \cdot AI_2O_3$, $12CaO \cdot 7AI_2O_3$, $CaO \cdot 2AI_2O_3$, $2CaO \cdot AI_2O_3 \cdot SiO_2$, FeO		40	0.314	[9,17,18]
	Gypsum and alumina expanding cement	70	$CaO \cdot AI_2O_3$, $12CaO \cdot 7AI_2O_3$, $CaO \cdot 2AI_2O_3$, $2CaO \cdot AI_2O_3 \cdot SiO_2$, FeO		40	0.314	[9,17,18]

Table 1 presents data on the approximate content of clinkers as the main cement component for the cements manufactured in Ukraine. These data show that the Portland cement clinker consists of 70-80% calcium silicate ($3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$).

3.3. GHG inventory estimation factors for high-temperature calcination

In addition to the CO_2 released during calcination, natural gas, coal and coke are combusted for high-temperature baking during clinker production. Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide N_2O are released when these fuels are combusted. This section presents adaptation of the GHG inventory methodology for the high-temperatures required for calcination [1].

Calculations of GHG emissions from fuel combustion by fuel types are started with conversion of coal-equivalent units into TJ. Fuel burned for the high-temperature calcination in the cement sector of Ukraine is presented in the Ukrainian statistical forms in tons of coal-equivalent. To convert these data into TJ, conversion factor 29.309 (1000 t c.e/TJ) is used.

Table 2 presents IPCC [1] carbon (C) emission estimation factors for fuels combusted in the cement sector of Ukraine in 2001. The next stage is to make corrections for unoxidised carbon. Results of this operation are multiplied by the factor 44/12 to convert GHG emissions into CO_2-equivalent.

Table 2. Carbon emission estimation factors

Fuel	Factors	
	Carbon emissions from fuel combustion, t C/TJ	Correction for unoxidised carbon
Natural gas	14.96	0.995
Coal	26.2	0.98
Coke	29.5	0.98

Table 3 presents IPCC [1] methane and nitrous oxide emission estimation factors for fuel combusted to ensure high-temperature calcination in the cement sector of Ukraine in 2001. To estimate methane (CH_4) and nitrous oxide (N_2O) emissions, the amount of combusted fuel in TJ should be multiplied by the relevant factors presented in Table 3.

Table 3. Methane and nitrous oxide emission estimation factors

Fuel	GHG estimation factor, kg/TJ	
	Methane (CH_4)	nitrous oxide (N_2O)
Natural gas	5	0.1
Coal	10	1.4
Coke	10	1.4

Methane and nitrous oxide emissions (kg/TJ) were converted into CO_2-equivalent (Gg) using factors 21×10^{-6} and 310×10^{-6}, respectively.

4. Instruction for filling the worksheets on the GHG inventory in the cement sector of Ukraine

4.1. CO_2 emissions from calcination process

Annex 1 contains two linked Excel worksheets to calculate CO_2 emitted from the calcination process. Worksheet A.1.1 provides an overview of cement production and CO_2 emissions by the 12 administrative units and 23 cement types, and worksheet A.1.1.1 provides more detail on the clinker and CO_2 content for each of the administrative units and cement types.

The 'A' columns of Worksheet A.1.1., "Inventory of CO_2 emissions in the cement production sector of Ukraine from the technological processes of calcination," are used to enter the information on the production of 23 different cement types (tonnes) by the 12 administrative units. The quantities of CO_2 emissions (tonnes) appear automatically in the 'B' columns. The data in the 'B' columns are automatically converted into CO_2, emissions (Gg) as shown in the 'C' columns. The last column, "D," of Worksheet A.1.1 contains the sum of CO_2 emissions in Gg by administrative unit, and the last cell of this column (BS23[8]) contains the total quantity of CO_2 emissions from the calcination process in the Ukraine's cement production sector.

The data from the 'A' columns of Worksheet A.1.1 are automatically transferred to the 'A' columns of Worksheet A.1.1.1, "Additional sheet for calculation of CO2 emission from technological processes of calcination in the cement industry of Ukraine". The 'B' columns of Worksheet A.1.1.1 contain information on the clinker fraction in each cement type based on the highest values. The 'C' columns contain the amount of clinker (tonnes) for each cement type, which is estimated as the product of the data in columns "A" and "B." Column "D" contains the highest CO_2 emission factor (tonnes of CO_2/t clinker) for each cement type from Table 1 that includes the CKD correction factor. The statistics of Ukraine do not provide information on the lost CKD, which is why the ratio suggested by the IPCC in [2] – 1.05 was used by default. Column "E" contains CO_2 emissions (tonnes), which are estimated as the product of data in columns "C" and "D'. Column "F" contains the quantities of CO_2 emissions from the calcination process in Gg as a result of multiplying the data from columns "E" by 10^{-3}.

[8] The number of cell (BS23) in Excel worksheet.

Estimates of CO_2 emissions based on the lowest clinker content in the cement and CaO content in clinker can be obtained by copying these spreadsheets and replacing these by the lower values shown in Table 1.

4.2. GHG emissions from fuel combustion for providing high-temperature conditions of calcination

4.2.1. CO_2 emissions from fuel combustion for providing high-temperature conditions of calcination

Annex II, "Inventory of GHG emissions from fuel combustion for providing high-temperature conditions of calcination in cement production sector of Ukraine," contains three spreadsheets to calculate emissions of CO_2, CH_4, and N_2O from fuel combusted to provide the high temperatures needed for the calcination process. The spreadsheets are in accord with the Revised 1996 IPCC Guidelines for national Greenhouse Gas Inventories [1] and all emissions are expressed in CO_2 equivalent.

The calculations of emissions begins with CO_2 in Worksheet A.2.1., "Inventory of CO_2 emissions from fuel combustion in cement production sector of Ukraine". The calculation of CO_2 emissions associated with fuel combustion is made in 6 steps with the entry of fuel combustion by fuel type in Step 1, and the emissions are subsequently calculated automatically in the following five steps.

Specifically, the six steps for calculating CO_2 emissions in spreadsheet A.2.1 are:

Step 1. Fuel combustion by fuel types.

Column "A" (Spreadsheet A.2.1, Appendix 2) contains the total amount of fuel in thousand t.c.e., which is entered by the user.

Step 2. Convert to common energy units (TJ)

Enter the conversion factor common for each fuel (29.309 TJ/thousand t.c.e.) into column "B" to convert fuel combustion in tetra-joules (TJ); enter the results into column "C".

Step 3. Multiply by carbon emission factor

The carbon emission factors for each fuel presented in Table 2 are entered into column "D." Fuel combustion in TJ (column "C") is multiplied by the carbon emission factor (column "D") to obtain carbon content in tons, which is entered in column "E". The carbon content in tons is multiplied by 10^{-3} to give gigagrams (Gg), which is than entered in column "F".

Step 4. Calculate carbon stored

No carbon is stored during fuel combustion, so no calculations are performed, and information from column "F" is transferred to column "I". Step 4 is preserved in order to comply with the requirements of IPCC Guidelines for format of the worksheets.

Step 5. Correction for carbon unoxidised

The fraction of unoxidised carbon from Table 2 for each fuel is entered in column "J" of Worksheet 2-1, which is multiplied by net carbon emissions (column "I") and the result is entered in column "K" – "Actual carbon emissions". The remainder is emitted as soot.

Step 6. Converting to CO_2 emissions

The actual carbon emissions from column 'K" are multiplied by 44/12 and the result is entered into column "L" – "Actual CO_2 emissions". The sum of CO_2 emissions from all fuels is the total emissions of CO_2.

4.2.2. Methane and nitrous oxide emissions from fuel combustion for providing high-temperature conditions of calcination

The calculations of methane and nitrous oxide emissions use the corresponding Worksheets A.2.2., "Inventory of CH_4 emissions from fuel combustion in the cement production sector of Ukraine," and A.2.3., "Inventory of N_2O emissions from fuel combustion in the cement production sector of Ukraine." The calculation of the emissions of these two GHGs is performed automatically by the Excel spreadsheets.

The four steps for calculating emissions of CH_4 and N_2O are:

Step 1. Estimate combustion for each fuel

Data on consumption of each fuel (in TJ) in the cement production sector of Ukraine is entered automatically into the appropriate sections of columns "A" of Worksheets A.2.2 and A.2.3 from A.2.1.

Step 2. Estimate methane and nitrous oxide emissions ratios for each fuel

The GHG emission factors (in kg/TJ) shown in Table 3 for each gas (CH_4 and N_2O) are then entered into columns "B" of Worksheets A.2.2and A.2.3.

Step 3. Calculation of methane and nitrous oxide emissions

In both Worksheets (A.2.2. and A.2.3.) the fuel combustion data (TJ) is multiplied by the GHG emissions factors and the results are entered in columns "C" (kg methane in Worksheet A.2.2. and kg nitrous oxide in Worksheet A.2.3.). The total emissions of CH_4 and N_2O in Gg (columns "D") are calculated by multiplying columns "C" by 10^{-6}.

The sum of emissions for each gas by fuel provides the total emissions of each gas from fuel combustion in the cement production sector in Ukraine.

Step 4. Convert each gas emissions to CO_2 equivalent.

The 'E' columns of Worksheets A.2.2. and A.2.3. contain conversion factors for each gas for calculating the equivalent in CO_2 emissions, Gg – for methane this factor is 21 and for nitrous oxide this factor is 310. Emissions of each gas from columns "D" are multiplied by the factors and the products are entered into column "F".

The sum of emissions in column "L" of Worksheet A.2.1 and columns "F" of Worksheets A.2.2 and A.2.3 is the total GHG emissions in CO_2 equivalent (Gg) from fuel combustion in Ukraine's cement production sector.

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