

**Technical Support Document for the
Miscellaneous Uses of Carbonate Sector:
Proposed Rule for Mandatory Reporting of
Greenhouse Gases**

Office of Air and Radiation

U.S. Environmental Protection Agency

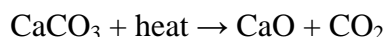
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1. Industry Description

As described in the *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006* (EPA 2008), limestone (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy, glass manufacture, and environmental pollution control. Large deposits of limestone of varying sizes and degrees of purity occur in nearly every state in the United States, and significant quantities are extracted for industrial applications. The five leading limestone and dolomite producing states are (in descending order of tonnage) Texas, Florida, Missouri, Pennsylvania, and Oklahoma (USGS 2007). For some of these applications, limestone undergoes a calcination process in which the limestone is sufficiently heated, generating CO_2 as a by-product. For example, the calcination of pure limestone is as follows:



There are a variety of emissive and non-emissive uses of limestone. Examples of such emissive applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization systems for utility and industrial plants, and as a raw material in the production of mineral wool or magnesium. The manufacture of cement, lime, and glass also result in process emissions; these applications are elaborated upon elsewhere since they are relatively significant emitters. Non-emissive applications include limestone used in poultry grit, as asphalt filler, and in the manufacturing of paper. The most common applications of limestone are use as a construction aggregate (78% of specified national consumption in 2006), the chemical and metallurgy industries (18%), agricultural uses (2%) and other specialized applications (1%) (USGS 2007). The breakdown of reported specified dolomite national consumption was similar to that of limestone; 87% of consumption was used as a construction aggregate, 9% was used in chemical and metallurgical applications, and 3% was used for agricultural use (USGS 2007).

2. Total Emissions

As estimated in the *U.S. Inventory* (EPA 2008), national process emissions from other limestone and dolomite uses (i.e. excluding cement, lime, and glass manufacturing) were 7,868,068 metric tons (mt) of CO₂ in 2006. These emissions increased 13% over the previous year and have increased 48% since 1990. The *U.S. Inventory* does not specify stationary combustion emissions for this source. Major emissive applications are presented in Table 1.

Table 1. Breakdown of 2006 CO₂ Process Emissions by Application

Application	Emissions (metric tons CO₂)	Percent of Total
Flux Stone	5,072,122	64%
Sulfur Oxide Removal	2,060,545	26%
Other Miscellaneous Uses	735,401	9%
TOTAL	7,868,068	100%

Source: U.S. EPA (2008) *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006*

Facility-level information on other limestone uses is not estimated here, due to the difficulty in obtaining this information from a wide variety of emissive applications and the myriad associated facilities. **Consequently, we have not estimated either process or stationary combustion emissions at the facility level, or conducted the subsequent threshold analysis.**

3. Review of Existing Programs and Methodologies

Protocols and guidance review for this analysis include the *2006 IPCC Guidelines, U.S. Inventory*, the Technical Guidelines for the Voluntary Reporting of Greenhouses Gases (1605(b)) Program, and the Australian National Greenhouse Gas Reporting Program. These methodologies are all based upon the IPCC methodology of measuring the consumption of carbonate inputs, but differ in their use of default values. These values are based on differing assumptions of the carbonate weight fraction in process inputs; for example, the IPCC Tier 1 and 2 assume that carbonate inputs are 95% pure (i.e., 95% of the mass consumed is carbonate), whereas the Australian Program assumes a default purity of 90% for limestone, 95% for dolomite, and 100% for magnesium carbonate (Australian DCC 2007, IPCC 2006).

3.1 2006 IPCC Guidelines for National Greenhouse Gas Inventories

The IPCC considers three tiers of consumption-based methodologies that differ in their assumptions of the types of carbonates consumed. Specifically, the Tier 1 and 2 methods assume that only limestone and dolomite are used as carbonate inputs. In addition, the Tier 1 method assumes a default limestone versus dolomite consumption fraction. The Tier 1 equation is as follows:

$$E_{CO_2} = M_c \cdot (0.85 EF_{LS} + 0.15 EF_D)$$

Where:

E_{CO_2} = process emissions of CO₂ (metric tons)

M_c = mass of carbonate consumed (metric tons)

EF_{LS} = emission factor for limestone (metric tons CO₂ / metric tons limestone)

EF_D = emission factor for dolomite (metric tons CO₂ / metric tons dolomite)

The Tier 2 method is the same as the Tier 1 method, except that the fraction of limestone versus dolomite consumed is not a default value. The calculation is as follows:

$$E_{CO_2} = (M_{LS} \cdot EF_{LS}) + (M_D \cdot EF_D)$$

Where:

E_{CO_2} = process emissions of CO₂ (metric tons)

M_{LS} = mass of limestone consumed (metric tons)

EF_{LS} = emission factor for limestone (metric tons CO₂ / metric tons limestone)

M_D = mass of dolomite consumed (metric tons)

EF_D = emission factor for dolomite (metric tons CO₂ / metric tons dolomite)

IPCC also considers a Tier 3 method, which does not assume the specific type(s) of carbonate input. This approach requires facilities to conduct a chemical analysis to determine the weight fraction of carbonates in their inputs, and then apply this information to the product of the stoichiometric emission factors and the fraction of calcination achieved. In other words:

$$E_{CO_2} = \sum_i (M_i \cdot EF_i \cdot F_i)$$

Where:

E_{CO_2} = process emissions of CO₂ (metric tons)

M_i = mass of carbonate *i* consumed (metric tons)

EF_i = emission factor for carbonate *i* (metric tons CO₂ / metric tons carbonate)

F_i = fraction of calcination achieved for carbonate *i*, fraction

Emission factors for common carbonates are presented in

Table 2.

Table 2. CO₂ Emission Factors for Common Carbonates

Mineral Name - Carbonate	CO₂ Emission Factor (tons CO₂/ton carbonate)
Calcite/aragonite - CaCO ₃	0.43971
Magnesite - MgCO ₃	0.52197
Dolomite - CaMg(CO ₃) ₂	0.47732
Siderite - FeCO ₃	0.37987
Ankerite - Ca(Fe,Mg,Mn)(CO ₃) ₂	0.40822-0.47572
Rhodochrosite - MnCO ₃	0.38286
Sodium Carbonate/Soda Ash - Na ₂ CO ₃	0.41492

Source: IPCC (2006) *2006 IPCC Guidelines for National Greenhouse Gas Inventories*

3.2 Australian Government's National Greenhouse and Energy Reporting System

The Australian Government's National Greenhouse and Energy Reporting System require reporting of CO₂ emissions from other uses of carbonates. Registration and reporting under this system is required for corporations if: they control facilities that emit at least 25,000 metric tons of CO₂ equivalent (CO₂e) or produce or consume at least 100 terajoules of energy; or their corporate group emits at least 125,000 metric tons CO₂e, or it produces or consumes at least 500 terajoules of energy (Australian DCC 2007). The higher-order method used for estimating emissions from other limestone uses is the IPCC Tier 3 method, albeit with emission factors in three significant figures instead of five as used by the IPCC.

4. Options for Reporting Threshold

Thresholds of 1,000, 10,000, 25,000, and 100,000 metric tons of CO₂ were considered, as well as inclusion of all facilities (i.e., 100% of facilities).

Despite the relatively small amount of CO₂ emissions generated by other applications of limestone (less than 3% of total national process emissions from industrial processes¹), a threshold is considered feasible because of the straightforward associated emissions estimation methodology. This methodology, which is based on measuring the consumption of carbonate inputs, is simple, widely accepted among existing protocols, and is relatively certain since it is based upon stoichiometry. The 25,000 metric ton threshold was chosen to reduce the compliance burden on small businesses, which are likely not consuming these carbonates (and thus emitting CO₂) in quantities large enough to justify the cost of compliance. In addition, the multiple emissive and non-emissive uses of these carbonates may create confusion over which facilities are required to report. Because of the wide variety of emissive applications, a facility-specific threshold analysis of emissions has not yet been conducted.

¹ As estimated in the *U.S. Inventory* (EPA 2008), total 2006 process emissions from industrial processes were 320.9 Tg CO₂ equivalent; process emissions from other limestone uses were 7.87 Tg CO₂ equivalent.

5. Options for Monitoring Methods

As previously stated, existing methodologies for estimating emissions from other limestone and dolomite uses are generally simple, easy to implement, and coalesce around the IPCC guidelines, but differ in their assumption of carbonate input types. Specifically, Tier 1 and 2 assume only limestone and dolomite are used as inputs and are 95% pure. A Tier 3 methodology requires facility specific information. Application of this methodology requires facilities to conduct a chemical analysis to determine the weight fraction of carbonates in their raw materials, a relatively simple additional requirement. The uncertainty involved in using the more exact Tier 3 methodology is 1-3 % (IPCC 2006). IPCC does not provide the uncertainty associated with using a Tier 1 or 2 methodology for estimating emissions from other limestone and dolomite uses, but does estimate that the uncertainty is as high as 60% for other mineral applications (e.g., glass manufacture) that require similar assumptions in input purity.

The discussion below outlines the specific monitoring methods considered for this technical support document: a simplified emission calculation (Option 1), a facility specific calculation (Option 2), and direct measurement (Option 3). All of these options require annual reporting and require each facility to internally develop the methodology and monitoring plan for calculating emissions from other limestone and dolomite uses. For reporting options for stationary combustion emissions (CO₂, N₂O, and CH₄), refer to EPA-HQ-OAR-2008-0508-004.

5.1 Option 1: Simplified Calculation Method

Option 1 follows the IPCC's Tier 1 protocol. The Tier 1 monitoring method uses default values for both the emission factors and the relative consumption of limestone and dolomite, as previously detailed in section 3.1.

5.2 Option 2: Facility Specific Calculation

This option is similar to the IPCC Tier 3 method. In order to successfully implement this methodology, a reporting facility will need to know the mass of each carbonate consumed. It is assumed that a facility will need to send samples of each carbonate consumed to an off-site laboratory for a chemical analysis of the carbonate weight fraction. Emission factors are based on stoichiometry and are presented in

Table 2. The methodology for calculating the fraction of calcination achieved can be determined based on sampling and analysis conducted by a certified laboratory using a suitable method such as an x-ray fluorescence test or other enhanced testing method published by a consensus standards organization (e.g., ASTM, ASME, API). The more detailed (i.e., Tier 3) methodology has a relatively low uncertainty and a minimal additional reporting burden compared to other methods.

The Tier 3 monitoring method involves the aforementioned facility-level calculation and sampling on an annual basis, at minimum. This method involves the following steps:

- Facility managers review samples of the carbonate input annually.
- Each facility sends samples of their inputs to an off-site laboratory, in order to conduct an analysis of the carbonate weight fraction. A facility is assumed to need to analyze, at most, seven types of input, one for each of the common carbonates listed in

Table 2.

5.3 Option 3: Direct measurement

In facilities where process emissions and/or combustion GHG emissions are contained within a stack or vent, direct measurement constitutes either measurements of the individual GHG concentration in the stack gas and the flow rate of the stack gas using a Continuous Emissions Monitoring System (CEMS), or periodic measurement of the individual GHG concentration in the stack gas and the flow rate of the stack gas using periodic stack testing. Under either a CEMS approach or a stack testing approach, the emissions measurement data would be reported annually. Given the diverse set of industries that use carbonates, it is not possible to assume clearly whether both process and combustion related CO₂ emissions would be emitted through a single stack.

Elements of a CEMS include a platform and sample probe within the stack to withdraw a sample of the stack gas, an analyzer to measure the concentration of each GHG pollutant (e.g., CO₂) in the stack gas, and a flow meter within the stack to measure the flow rate of the stack gas. The emissions are calculated from the concentration of the specific GHG pollutant in the stack gas that is monitored using the concentration monitor for that pollutant and the flow rate of the stack gas. The CEMS continuously withdraws and analyzes a sample of the stack gas and continuously measures each of the individual GHG pollutant concentration and flow rate of the stack gas.

For direct measurement using stack testing, sampling equipment would be periodically brought to the site and installed temporarily in the stack to withdraw a sample of the stack gas and measure the flow rate of the stack gas. Similar to CEMS, for stack testing the emissions are calculated from the concentration of GHGs in the stack gas and the flow rate of the stack gas. The difference between stack testing and continuous monitoring is that the CEMS data provide a continuous measurement of the emissions while a stack test provides a periodic measurement of the emissions. Stack testing could also capture both process and combustion related CO₂ emissions.

6. Options for Estimating Missing Data

Options and considerations for missing data vary will vary depending on the proposed monitoring method. Each option would require a complete record of all measured parameters as well as parameters determined from company records that are used in the GHG emissions calculations (e.g., carbonate consumption).

In the occasion that a facility lacks carbonate input data for a certain time period, that facility would apply their typical mix of carbonates consumed by mass during times of known data to the period of missing data. However, the likelihood for missing data is low, as businesses closely track their purchase of production inputs.

For Option 2, if the results of the chemical analysis on the calcination fraction of carbonates consumed were lost or missing, the analysis would have to be repeated. For units using direct measurement to measure CO₂ emissions, the equipment would be tested for accuracy and calibrated as necessary by a certified third party vendor. These procedures would be consistent in stringency and data reporting and documentation adequacy with the quality assurance procedures for CEMS described in Part 75 of the Acid Rain Program.

7. QA/QC Requirements

Facilities would conduct quality assurance and quality control (QA/QC) of the production and consumption data, and emission estimates reported. Specific QA/QC requirements will vary depending on the monitoring methods, but facilities would prepare an in-depth QA/QC plan which would include checks on production data (quantities of carbonates consumed, by type), the calcination fraction information received from the lab analysis, and calculations performed to estimate GHG emissions.

In order to ensure accurate emissions estimates, a facility could compare emissions estimates using the proposed (i.e., Tier 3) methodology to the IPCC Tier 1 and 2 approaches. The facility could also track its carbonate consumption and emissions over time.

8. Types of Emissions Information to be Reported

To ensure completeness, facility owners or operators would report annual GHG emissions from other carbonate uses, including both combustion-related (CO₂, CH₄, and N₂O) emissions and process-related CO₂ emissions. For reporting options for stationary combustion refer to EPA-HQ-OAR-2008-0508-004.

Along with their formal report, facilities would submit carbonate consumption data (in metric tons, by carbonate), the fraction of calcination achieved (for each carbonate), and the average annual mass fraction of carbonate-based mineral in carbonate-based raw material by carbonate type (i.e., the average annual quantity of carbonate (CO₃) in the raw material either based on stoichiometric analysis or measurement).

9. References

Australian DCC (2007). *National Greenhouse and Energy Reporting System: Technical Guidelines for the Estimation of Greenhouse Emissions and Energy at Facility Level*.

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