Determination of carbonate content-as carbon dioxide-in coal using a new pressure method with temperature compensation

Dimitrios Sotiropoulos [1], Vasilios Koulos [2], Ioannis Katsoyiannis [3]

(1) Public Power Corporation, Kozani Greece, (2) BD Inventions P.C, Thessaloniki, Greece,

(3) Assistant professor, Aristotle University of Thessaloniki, Department of Chemistry

ABSTRACT

The determination of carbonate content, as carbon dioxide, in coal and lignite is achieved by a new technique using the FOGL Digital Soil Calcimeter / BD Inventions. This technology is innovative and complies with EN ISO 10693:2013, ASTM D4373-02(2007), ASTM D1756-02(2007) and Soil Science Society of American standard test methods for calcium carbonate content in soils and sediments. The Carbon Dioxide analysis is based on a pressure method that utilizes the FOGL Digital Soil Calcimeter, which is a bench-top apparatus. The Carbon Dioxide determined by treating a 1.000 g (+/- 0.001 g) dried sample specimens with 1-3N hydrochloric acid (HCL) reagent grade, in an enclosed reaction vessel. Carbon Dioxide gas evolved during the reaction between the acid and carbonate fraction of the specimen, was measured by the resulting pressure generated, taking into account the temperature conditions during the reaction. The results of the FOGL experiment were compared with those obtained from the TGA Thermogravimetric Analysis.

CONTACT

Vasilios Koulos

BD Inventions P.C, Thessaloniki, Greece

Email:

vasilios.koulos@bd-inventions.com

Phone:

+30231 2207188

Website:

www.bd-inventions.com

INTRODUCTION

The quick method used for carbonates determination in lignites with high CO_2 content involves a thermogravi-metric analysis which in most cases fails, due to the sulfur content and carbonate types contained in lignite. An alternative new technique was applied based on a pressure method that utilizes the FOGL Digital Soil Calcimeter (BD Inventions), which is a bench-top apparatus that gives more consistent and rapid results.

METHODS AND MATERIALS

A quick method for carbonates determination in lignites and coals in general is a two-step thermogravi-metric analysis (after moisture removal) involving the combustion (in oxygen atmosphere) of samples at 510 ^oC and then the heating of the remainder at 815 ^oC. In the first step all volatile and combustible constituents are removed from the sample, while in the second step the carbonates are decomposed, freeing the containing CO_2. This method cannot be a standard method, as the carbonates' type has a great impact on the final result.

For the determination of carbonate content (as carbon dioxide) in coal and lignite a new technique was applied using the FOGL Digital Soil Calcimeter/BD Inventions. This technology is innovative and complies with EN ISO 10693:2013, ASTM D4373-02(2007), ASTM D1756-02(2007) and Soil Science Society of American standard test methods for calcium carbonate content in soils and sediments. The Carbon Dioxide analysis is based on a pressure method that utilizes the FOGL Digital Soil Calcimeter, which is a bench-top apparatus. The Carbon Dioxide determined by treating a 1.000 g (± 0.001 g) dried sample specimens with 1-3N hydrochloric acid (HCL) reagent grade, in an enclosed reaction vessel. Carbon Dioxide gas evolved during the reaction between the acid and carbonate fraction of the specimen, was measured by the resulting pressure generated, taking into account the temperature conditions during the reaction. The results of the FOGL experiment were compared with those obtained from the TGA Thermogravimetric Analysis.

RESULTS

Two different tests conducted to compare the results of the above mentioned methods:

1. A series of $MgCO_3$ and $CaCO_3$ mixtures (reagent grade),
2. A series of lignite samples

1. $MgCO_3$ - $CaCO_3$ mixtures

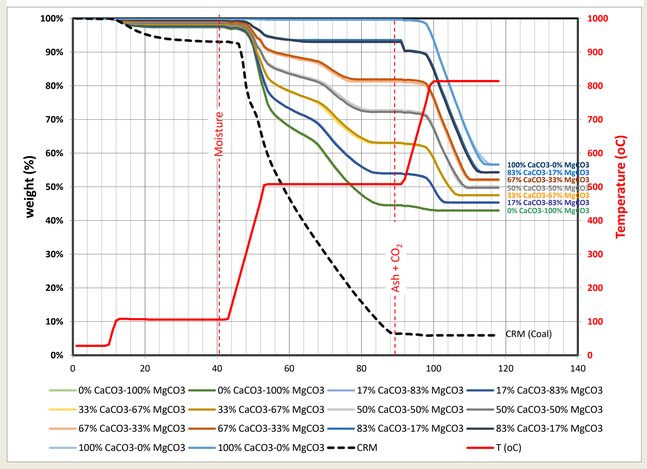

Chart 1. Weight loss of mixtures by TGA

As found in the thermogravimetric analysis the final result depends on $MgCO_3$ and $CaCO_3$ ratio, due to different temperature of decompo-sition of carbonates. As seen in the Chart 1, the TGA method behaves properly only in case that the carbonates are of calcite or aragonite type (pure $CaCO_3$). This is because the $MgCO_3$ decomposes prior or during the first step (510 ^oC), which leads to a false CO_2 calculation (Table 1).

Table 1. CO_2 content results by TGA and FOGL

Percent of $CaCO_3$ in mixture	Theoretical CO_2 content	TGA CO_2 result	FOGL CO_2 result
	%	%	%
0,0%	37,45	1,59	37,7
16,7%	38,50	8,86	38,7
33,3%	39,55	15,78	39,2
50,0%	40,60	22,90	40,5
66,7%	41,65	29,80	41,1
83,3%	42,70	39,10	41,0
100,0%	43,75	43,08	41,8

2. Lignite samples

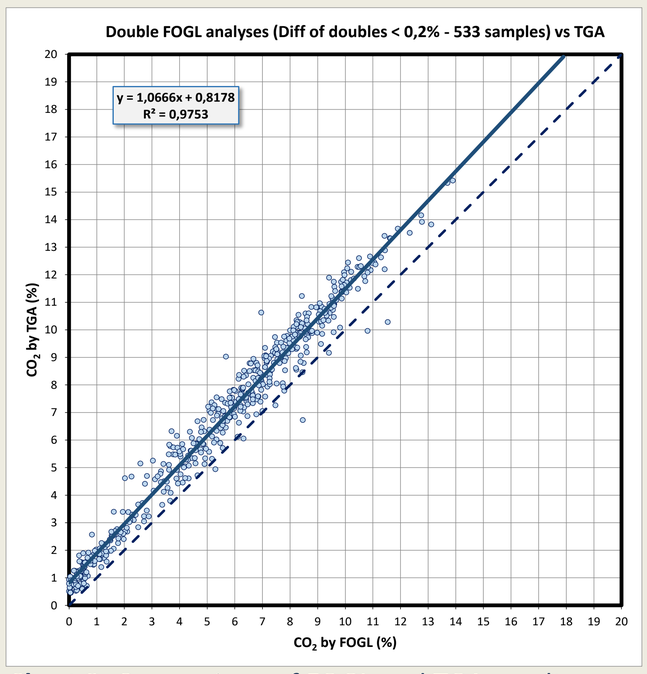

Chart 2. Comparison of FOGL and TGA results

More than 500 lignite samples were analyzed with FOGL Digital Soil Calcimeter in duplicates and their results compared to the respective ones conducted by TGA analyzers.
Surprisingly, although consistent with each other, the results provided by TGA were systematically higher than the ones obtained with the FOGL by 1%-2%, with difference increasing by the real carbonate content (Chart 2).

DISCUSSION

According to A. Khan et al[(1)] the $MgCO_3$ decomposes at 440 to 460 ^oC in an endothermic reaction, leading to respective CO_2 loss before the second step of heating. On the other hand, if the sulfur contained in lignite is in the form of ferrous sulfate (mainly from oxidized pyrites at the 1st step) its decomposition starts at 550 ^oC and increases rapidly at 600 ^oC[(2)], expelling SO_2 which is accounted as CO_2 by the TGA method. It is noted that the sulfur content of lignite is 1%-2% in dry basis.
By using the alternative method of FOGL Digital Soil Calcimeter, the CO_2 content result does not depend on type of carbonates nor on other lignite constituents as sulfur, thus preserving more consistent and accurate results.

CONCLUSIONS

The determination of CO_2 content in lignites and coals performed by thermogravimetric analysis exhibits error coming from their sulfur type and content as well as the type of carbonates. The alternative method of FOGL Digital Soil Calcimeter (from BD Inventions) not only confronts these issues but also complies with EN ISO and ASTM standards, giving more consistent and accurate results, making it ideal not only for soil samples but also for lignite and coal samples, especially with CO_2 content higher than 1%

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