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PHASE ANALYSIS OF HIGH-CALCIUM LIME BY TG

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Abstract

A thermogravimetric method has been developed and is suggested for both the qualitative and quantitative phase analyses of high-calcium lime and calcium speciation as well. Two complementary TG measurements are proved to be satisfactory for the determination of moisture, calcium oxide, calcium hydroxide and calcium carbonate contents as well as total mineral impurities in high-calcium limes: quicklime, hydrated lime and limestone.

Keywords: (high-calcium) lime, phase analysis, speciation analysis, TG

Introduction

Limestone is a general term denoting both carbonate rocks and fossils. It is composed mostly of calcium carbonate (high-calcium limestone) or is a combination of calcium and magnesium carbonates (dolomitic limestone, dolomite) with varying amounts of impurities. Lime (quicklime) is a calcinated form of limestone. Hydrated (slaked) lime is created from it upon addition of water. The term of ‘lime’ is understood to represent both quicklime and hydrated lime. The lime may be high-calcium or dolomitic type, dependently on the type of raw limestone. The high-calcium systems are only considered in this paper.

Contrary to calcium carbonate which is among the most chemically stable compounds, calcium oxide and calcium hydroxide are not stable under atmospheric air – they are hygroscopic and react with moisture and/or carbon dioxide. This is the main reason why a quicklime is usually a mixture of the three compounds mentioned above, and a hydrated lime contains calcium carbonate. Also, quicklime and hydrated lime may change their phase compositions during storage and handling. Being derived from natural limestone, they may also contain mineral, usually ‘non-calcium’ impurities, mostly silica and alumina and also magnesium compounds from the dolomitic impurities of limestone [1].

The use of limestone, quicklime or hydrated lime in chemical syntheses (as a raw material or catalyst) calls for the high-grade specifications for these materials. This requirement refers in most cases to the low level of impurities, in particular no magnesium compounds and/or some specific phase composition of lime.

A number of test procedures and analytical methods for limes and limestone composition analysis have been described [1, 2]. Most of them, however, are highly

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labour- and time-consuming standard methods and do not provide information on the phase composition and hence make speciation of calcium impossible.

In the present paper a quick thermogravimetric method for the qualitative and quantitative phase analysis of high-calcium limes, enabling the principal components, namely calcium oxide, calcium hydroxide and calcium carbonate, as well as moisture and total mineral impurities (X_m) to be determined at a time, has been developed and is proposed.

The principle of the method

The determination is based on the findings in two complementary TG measurements: for the lime 'as-delivered' and after its slaking and then drying. The first TG measurement provides data for the determination of water (moisture), calcium hydroxide and calcium carbonate contents as well as the total content of free calcium oxide and mineral impurities. The thermogravimetric analysis of lime after its slaking and then drying is employed to determine the mass fraction of mineral impurities in the calcination product. This makes it possible to split the total content of free calcium oxide and mineral impurities as found in the first measurement into the individual contents for these two components.

After its slaking followed by drying, lime being, in general, a quasi-five-component system is converted to a quasi-four-component one which contains: water (moisture), calcium hydroxide, calcium carbonate and mineral impurities, and which virtually contains no calcium oxide. The chemical and phase compositions of the products obtained from complete calcination of both lime samples considered (i.e. 'as-delivered' and after slaking) are always identical (the same) as regards their quality and quantity ($CaO+X_m$), irrespective of the $Ca(OH)_2/CaCO_3$ ratio obtained in the slaked and dried lime under question. The calcination product contains always the total amount of calcium as CaO and mineral impurities, X_m.

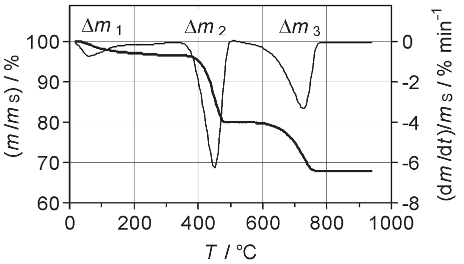

Fig. 1 TG and DTG curves of a high-calcium lime after its slaking and then drying

The water (moisture), calcium hydroxide and calcium carbonate contents are determined on the basis of the mass loss steps (Fig. 1) and stoichiometry of the corresponding thermal decomposition reactions of calcium compounds:

$-\Delta m_1$: $H_2O_{(l)} \longrightarrow H_2O_{(g)}$

$-\Delta m_2$: $Ca(OH)_2 \longrightarrow CaO+H_2O$

$-\Delta m_3$: $CaCO_3 \longrightarrow CaO+CO_2$

The total content of free calcium oxide and mineral impurities ($CaO+X_m$) in the ‘as-delivered’ lime is found as the difference between the calcination product content and calcium oxide generated in the thermal decomposition processes of calcium hydroxide and calcium carbonate. For the slaked lime, this difference represents the mineral impurities content only.

Experimental

Materials studied

- Calcium oxide, p.a., from Loba Feinchemie, AG,
- Hydrated lime, as per Polish Standard PN-90/B-30020, from Zakłady Wapiennicze at Trzuskawica, Poland.

The chemically pure calcium oxide from Loba (powder) was taken for the analysis right after opening the original plastic container while hydrated lime was collected from the central section of a paper bag right after it was opened.

Thermogravimetric analysis

The TG measurements were carried out by using the Mettler TG-50 thermobalance operated in the TA-4000 Thermal Analysis System. About 20 mg sample was subjected to heating in the dynamic air from ambient temperature to 950°C, at the heating rate of $\beta=24°C\ min^{-1}$. The quantitative interpretation of TG curves involved the use of the blank correction.

Lime slaking

5–10 ml of distilled water were added to about 1–2 g of the lime studied and then mixed till the homogeneous (visually) suspension was obtained. After a few minutes, the product was placed in a drier, at ~100°C, and dried (about 15 min) to give a solid. The sample was then averaged in a mortar.

Results

The materials studied here were selected to form an example, in particular for the purpose of illustrating the thermogravimetric method discussed for the quantitative phase analysis of quicklime and hydrated lime. The magnesium content was determined for both the materials studied (with AAS method, after they have been dissolved in hydrochloric acid). The hydrated lime was found to contain ~0.33% Mg while the investigated calcium oxide contained less than 0.01% Mg. Hence, these substances may be regarded high-calcium lime materials.

The findings from the quantitative phase analyses for both the materials studied have been presented in columns 2 and 4 of Table 1, respectively. Columns 3 and 5 of this Table provide the results from the quantitative speciation of calcium for the materials studied.

Table 1 Results of phase analysis of and speciation of calcium in the limes studied

Component	CaO, p.a., Loba		Hydrated lime, Trzuskawica	
	Component content	Calculated Ca content	Component content	Calculated Ca content
	% (m/m)			
Moisture	0.40	0	1.39	0
$Ca(OH)_2$	8.55	4.62	80.08	43.29
$CaCO_3$	4.70	1.88	14.30	5.72
CaO	83.19	59.42	0.45	0.32
Mineral impurities	3.16	0	3.78	0
Total (±SD)	100.00	65.92 (0.29)	100.00	49.33 (0.38)
Titration (±SD)	–	66.07 (0.45)	–	49.58 (0.40)

(±SD) – standard deviation, s_{n-1}, for n=4

The total calcium contents resulting from the speciation analyses of both the materials considered were compared to the calcium contents which were found by the titrimetric determination of the active (available) calcium oxide content ([2], back titration was employed) – last raw in Table 1. Very good conformity was found for the results.

Concluding remarks

The conformity found for total calcium contents resulting from the speciation analyses by TG method in question and by standard titration proves that the discussed thermogravimetric method for phase analysis of high-calcium lime is correct. This rapid method may be especially helpful for quality-control testing of high-calcium lime by producers and consumers alternatively to the standard, e.g. ASTM, methods as many of which are too labour- and time-consuming ones for such purposes.

References

1 R. S. Boynton, ‘Chemistry and Technology of Lime and Limestone’, 2nd ed., Wiley and Sons, Inc., New York 1980.
2 Polish standard PN-76/B-04350.