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USE OF THERMAL ANALYSIS IN THE STUDY OF SODIUM CARBONATE CAUSTICIZATION BY MEANS OF DOLOMITIC LIME

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Abstract

Dolomitic lime samples were treated with sodium carbonate solution and the causticizing process was followed at different temperatures by recording the TG and DTA curves of the solid-phase products that separated after different time intervals. The chemical reactions occurring during causticization are discussed. From the TG curves, apparent kinetic parameters were derived. Some aspects of the kinetic compensation effect are discussed.

Keywords: causticization of sodium carbonate, dolomitic lime, kinetic compensation effect, kinetic parameters of thermal decompositions

Introduction

The causticization of sodium carbonate, i.e. the transformation of Na_2CO_3 into NaOH, is generally performed by using lime:

$$Na_2CO_3+Ca(OH)_2=2NaOH+CaCO_3 \qquad (1)$$

On the other hand, MgO is frequently obtained from calcined dolomite by means of the Pattinson procedure, involving the reaction:

$$Ca(OH)_2+Mg(OH)_2+3CO_2=Mg(HCO_3)_2+CaCO_3+H_2O \qquad (2)$$

This procedure is not advantageous, since it does not utilize the CaO and it needs a large amount of CO_2. This is why a combination of Na_2CO_3 causticization with the Pattinson procedure has been proposed, i.e. the use of dolomitic lime in causticization (e.g. [1]). In this case, the causticization involves two parallel processes:

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a) Hydration of magnesium oxide:

$$MgO+H_2O=Mg(OH)_2 \qquad (3)$$

Reaction (3) occurs in two stages, $Mg(OH)_2$ first being formed in a metastable form as a gel, which is further transformed into the stable, hexagonal crystalline modification [2].

b) Causticization, also occurring in two stages:

$$CaO+H_2O=Ca(OH)_2 \qquad (4)$$

followed by reaction (1). Characterization of the heterogeneous reactions (1), (3) and (4) with respect to both their equilibria and their kinetics is not at all simple, since all these features are greatly influenced by the source of the dolomite and by the working conditions during the production of the dolomitic lime. There are many literature data concerning the rates of hydration of lime and magnesia [2, 3, 6–8], but these tell us nothing with respect to the rates of hydration of miscellaneous dolomitic limes. The rate of hydration of CaO is much higher than that of MgO, but the kinetics of hydration of CaO and of MgO are both influenced by each other and by the presence of impurities [3]. Thus, the rate of hydration of MgO increases in the presence of CaO, but it nevertheless remains much lower than that of pure CaO [6]. Similarly, causticization by means of CaO as a component of dolomitic lime occurs in a different way than with pure CaO. In such systems, an undesired secondary product, pirssonite, $CaCO_3 \cdot Na_2CO_3 \cdot 2H_2O$, may also appear, especially at low temperatures and high lye concentrations [4].

Obviously, the rate of the causticization process must be studied separately for each dolomitic lime. In these studies, thermoanalytical methods may be very useful [5, 6].

In the work reported in the present paper, dolomitic lime samples were treated with Na_2CO_3 solutions and samples of the resulting solid phase were subjected to TG, DTG and DTA.

Experimental

Material

A dolomite from Voslobeni (Romania) was used. Ten samples were subjected to chemical analysis. The composition given in Table 1 represents the mean value of the results. The mean density is 2.82 g cm^{-3}. The dolomite was calcined under industrial conditions in the 'Solvay' soda factory at Ocna Mureş (Romania). Before the experiments, the dolomitic lime was recalcined by maintaining it for 2 h at 1050°C. It was crushed in a mortar and the 0.1–0.25 mm fraction was selected by means of appropriate sieves.

Table 1 Chemical composition of the dolomite Voşlobeni

Component	Content wt%
CaO	33.1
MgO	21.8
SiO_2	1.06
Al_2O_3	0.14
Fe_2O_3	0.16
K_2O	0.04
Na_2O	0.16
SO_3	traces
P_2O_5	traces
mass loss at calcination	43.87

Method

Causticization was performed in a reactor at a controlled temperature, under continuous stirring. The concentration of the aqueous solution of Na_2CO_3 was 205 g l^{-1} and it was used in an excess of 10%. The reaction occurred at constant temperatures of 59, 70 or 84°C. Samples removed after various time intervals were filtered, and the solid was washed rapidly with warm water and with acetone, and dried at 80°C.

Thermal analysis was performed with a MOM Derivatograph. Sample mass: 800 mg. Heating rate: 6 K min^{-1}.

Results and discussion

TG and DTA curves of a sample causticized during 7 min at 59°C are presented in Fig. 1. A small mass loss is observed up to 200°C, this endothermal process presumably consists in the loss of pirssonite crystallization water.

The endothermal decomposition between 240 and 420°C may be assigned to the dehydration reaction

$$Mg(OH)_2=MgO+H_2O \qquad (5)$$

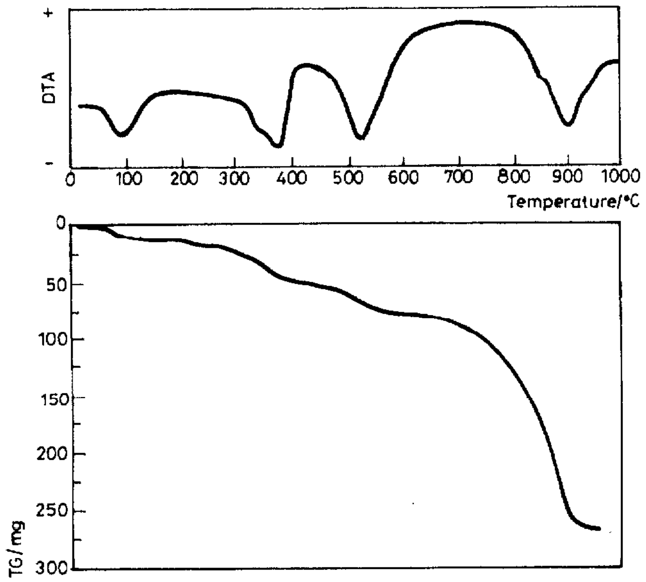

Fig. 1 DTA and TG curves of dolomitic lime causticized during 7 min at 59°C

The DTA curve reveals an inflexion at 330–340°C, which might be due to the transition of the metastable gel into the crystalline modification.

The endothermal decomposition between 420 and 660°C corresponds to the dehydration

$$Ca(OH)_2=CaO+H_2O \tag{6}$$

Reaction (6) begins before reaction (5) [5, 9, 10] and it has been found that, under working conditions similar to ours, only 90% of the $Mg(OH)_2$ is dehydrated up to the cessation of mass loss at about 380–400°C [5].

The last stage of the thermal decomposition, the endothermal process between 660 and 920°C, can be assigned to the pyrolysis process.

$$CaCO_3=CaO+CO_2 \tag{7}$$

The mass losses observed in the various stages of the thermal decomposition allow calculation of the compositions of the samples and the transformation degrees, viz. α_{Mg} of MgO into $Mg(OH)_2$ and α_{Ca} of CaO into pirssonite, $Ca(OH)_2$ and $CaCO_3$, due to the causticizing process. In these calculations , corrections were made to eliminate the errors due to the overlap of reactions (5) and (6). As suggested in the literature [5], 11% of the mass loss observed between 240 and 420°C was added to this mass loss and subtracted from the mass loss between 420 and 660°C. Results are presented in Table 2.

Table 2 Transformation degrees of MgO and of CaO into products during the causticizing process

T/°C	t/min	$Mg(OH)_2$	$Ca(OH)_2$	$CaCO_3$
59	7	0.236	0.174	0.542
59	14	0.278	0.101	0.591
70	7	0.259	0.148	0.568
70	14	0.305	0.096	0.602
84	7	0.281	0.063	0.579
84	14	0.383	0.025	0.631

Inspection of Table 2 shows that reaction (3) progresses in time, i.e. α_{Mg} increases in time and the rate of reaction (3) also increases with increasing temperature. The same feature is observed with reaction (1). In the case of reaction (4), the situation is quite different. The corresponding α_{Ca} value diminishes in time and with increasing temperature. It is easy to understand this behaviour since reaction (3) leads to one of the final products of the causticizing process, but reaction (4) yields only an intermediate and is followed by reaction (1). On the other hand, reaction (4) is very rapid and, at our working temperatures, it occurs practically totally in the first few minutes. Obviously, the causticization is not completed in 14 min, but it proceeds to an important extent even in the first few minutes of the reaction. The formation of pirssonite is not important under these working conditions and the amount of CaO transformed into pirssonite does not exceed 2–3% in our experiments. The corresponding α_{Ca} values are not given in Table 2 since the mass losses cannot be determined accurately and reproducibly.

At any rate, it is obvious that thermal analysis is a suitable method for investigations of the causticization process. The above results are in good agreement with our earlier observations [11].

Kinetic parameters

The portions of the TG curves corresponding to reactions (5)–(7) were used to derive the apparent kinetic parameters, viz. the apparent reaction order n, activation energy E and pre-exponential factor A. For this purpose, our nomogram method [12–14] was used. Results are presented in Tables 3–5.

In these Tables, the position parameter τ means

$$\tau = 10^3 T_{0.1}^{-1}$$

where $T_{0.1}$ is the temperature at which the transformation degree attains α=0.1.

As observed in our earlier papers, the kinetic parameters derived from the TG curves frequently obey a linear kinetic compensation law:

$$\log A = aE+b \tag{8}$$

which is the expression of the isokinetic relation

$$\log A = (RT_i \ln 10)^{-1}E + \log k_i \tag{9}$$

implying the existence of an isokinetic temperature T_i at which the rate constant of all reactions has the same value k_i. This isokinetic temperature has been presumed to be the decomposition temperature [15]. Since the decomposition temperature cannot be defined exactly, we proposed to take $T_{0.1}$ for the decomposition temperature [13]. In this case, according to (9), the compensation parameter a will be equal to

$$a' = (RT_{0.1} \ln 10)^{-1} \tag{10}$$

The analysis of a large number of kinetic parameters showed that, for TG curves corresponding to $T_{0.1}$ values in a narrow temperature interval, a linear compensation law is valid and compensation parameter a derived from the straight line $\log A$, *vs.* E is very near to the a' value calculated via Eq. (10) by using the mean value of $T_{0.1}$. In all these cases, the parameter b of Eq. (8) was found to be near to –3 [16]. These results allowed us to define, as a first approach, a 'theoretical' pre-exponential factor, given by the relation

$$\log A' = (RT_{0.1} \ln 10)^{-1}E - 3 \tag{11}$$

The $\log A'$ values are also indicated in Tables 3–5 and are indeed quite near to the $\log A$ values derived directly from the TG curves.

Analysis of the equations of the TG curves showed that the correlation between $\log A$, E and $T_{0.1}$ is more complicated than expressed by Eq. (11) viz. it may be given [17] as

$$\log A'' = (RT_{0.1} \ln 10)^{-1}E + \log(qET_{0.1}^{-2}) - 1.85 \tag{12}$$

where q is the heating rate expressed in K s^{-1} and E is expressed in J mol^{-1}. The $\log A''$ values are also presented in Tables 3–5; it is obvious that A'' is a much better approximation of A than is A'.

Inspection of Tables 3–5 shows that there is no clear correlation between the working conditions and the kinetic parameters derived. An attempt was made to find a correlation between the nature of the process and the kinetic parameters. Accordingly, mean values were calculated for each reaction (Table 6). Although these mean values are rather different, a reasonable interpretation of them is not possible. Nevertheless, the mean values of $\log A'$, calculated by means of Eq. (11), denoted $\overline{\log A'}$, are very near to the $\log\overline{A'}$ values also calculated by means of Eq. (11), but by using the mean values $\bar{\tau}$ and $\bar{E}$, presented in Table 6, i.e.

$$\overline{\log A'} \approx \log\overline{A'}$$

Similarly, the mean values of $\log A''$, i.e. $\overline{\log A''}$, are very near to the $\log\overline{A''}$ values calculated via Eq. (12) by using the mean values $\bar{\tau}$ and $\bar{E}$ given in Table 6.

Table 3 Kinetic parameters of reaction (5) derived from TG curves

T/°C	t/min	τ	n	E/kJ	lg$A$	lgA'	lgA''
59	7	1.745	0.68	109.8	6.64	7.02	6.70
59	14	1.623	0.76	150.5	9.34	9.78	9.52
70	7	1.698	0.42	118.2	7.15	7.50	7.18
70	14	1.642	0.72	162.1	10.57	10.92	10.71
84	7	1.658	1.01	162.1	10.73	11.06	10.86
84	14	1.600	1.18	215.4	14.73	15.03	14.92

Table 4 Kinetic parameters of reaction (6) derived from TG curves

T/°C	t/min	τ	n	E/kJ	lg$A$	lgA'	lgA''
59	7	1.414	0.51	129.6	6.13	6.58	6.15
59	14	1.418	0.52	158.0	8.32	8.72	8.37
70	7	1.342	1.26	325.8	19.90	19.87	19.79
70	14	1.383	2.24	329.8	20.70	20.86	20.81
84	7	1.443	0.86	152.6	8.14	8.52	8.17
84	14	1.403	1.87	278.8	17.33	17.45	17.34

Table 5 Kinetic parameters of reaction (7) derived from TG curves

T/°C	t/min	τ	n	E/kJ	lg$A$	lgA'	lgA''
59	7	0.969	0.21	142.2	3.47	4.21	3.48
59	14	0.951	0.35	160.5	4.31	4.98	4.30
70	7	0.958	0.17	173.8	5.16	5.71	5.06
70	14	0.951	0.46	170.1	4.76	5.46	4.80
84	7	0.957	0.16	167.2	4.62	5.37	4.70
84	14	0.958	0.25	144.2	3.60	4.23	3.50

Table 6 Mean values of the kinetic parameters

Reaction	$\bar{\tau}$	$\bar{n}$	$\bar{E}$/kJ	$\overline{\log A}$	$\overline{\log A'}$	$\overline{\log A''}$	$\log \overline{A'}$	$\log \overline{A''}$
(5)	1.661	0.79	153.0	9.86	10.22	9.98	10.29	10.07
(6)	1.400	1.21	229.1	13.42	13.67	13.44	13.78	13.58
(7)	0.957	0.27	159.7	4.32	4.99	4.31	4.99	4.31

The validity of the linear relation (8) may be expected separately for reactions (5)–(7). By means of linear regression, the a and b parameters presented in Table 7 were derived. As shown by the correlation coefficient r, the linearity is quite good. The same Table also contains the a' values calculated with Eq. (10). The agreement between the a and a' values is seen to be acceptable. As far as the b values are concerned, they are rather far from –3, i.e. Eq. (11) is a very rough approximation.

Table 7 Compensation parameters for reactions (5)–(7)

Reaction	b	a	a'	r
(5)	–1.986	0.0774	0.0869	0.9982
(6)	–2.896	0.0712	0.0732	0.9991
(7)	–3.519	0.0491	0.0501	0.9920

In order to compare the approximations expressed by Eqs (11) and (12), by means of linear regression the parameters a and b of the relations

$$\log A' = a\log A + b \quad \text{and} \quad \log A'' = a\log A + b \qquad (13)$$

were derived. The results are presented in Table 8, which also contains the correlation coefficient values r. The latter indicate excellent linearity in both cases. As concerns the parameters a and b, it is obvious that the nearer a is to unity and the nearer b is to zero, the better the approximation used. The parameter values given in Table 8 indicate that Eq. (12) is a far better approach than Eq. (11). Consequently, Eq. (12) may be considered the true expression of the 'compensation effect' observed in TG kinetics. Its validity indicates that the compensation effect in TG kinetics is only an apparent effect, which is due to the formal application of the Arrhenius equation in deriving the basic relations.

Table 8 Parameters of the relations (13)

	a	b	r
$\log A'$	0.958	0.795	0.9999
$\log A''$	1.003	0.012	0.9999

References

1 A. Lazăr, A. Kiss and V. Páczai, Romanian Patent, (1968) 53744.
2 G. L. Smithson and N. N. Bakhski, Can. J. Chem. Eng., 47 (1969) 876.
3 W. Bauer, Cement, Lime and Gravel, 23 (1949) 396.
4 C. Calistru and C. Leonte, Bul. Inst. Polit. Iaşi, 7/9 (1961) 117.
5 G. Dave and J. Masood, Zement-Kalk-Gips, 5 (1970) 219.
6 M. Hints and D. Păcurar, Rev. Chim, (Bucharest), 28 (1977) 688.
7 G. Babatschew and M. Kassalowa, Zement-Kalk-Gips, 1 (1969) 312.
8 G. K. Boreskov, V. A. Dzisko and M. S. Borisova, Zh. Fiz. Khim., 27 (1953) 1176.
9 D. F. Richardson, Ind. Eng. Chem., 19 (1926) 389.
10 L. G. Clark and R. S. Sprague, Anal. Chem., 24 (1952) 688.
11 C. Calistru and M. Hints, Rev. Chim. (Bucharest), 30 (1979) 234.
12 J. Zsakó, J. Thermal Anal., 15 (1979) 369.
13 J. Zsakó, M. Várhelyi and Cs. Várhelyi, J. Thermal Anal., 17 (1979) 123.
14 J. Zsakó, G. Marcu and M. Várhelyi, Rev. Roum. Chim., 27 (1982) 815.
15 P. D. Garn, J. Thermal Anal., 7 (1975) 475; 10 (1976) 99.
16 J. Zsakó, J. Thermal Anal., 47 (1996) 1679.
17 J. Zsakó, J. Thermal Anal., in press.