

HEAT OF HYDRATION AS A METHOD FOR DETERMINING THE COMPOSITION OF CALCINED GYPSUM

M. ABDEL MAKSOUUD * and AZIZ ASHOUR

Material Testing Laboratory, Ministry of Public Works and Housing, Riyadh (Saudi Arabia)

(Received 7 January 1981)

ABSTRACT

The heat of hydration of a fresh, locally produced sample of some industrial gypsum (plaster of Paris, $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) was determined. An adiabatic calorimeter was used for this purpose. The obtained heat of hydration was -9 cal g^{-1} , which is higher than that for the hemihydrate (-5 cal g^{-1}). The calculated heat of hydration for calcium sulphate hemihydrate from the known heats of formation, and using ordinary thermochemical equations, is -5 cal g^{-1} . In the same manner, however, the calculated heat of hydration for the anhydrite (CaSO_4) is -29 cal g^{-1} . The higher heat of hydration (-9 cal g^{-1}) for the tested sample than that for the ordinary hemihydrate (-5 cal g^{-1}) was attributed to the presence of a certain percent of anhydrite. The composition of the tested sample was proposed by applying conventional chemical and rational analyses. The present work suggests the use of the heat of hydration as a tool for determining the composition of calcined gypsum.

INTRODUCTION

Industrial gypsum ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) is produced by the calcination of raw gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) at 150°C [1]. The calcination product, which is called plaster of Paris or calcium sulphate hemihydrate, contains 0.5 molecules of water of crystallization. Anhydrite (CaSO_4) may also form during the overburning of raw gypsum. Both the hemihydrate and the anhydrite liberate heat when they combine with water on rehydration, i.e., the reaction is exothermic.

A fresh sample of some industrial gypsum (plaster of Paris), produced by the National Gypsum Co., Riyadh, Saudi Arabia, was tested for its heat of hydration using an adiabatic calorimeter. The tested sample was obtained during a control phase of the calcination process of gypsum in the plant.

The heat of hydration of calcium sulphate hemihydrate was calculated theoretically from the known heats of formation by applying ordinary thermochemical equations. The heat of hydration of the anhydrite was calculated in the same way. Again, the heat of hydration determined experimentally for the tested sample was compared with that calculated, on a theoretical basis, for the calcium sulphate hemihydrate. The value of the

* Permanent address: The National Research Center, Dokki, Cairo, Egypt.

heat of hydration determined experimentally for the plaster of Paris is discussed with respect to the composition of the sample, i.e., the amounts of calcium sulphate hemihydrate and anhydrite. However, the composition of calcined gypsum is generally elucidated by DTA, X-ray diffraction and IR spectrometry [2].

EXPERIMENTAL

Material

A sample of calcined gypsum was obtained under the conditions mentioned above. It was tested for its heat of hydration using a suitable adiabatic calorimeter. Chemical analysis of the fresh sample was also carried out using the known analytical method.

Determination of the heat of hydration

Apparatus

An adiabatic calorimeter of the Tonindustrie type [3], West Germany, was used for the determination of the heat of hydration.

Preparation of the test sample

(1) A known quantity (W_1) of the plaster of Paris was added to a standard quantity of water (W_2) in a suitable mixing pan. The amount of mixing water was equal to 60% of the plaster of Paris on a weight basis. The material was homogenized using a couple of stainless steel standard trowels. Mixing took 2 min.

(2) The obtained paste ($W = W_1 + W_2$) was transferred as soon as possible into a cylindrical tin container of 16 cm diameter and 24 cm height. Any residual material still adhering to the inside of the mixing pan was wiped off by means of a piece of cotton, and this was then placed together with the material in the container.

(3) The container was then covered; it was placed in the calorimeter.

(4) The initial temperature (t_0) and the final temperature (t) were recorded as room temperature and the highest temperature attained when thermal equilibrium occurred, respectively.

(5) The rise in temperature ($\Delta t = t - t_0$) was calculated.

Calculation of the heat of hydration

The quantity of heat liberated (Q), expressed in calories, was calculated from the weight of the container's content (W) of hydrated plaster, its specific heat (C_p) and the rise in temperature (Δt), as well as the calorimeter constant (k) for tin, hence

$$Q = (WC_p \Delta t) + (k \Delta t)$$

The heat of hydration (q) was calculated by dividing the quantity of heat liberated (Q) by the weight of plaster (W_1). An example for calculating the heat of hydration is given in Appendix I.

TABLE 1

Constituents * of the plaster of Paris sample:

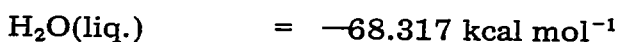
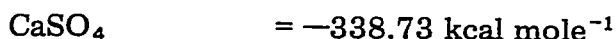
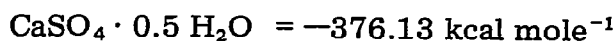
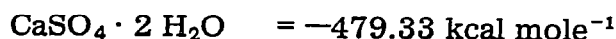
Constituents	%
CaSO ₄ · 0.5 H ₂ O	54.5
CaSO ₄	29.2
CaCO ₃	12.5
Other contaminations	3.8
Total	100.0

* Based on rational and chemical analyses (see also chemical analysis results, Appendix II).

RESULTS AND DISCUSSION

A value of -9 cal g^{-1} was obtained for the heat of hydration of the tested sample (Appendix I). Table 1 shows the composition of the plaster of Paris, and indicates that the sample contained mainly calcium sulphate hemihydrate and anhydrite. However, the amount of calcium sulphate hemihydrate (54.5%) present in this sample is much lower than the norm (90%) prescribed, for example, in the DIN specification [4]. On the other hand, the amount of anhydrite present in the tested sample is higher than that normally found in industrial gypsum. This is attributed to the overburning of the gypsum raw material from which the plaster originated [5].

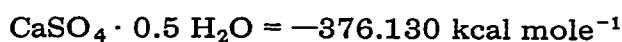
Both of the calcium sulphate hemihydrate and anhydrite liberate heat of hydration. The heat of hydration of the calcium sulphate hemihydrate and anhydrite could be calculated theoretically from the heats of formation at 25°C using ordinary thermochemical equations.



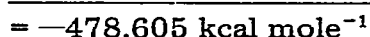
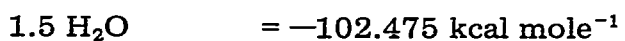
The calcium sulphate hemihydrate is hydrated to gypsum in accordance with the following equation



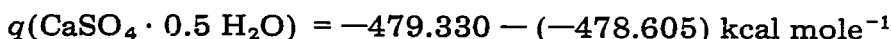
Substituting for the heats of formation, therefore



+



Since the heat of formation of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = -479.330 \text{ kcal mole}^{-1}$



The anhydrite (CaSO_4) is hydrated to gypsum in accordance with the equation



In the same manner, the heat of hydration $q_{(\text{CaSO}_4)}$ could be calculated from the heats of formation.

$$\begin{aligned} q_{(\text{CaSO}_4)} &= -3.966 \text{ kcal mole}^{-1} \\ &= -29.0 \text{ cal g}^{-1} \text{ (M.W. of CaSO}_4 = 136 \text{ g)} \end{aligned}$$

In summary,

$$\begin{aligned} q_{(\text{tested sample})} &= -9.0 \text{ cal g}^{-1} \text{ (determined experimentally)} \\ q_{(\text{CaSO}_4 \cdot 0.5 \text{ H}_2\text{O})} &= -5.0 \text{ cal g}^{-1} \text{ (calculated theoretically)} \\ q_{(\text{CaSO}_4)} &= -29.0 \text{ cal g}^{-1} \text{ (calculated theoretically)} \end{aligned}$$

Again, the above mentioned results indicate that the heat of hydration of the plaster of Paris (-9.0 cal g^{-1}) is higher than that calculated theoretically for the ordinary calcium sulphate hemihydrate (-5.0 cal g^{-1}). This was attributed to the presence of a certain percent of anhydrite (29.2%) in the sample. The theoretically calculated heat of hydration assigned to anhydrite (-29.0 cal g^{-1}) is, however, much higher than that of the calcium sulphate hemihydrate (-5.0 cal g^{-1}).

The proposed percent of anhydrite (29.2%) in the sample should be based on theoretically calculated excess heat of hydration, which should consequently agree with that determined experimentally. This could be followed by multiplying the ratios of the calcium sulphate hemihydrate and anhydrite by their corresponding heats of hydration. Of course, the calcium sulphate hemihydrate and anhydrite are those phases which are responsible for the liberation of heat when the sample is hydrated; let us call them the hydratable phases. On the other hand, the calcium carbonate and other contaminants, which totalled 16.3% in the sample, liberate no heat since they are unhydratable. Ratios of hydratable phases were obtained by multiplying phase percent by 83.7/100, which represents the proportionality of the hydratable phases in the sample. This can be illustrated below.

Hydratable phases	Ratio		q (cal g^{-1})		Result
$\text{CaSO}_4 \cdot 0.5 \text{ H}_2\text{O}$	$\left(\frac{54.5}{100} \times \frac{83.7}{100} \right)$	\times	-5.0	=	-2.28 cal g^{-1}
CaSO_4	$\left(\frac{29.2}{100} \times \frac{83.7}{100} \right)$	\times	-29.0	=	-7.08 cal g^{-1}
				=	-9.36 cal g^{-1}
				\approx	-9.0 cal g^{-1}

Therefore, the theoretically calculated heat of hydration of the sample (-9.36 cal g^{-1}) compares well with that determined experimentally (-8.8 cal

g^{-1}). By approximation, a value of -9.0 cal g^{-1} is obtained for both theoretically calculated and experimentally determined heats of hydration. This shows that the stated percent of anhydrite in the sample, which caused excess heat of hydration, is correct. The estimation of the heat of hydration of calcined gypsum in this way could therefore be used for assessing the phase composition of any type of calcined gypsum to clarify the hemihydrate/anhydrite ratio.

In conclusion, the amount of anhydrite in the plaster of Paris should be at a minimum. This can be achieved by providing controlled burning of the gypsum raw material. In this way overburning can be avoided. However, a high percent of anhydrite in the plaster of Paris will cause excess heat of hydration. If a large batch of some plaster of Paris having excessive anhydrite is utilized, the heat liberated on addition of water would be considerable. This could cause many problems, especially in the formation of gypsum plaster products, e.g., plaster boards and similar prefabricates [6]. It is visualized that microcracks would occur in the finished product due to the stresses created in the plaster mass. Similarly, if gypsum plaster having a high percent of anhydrite is used in plastering walls or ceilings, the plaster finish will have irregularities and microcracks, and the application of paint to such a plaster finish would be affected.

REFERENCES

- 1 D.A. Holdridge, *Trans. Br. Ceram. Soc.*, 64 (1965) 211.
- 2 A.A. Khalil, A.T. Hussein and G.M. Gad, *J. Appl. Chem. Biotechnol.*, 21 (1971) 313.
- 3 Chemisches Laboratorium für Tonindustrie, Berlin, West Germany (Catalogue).
- 4 DIN Specification No. 1168 on Industrial Gypsum.
- 5 R.C. Smith, *Materials of Construction*, McGraw-Hill, New York, 1966.
- 6 The National Co. for Gypsum, *Industrial Gypsum — A Basic Constructional Material*, Informative Report, Riyadh, Saudi Arabia, 1972.

APPENDIX I

The experimental data from which the heat of hydration of the tested sample was calculated are given below.

Wt. of plaster of Paris (W_1) = 5000 g
 Wt. of added water (60%) (W_2) = 3000 g
 Wt. of hydrated plaster ($W = W_1 + W_2$) = 8000 g
 Specific heat of hydrated plaster (C_p) = $0.27 \text{ cal C}^{-1} \text{ g}^{-1}$
 Initial temp. (t_0) = 30°C
 Final temp. (t) = 50°C
 Rise in temp. ($\Delta t = t - t_0$) = 20°C
 Calorimeter constant (tin), (k) = $43 \text{ cal } ^\circ \text{C}^{-1}$

The heat liberated (Q) is calculated by substituting the above data into eqn. (1)

$$Q = (WC_p t) + (kt)$$

$$= (8000 \times 0.27 \times 20) + (43 \times 20) = 44\,060 \text{ cal}$$

The heat of hydration (q) is calculated using eqn. (2)

$$\begin{aligned}
 q(\text{tested sample}) &= \frac{Q}{W_1} && (2) \\
 &= \frac{44\,060}{5000} = -8.8 \text{ cal g}^{-1} \text{ (hence exothermic)} \\
 &\approx -9.0 \text{ cal g}^{-1}
 \end{aligned}$$

APPENDIX II

Chemical analysis results of the plaster of Paris sample

Moisture	
Combined water	3.5%
Ignition loss at 1000°C	9.80%
Insoluble residue	3.10%
Fe ₂ O ₃ /Al ₂ O ₃	1.00%
CaO	40.00%
SO ₃	47.16%
CaO/SO ₃	0.847%
MgO	
NaCl	0.01%