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DTA DETERMINATION OF THE ANHYDRITE CONTENT IN ROCK SALTS

A. Swiątek and *I. Wacławska*

INSTITUTE OF BUILDING MATERIALS AND REFRACTORIES,
ACADEMY OF MINING AND METALLURGY, AL. MICKIEWICZA 30,
30–059 CRACOW, POLAND

The DTA method was used to determine the phase diagram of the NaCl—$CaSO_4$ system over the range 0.55 wt.% of $CaSO_4$ in air atmosphere. The effects of SiO_2, $CaCO_3$ and Fe_2O_3 on the melting temperatures of pure NaCl and the eutectic were determined. On the basis of the above temperatures, a method of quantitative determination of the anhydrite content in rock salts has been developed.

Anhydrite frequently occurs as the main impurity of rock salts in the majority of deposits. It is also found in the rock salt from Bochnia, samples of which have been used as materials for quantitative examination.

A knowledge of the $CaSO_4$ content in natural salts is necessary for the correct process of their purification. Its amount in the final product determines the purity of the salt obtained. Besides the diffractometric method, the DTA method is one of the quick and reliable methods of determining the $CaSO_4$ content in rock salts without the need to carry out chemical analysis. It can be applied when the $CaSO_4$ content in the NaCl is 0.5–25.0 wt.%.

Experimental

Quantitative determination of the $CaSO_4$ was carried out on the basis of the phase diagram of the NaCl—$CaSO_4$ system in the range 0–55.0 wt.% of $CaSO_4$, determined by the DTA method. The effects of rock salt impurities such as Fe_2O_3, SiO_2 and $CaCO_3$ on the phase equilibrium in the discussed system were also established.

According to [1], the onset temperature of the first peak in the DTA heating curves was utilized to determine the solidus line, whereas the liquidus line was traced on the basis of the onset temperature of the first peak during cooling of the liquid phase. For this purpose, standard mixtures with the compositions 0.5, 1.0,

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2.5, 5.5, 12.5, 17.6, 25.0, 35.0 and 55.0 wt.% of $CaSO_4$ were prepared using chemically pure reagents. Thermal analysis (DTA) was carried out with a Q–1500 D derivatograph. 400 mg samples were heated and cooled at a rate of 2.5 deg/min in platinum crucibles and in air atmosphere. The effects of SiO_2, Fe_2O_3 and $CaCO_3$ were determined by the DTA method on the basis of the reactions with pure NaCl and with the mixture NaCl—5.5 wt.% of $CaSO_4$. Additions of 2.5, 5.0 and 10.0 wt.% of the above compounds were applied.

Results

The NaCl—$CaSO_4$ diagram represents a simple eutectic system in which, in the range 0–46.0 wt.% of $CaSO_4$, two endothermic peaks occur during heating and two exothermic ones during cooling [2]. The first endothermic peak during heating corresponds to the melting of the eutectic. The other endothermic effect accompanies the solution of the NaCl crystals in liquid of the given composition. During cooling, the first exothermic peak corresponds to the crystallization of NaCl from the liquid, while the other one corresponds to the crystallization of the eutectic. Part of the NaCl—$CaSO_4$ phase diagram worked out by the given method is shown in Fig. 1.

It was found that, in the range 0–27.0 wt.% of $CaSO_4$ in a mixture with NaCl, two separate exothermic peaks appear in the DTA curves for cooling. Near the eutectic point, a single strong peak can be observed (Fig. 2).

When this system is compared with that described in the literature [2], the following differences are found:

— the solidus temperature is lower by 36 degrees, at 695°,

— the eutectic point occurs at a lower content of $CaSO_4$, i.e. 38.0 wt.%.

No effect of SiO_2, Fe_2O_3 or $CaCO_3$ on the melting temperature of pure NaCl was observed. The effects of these additions, however, are detectable in the mixture

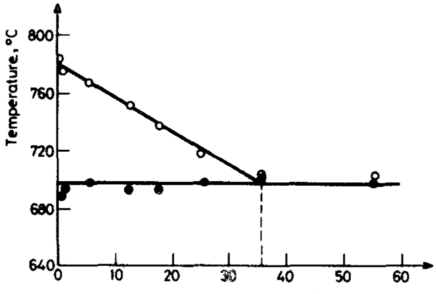

Fig. 1 Phase diagram of NaCl—$CaSO_4$ system

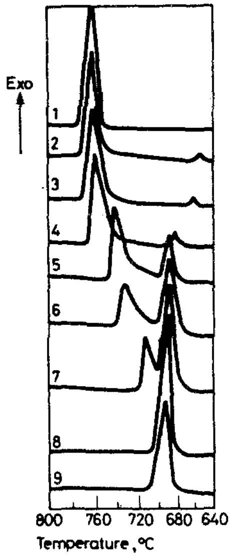

Fig. 2 DTA curves of cooling standard mixtures NaCl—$CaSO_4$; 1 – 0.5, 2 – 1.0, 3 – 2.5, 4 – 5.5, 5 – 12.5, 6 – 17.6, 7 – 25.0, 8 – 35.0, 9 – 55.0 wt.% of $CaSO_4$

NaCl—5.5 wt.% of $CaSO_4$. This refers mainly to the peaks connected with the melting or crystallization of the eutectic, which are shifted towards temperatures lower by about 10–20 degrees. The temperature of the other peak remains unchanged, independently of the amount and type of the added compound.

Quantitative determination of the $CaSO_4$ content in rock salt may be carried out on the basis of the temperature differences between the minima of the first and the second endothermic peaks in the DTA curves, or directly from the temperature shift of the second peak. The basis of the first assumption is the linearity of the liquidus in the NaCl—$CaSO_4$ system, and hence the temperature difference between the minima of the two peaks is proportional to the $CaSO_4$ content of the mixture. This method, however, contains an error resulting from the influence of other impurities on the position of the first peak in the DTA curves.

The other method, which consists in the determination of the temperature of the second endothermic peak, is much more accurate. The temperature of the above peak is stable and practically independent of the admixtures within the range of their content up to 10 wt.%, and it clearly decreases when the $CaSO_4$ content in the mixtuse increases. From the DTA curves for standard mixtures, it has been found that a decrease in the melting temperature of pure NaCl by about 5 degrees occurs at a $CaSO_4$ content of 0.5 wt.%. On the basis of the temperature of the second endothermic peak in the DTA heating curves of the standard mixtures, the calibration curve for the determination of the anhydrite content in rock salt was plotted. The $CaSO_4$ content in the salts was determined from the DTA curves in parallel to the diffractometric quantitative analysis of this mineral and chemical analyses. A comparison of the results obtained revealed that for salts containing more than 1.5 wt.% of $CaSO_4$ the differences between the determinations of this mineral by the particular methods are lower than 5 wt.%.

References

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Zusammenfassung — DTA wurde benutzt, um in Luft im Bereich 0 bis 55,0 Gew.% $CaSO_4$ das Phasendiagramm des Systemes NaCl—$CaSO_4$ zu bestimmen. Es wurde auch der Einfluß von SiO_2, $CaCO_3$ und Fe_2O_3 auf die Schmelztemperatur von reinem NaCl bzw. des Eutektikums bestimmt. Auf der Grundlage obiger Temperaturen wurde eine Methode zur quantitativen Bestimmung des Anhydritgehaltes in Steinsalzen entwickelt.

Резюме — Методом ДТА в атмосфере воздуха определена фазовая диаграмма для системы хлористый натрий—сульфат кальция с содержанием сульфата кальция 0—55,0 весовых процента. Было также изучено влияние двуокиси кремния, карбоната кальция и оксида трехвалентного железа на температуры плавления чистого хлорида натрия и его эвтектики. Исходя из найденных температур, разработан метод количественного определения содержания ангидрита (сульфата кальция) в каменной соли.