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INFLUENCE OF PRESSURE REDUCTION ON THE SHAPES OF THERMOANALYTICAL CURVES OF RED MUDS*

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The effect of reduction of pressure on the shapes of the TG, DTG and DTA curves and the mass-spectra of hydroxide and carbonate phases was investigated in some typical Hungarian red muds. The pressure change caused different decomposition rates of the phases and resulted in better separation of the overlapping thermal curves; this led to advantages as regards phase analysis. For phase analysis the red muds were extracted with water, and the extracts and solid residues were identified by IR-and X-ray methods.

Investigations connected with the utilization of the derivatives of alumina manufacture made improvement of the phase analysis of red mud imperative. The possibilities of derivatographic analysis were previously exploited [1]. We hoped to make advances with regard to thermal phase analysis by carrying out research with an apparatus of high sensitivity which provides an atmosphere of low pressure reliably adjustable in the analytical range.

Experimental

Red mud originating from the Alumina Factory in Almásfüzitő was used. This basic material is the V_0 red mud. After being freed from sodium by leaching combined with special oxidation, the material is named V_1. Both samples (V_0, V_1) were washed with distilled water and dried. The water phase was evaporated. The two solid phases were used for identification of the dissolved and the residual materials.

A Mettler TA-1 thermobalance connected to a QMG 311 quadrupole gas analyser was used for the investigations. An examination was made of the additional information given by reduction of pressure, the gaseous decomposition products being analysed.

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Observations extended to the TG, DTG and DTA curves and the mass-spectra of the gases. Generally, recordings were made of the peak temperatures characteristic of the thermal transformations from the DTG and mass-spectrometric curves, because the DTA baseline was rather questionable in vacuum, and hence detection of minor or medium thermal effects was difficult.

20 mg material was weighed into an alundum crucible in all cases except the mass-spectrometric measurements, which were carried out at atmospheric pressure by capillary techniques, where, because of the sensitivity reduction, a larger quantity was required. The heating rate was 4° per min.

The samples were investigated by IR-spectroscopy using a UR-20 Zeiss spectrophotometer and KBr pellets.

Results and discussion

V_0 red mud

We shall disregard the weight loss under 100°, resulting from the departure of loosely-bound water, as from the point of view of our discussion this is not important. Above 100° two processes occur involving the departure of H_2O: the decompositions of goethite and sodalite [2]. The results at atmospheric pressure and in vacuum are compared in Table 1.

Table 1

Thermal properties of some minerals at various pressures

Phase	DTG peak temperature °			
	at 760 torr	ΔT	at $3 \cdot 10^{-5}$ torr	ΔT
Goethite	330	75	290	90
Sodalite	255		200	

According to expectations the peak temperatures shift towards lower values in vacuum; this is natural, since a partial pressure of the decomposition products large enough to retard the progress of the reaction is not attained above the solid phase. At the same time, some thermal decomposition processes take place more quickly, hence the processes become more separated from one another, so that recognition of the phases is easier [3]. This is verified by the ΔT values in Table 1.

In the range of decomposition of carbonates in red mud (calcite, sodalite, etc.). It is interesting that at atmospheric pressure the DTG curve registers only one decomposition process, whereas in vacuum two definite and well-separated DTG peaks form. Mass-spectrometric analysis of the gases above the solid phase also gives completely congruent results (Fig. 1). For the time being let us leave the question of whether this is the separation of the decompositions of two different carbonate phases or some other reaction-kinetics phenomenon.

At much more elevated temperatures, 1000–1500°, the TG curves do not indicate any other characteristic process, but the weights of the samples gradually decrease considerably. As shown in Fig. 2, this decreasing tendency is greater by several orders of magnitude in vacuum than at atmospheric pressure. We first attributed this weight loss to the Na_2O content of the red mud, for this is the only volatile oxide present. However, the small Na_2O content of the V_0 red mud (under the detection limit of X-ray spectrometric analysis) in itself cannot cause the weight loss observed in vacuum (Fig. 2). Thus, some other process also plays

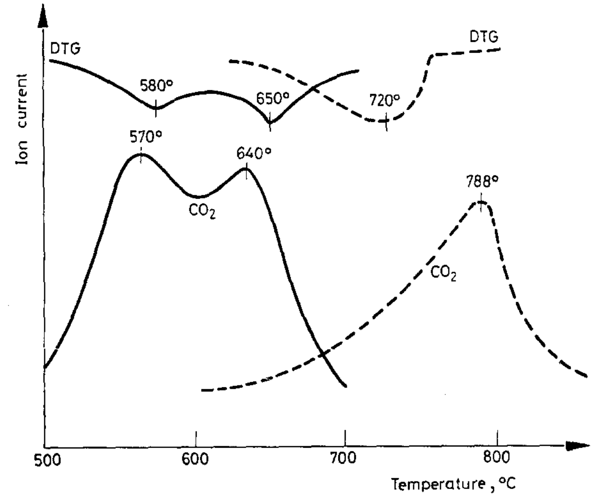

Fig. 1. Change of the partial pressure of CO_2 in the gas phase, and the DTG curves of V_0 red mud; ——: at 10^{-5} torr, — —: in air

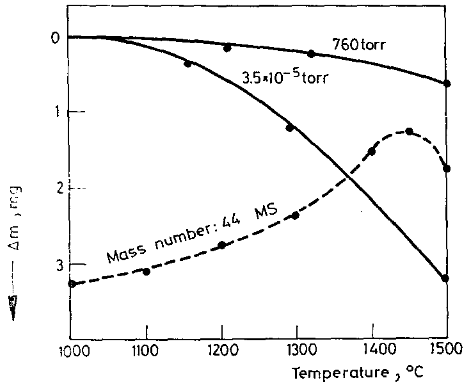

Fig. 2. TG and MS curves of V_0 red mud

a role in the temperature range in question. Finally, mass-spectrometric analysis of the gases gave the answer to the question: an intense peak at mass number 44, with 1450° maximum. Since the presence of undecomposed carbonate, and consequently carbon dioxide formation, cannot be assumed under the given conditions (the character of the weight loss curve also shows this), the mass number 44 must correspond to some other gaseous product, most probably silicon monoxide (SiO). We know from X-ray analysis that the approximately 14% SiO_2 content of V_0 red mud originates from about 11% silicate compound and 3% crystalline quartz. Pliskin [4] showed that SiO_2 evaporates, chiefly in the form of SiO, in a vacuum better than 10^{-4} mm Hg. Though he does not give accurate temperature data for the equilibrium of the reaction $SiO_2 \rightleftharpoons SiO + 1/2O_2$, our experience in other fields [5] supports the supposition that above 1100° the reaction shifts considerably towards SiO formation.

We identified the gas product with mass number 44 as silicon monoxide by infrared spectrophotometry. Potassium bromide was placed in an appropriately chosen colder place in the path of the gases leaving the reaction zone, and the spectrum of the product deposited on the window was found to consist of a single broad band the character and frequency of which coincide almost exactly with the literature data on SiO [6].

V_1 red mud

Treatment of the V_0 basic material with vitriolic iron(III) sulfate solution yielded the V_1 red mud [7], which can be expected to consist of phases containing sulphate instead of carbonate ions.

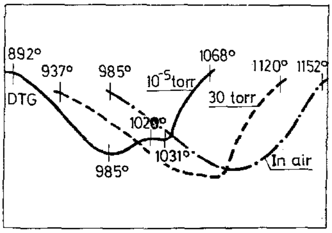

Fig. 3. DTG curves of V_1 red mud

The characters of the decomposition reactions of the phases containing residual hydroxyl groups, as well as of goethite and sodalite, and the tendencies of the temperature data agree exactly with those reported in connection with the V_0 basic material. It is also noteworthy that at atmospheric pressure between 800 and 1150° the TG and DTG curves indicate only one process. At the same time, on reduction of the pressure the reaction starts at lower and lower temperatures and, as the shapes of the DTG curves in Fig. 3 indicate, at 30 torr a minor reaction stop appears; however, at 10^{-5} torr the process divides definitely into two parts with maxima at 985 and 1031°.

Mass-spectrometric analysis of the gases gave information about the high-temperature processes (Fig. 4). A maximum curve at mass number 64 proves unambiguously the decomposition of the enriched sulphates resulting from the treatment with sulfuric acid. In agreement with the DTG curves in Fig. 3, the sulfate decomposition is also resolved into two part-processes in high vacuum, and (Fig. 4) the corresponding DTG peak temperatures correlate with those of the mass spectra. It is interesting that slight sulfur dioxide peaks can be observed at 450 and 650°, but they are such slight effects that only very small inflexions are perceptible at these temperatures in the TG curve.

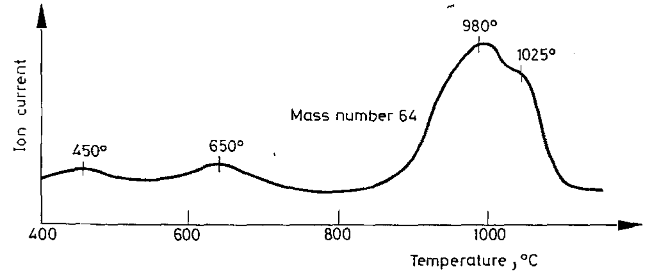

Fig. 4. Change of the partial pressure of SO_2 in the gas phase during heating of V_1 red mud

Effect of washing the V_0 mud with water

We previously left open the question of the reason for the separation of the carbonate steps of V_0 in vacuum. It was assumed that while carbon dioxide bound in the small quantities of calcite and sodalite or perhaps soda, leave together at atmospheric pressure, their decompositions separate in vacuum. Since the carbonate bound to sodium is water-soluble, it seemed practical to dissolve the assumed sodium carbonate of the V_0 material with water. Accordingly, the material was washed with water several times, and studies were then made on the residual red mud after filtration and drying under conditions identical with the former ones.

The characters of the thermoanalytical curves at atmospheric pressure remain practically unchanged after washing. However, in vacuum only one peak appears instead of two; this proves that the two DTG peaks of the untreated V_0 mud in vacuum are caused by two carbonate compounds decomposing at close temperatures. The water-extraction dissolves the phase decomposing at higher temperature, as the DTG peak corresponding to this does not recur (Fig. 5).

The infrared spectrum of the residue from evaporation of the aqueous phase (Fig. 6) shows that the bulk is sodium carbonate, with sodium sulfate in smaller amount. Hence, we can attribute the lower-temperature DTG peak to calcium carbonate with calcite structure, and the higher-temperature peak to sodium carbonate. Calcium carbonate was detected by X-ray phase analysis too. It can easily be seen from the foregoing that we can not detect sodium sulfate by appropriate thermal analysis. On the basis of the infrared spectrum it became clear that in the mass-spectrometric curve of the untreated V_0 sample we observed a slight sulfur dioxide maximum after the carbonate decomposition range 850–950°. This was confirmed by the results of the dissolution experiments. On the other hand, phases present in quantities less than 1% cannot be detected from the DTA-TG curves, so here we could expect information only from quadrupole gas analysis.

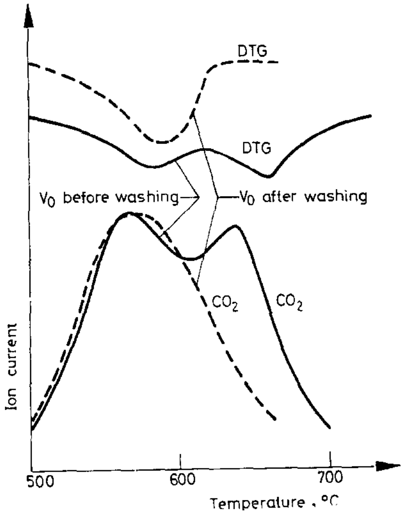

Fig. 5. DTG and MS curves of V_0 red mud before (——) and after (– –) washing with water

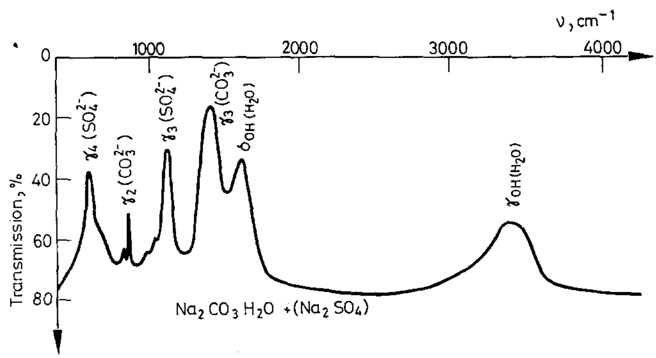

Fig. 6. IR spectrum after evaporation of the water extract of the V_0 red mud

Effect of washing the V_1 red mud with water

The infrared spectrum of the material left after the water treatment (Fig. 7) proves the presence of sulfate compounds exclusively. The double peak in both the DTG and the mass-spectrometric curves of the untreated red mud (Fig. 3) disappears after treatment with water; no signal indicative of a thermal process appears at all here, indicating the decomposition of water-soluble sulfate in this range.

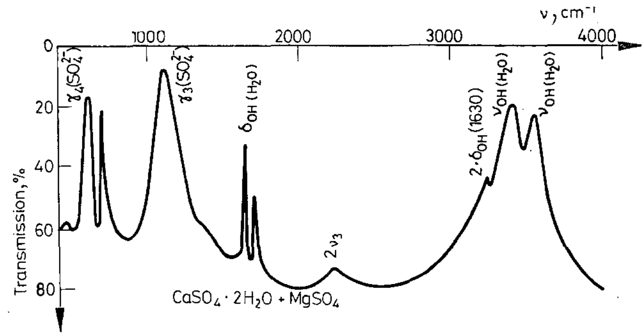

Fig. 7. IR spectrum after evaporation of the water extract of the V_1 red mud

From the spectrum in Fig. 7 it can be stated with complete certainty that the bulk of the water-soluble compound is $CaSO_4.2H_2O$ [8], i.e. gypsum. Further, magnesium was detected in major quantity and aluminium in minor quantity in the solution, but it is striking that the aqueous phase does not contain iron(III) ions even in traces. The analytical data suggest that smaller quantities of magnesium sulfate and aluminium sulfate, perhaps basic aluminium sulfate ($AlOHSO_4$) are the most probable impurities present beside gypsum. Because the aqueous extraction was not suitable for dissolving the sulfate selectively, in contrast to the situation with the carbonates we could not get any direct experimental evidence to explain the double DTG and MS peaks.

However, if we consider that calcium sulfate is transformed into calcium oxide in one step [9] and it is not presumable that sulphur dioxide would be evolved stepwise in vacuum either, we can justifiably assume on the analogy of the carbonates that the occurrence of the double DTG and MS peaks in vacuum is similarly connected to the separation of the decompositions of two sulfate compounds ($CaSO_4$ and $MgSO_4$), which decompose at very close temperatures.

The dissolution experiments called attention to the fact that, of the two minor mass-spectrometric maxima in Fig. 4, that at 650° corresponds to the decomposition of sulfate bound to aluminium, which can be found in the V_1 mud in small quantity. The aluminium sulfates, including basic aluminium sulfate, decompose at about 750° at normal pressure [10], and consequently it can be excluded that this reaction would relate to one of the double DTG or MS peaks at higher temperature; the decomposition temperature must be under 750° in vacuum.

To summarize we can draw the practical conclusion that with the application of a pressure of about 10^{-5} torr and detection of the gases released an opportunity arises for detecting minor part-processes and hence identifying low-quantity phases which generally remain in the background in the course of the usual thermoanalytical investigations.

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Résumé — On a étudié dans quelques espèces typiques de boues rouges de Hongrie l'effet des variations de pression sur la forme des courbes TG, TGD et ATD ainsi que les spectres de masse des phases hydroxyde et carbonate. La variation de la pression entraîne des vitesses de décomposition différentes. Il en résulte une meilleure séparation des phénomènes dans le cas où ceux-ci se chevauchent ainsi que des avantages du point de vue de l'analyse des phases. L'analyse des phases présentes dans les boues rouges a été effectuée par extraction à l'eau. Les extraits et les résidus solides ont été identifiés par spectrométrie infrarouge et par diffraction des rayons X.

Zusammenfassung — Die Wirkung der Druckänderung auf die Form der TG-, DTG- und DTA-Kurven, sowie der MS-Spektra der Hydroxid- und Carbonatphasen in einigen typischen ungarischen Rotschlamm-Sorten wurde geprüft. Die Druckänderung verursachte verschiedene Zersetzungsgeschwindigkeiten der Phasen, führte zur besseren Auftrennung der sich überlappenden thermischen Kurven, und war ausserdem auch hinsichtlich der Phasenanalyse vom Vorteil. Zur Phasenanalyse wurden die Rotschlämme mit Wasser extrahiert und die Extrakte und festen Rückstände mittels IR- und Röntgenmethoden identifiziert.

Резюме — Было исследовано влияние изменения давления на вид кривых ТГ, ДТГ и ДТА также как и масс-спектры гидроксидной и карбонатной фаз в некоторых образцах типичных венгерских красных грязей. Изменение давления вызывает различные скорости разложения фаз, в результате чего происходит лучшее разделение перекрывающихся термических кривых, что является преимуществом по отношению фазового анализа. Для фазового анализа красные грязи экстрагировались водой и экстракты и твердый остаток были идентифицированы рентгенографическим методом и инфракрасной спектроскопией.