

A STUDY OF THERMAL PREPARATION OF IRON (III) PIGMENTS BY MEANS OF THERMAL ANALYSIS METHODS

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The decomposition of hydronium jarosite occurs in two temperature ranges: first a loss of 8 moles of H_2O from 2 moles of jarosite, then in the second step one mole of H_2O and 4 moles of SO_3 are simultaneously evolved. $\text{Fe}(\text{OH})(\text{SO}_4)_2$ and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ are assumed intermediates. During the thermal treatment of Na or K jarosites, only $\text{Fe}_2(\text{SO}_4)_3$ appears as intermediate. The decomposition temperatures are significantly influenced by the type of crucible used (determination of partial pressure of gaseous decomposition products). The particle size distribution of the starting jarosite has no effect upon the temperature of the decomposition steps and of the reaction with ZnO .

The results of TG measurements were evaluated via calculations of the steps of the experimental activation energies for these partial decomposition jarosites and for their reaction with ZnO .

In accordance with current economic needs, a new method of production of iron(III) oxide by means of thermal decomposition of jarosite precipitates has been introduced. These hydroxide-sulphates are waste-products of Cu–Pb–Zn concentrates. The separation of iron in this form of jarosite precipitates is very advantageous, especially as concerns the economy of zinc production [1].

Different conditions of precipitation (the iron content, the free H_2SO_4 content in the solution, the temperature, etc.) may lead to different results [1]. Particularly the formation of hydronium and sodium jarosites (H–Ja, Na–Ja) in this technology is important. The jarosites form an isomorphous series of compounds: the cation H_3O^+ may be replaced by Na^+ , K^+ , NH_4^+ etc.

The mechanism of decomposition of NH_4^+ jarosite was studied in [2], while [3] deals with NH_4^+ , Na^+ and K^+ jarosites. The formation of $\text{Fe}_2(\text{SO}_4)_3$ as an intermediate is assumed. Many papers (e.g. [4, 5]) deal with the thermal decomposition of iron(II) sulphate. The formation of hydroxide-sulphate $\text{Fe}(\text{OH})(\text{SO}_4)$ and oxid-sulphate $\text{Fe}_2\text{O}(\text{SO}_4)_2$ as intermediates is usually presumed.

In this paper we present a study of the thermal decompositions of H–Ja and Na–Ja, and of their reactions with ZnO , when pigments of spinel type are formed.

Experimental

Samples of various jarosites test-produced in hydrometallurgical works were analysed for Fe and S (Table 1). The sample of H-Ja contains about 1 wt.% of Na-Ja, Na-Ja contains 1.5 wt.% of K-Ja contains about 1 wt.% of Ha-Ja.

Table 1 Analyses of jarosites used, in wt.%

| Jarosite | Symbol | Contents of Fe ₂ O ₃ and SO ₃ , wt.% | | | | | Wt.loss % on calculation to 1100° |
|--|--------|---|-----------------|------------------|--------------------------------|-----------------|-----------------------------------|
| | | theoretically | | | determined | | |
| | | Fe ₂ O ₃ | SO ₃ | H ₂ O | Fe ₂ O ₃ | SO ₃ | |
| H ₃ O[Fe ₃ (SO ₄) ₂ (OH) ₆] | H-Ja | 49.82 | 33.28 | 16.85 | 50.1 | 32.9 | 47.7 |
| Na[Fe ₃ (SO ₄) ₂ (OH) ₆] | Na-Ja | 49.41 | 24.78 | 11.14 | 48.8 | 24.8 | 37.3 |
| K[Fe ₃ (SO ₄) ₂ (OH) ₆] | K-Ja | 47.83 | 23.98 | 10.79 | 47.9 | 23.8 | 35.1 |

The jarosite samples were calcined in an electric muffle kiln under isothermal or dynamic (linear temperature increase 5 deg · min⁻¹) conditions in air atmosphere. Thermal analyses were carried out with a Q-1500 D derivatograph. X-ray analyses showed only the diffraction maxima of jarosites (ASTM 11-302).

The particle size distribution curves of the samples of jarosites are shown in Fig. 1 (Joyce Loebel disc centrifuge). The specific surface areas of H-Ja, Na-J and K-Ja

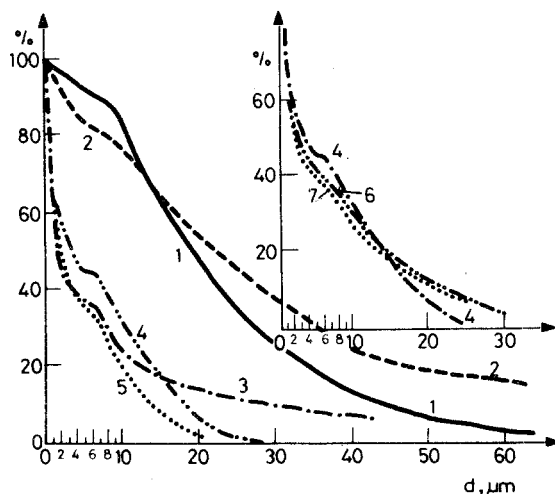


Fig. 1 Particle size distribution: 1 – H-jarosite, 2 – Na-jarosite, 3, 4 – Na-jarosite pre-fired to 650 and 800°, 5 – H-jarosite pre-fired to 800°, 6, 7 – Na-jarosite pre-fired to 700°, when the starting material was coarse ($d > 60 \mu\text{m}$) or fine ($d < 20 \mu\text{m}$)

were 2.2–2.6 and 1.7 m² g⁻¹ (thermal desorption of N₂). H-Ja and Na-Ja were divided into three fractions by sedimentation (Schöne apparatus). The larger particles ($d > 60 \mu\text{m}$) had a regular crystalline form, while the smaller particles ($d < 20 \mu\text{m}$) were sticklike in form. On calcination (temperature increase 5 deg·min⁻¹) to various temperatures, iron(III) oxide was formed. The changes in the Fe₂O₃ particle size distribution are also shown in Fig. 1 (curves 6 and 7). It can be seen that the size distribution of the starting jarosite has only a negligible influence on the size distribution of the decomposed product.

Results and discussion

The DTA curves of H-Ja, Na-Ja and K-Ja are shown in Fig. 2. The decomposition reactions proceed independently of the size distribution of the

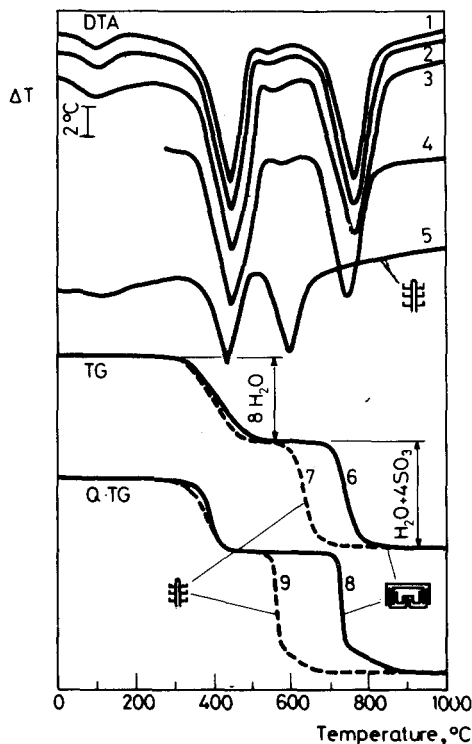


Fig. 2 DTA (1–5 and TG curves (6–9) of the decomposition of J-jarosite.

1 – H-jarosite (standard sample), 2, 3 – fine and coarse fractions of H-jarosite, 4 – measurement of ΔH , Perkin-Elmer 1700, 5 – multiplate crucible, 6, 7 – TG, 8, 9 – Q-TG, two types of crucible

Table 2 DTA peaks of decomposition reactions

| Jarosite | Reaction I | | Reaction II | | Type of crucible, increase of temp., \emptyset |
|---|------------------------------|-------|-------------------------------|-------|--|
| | t_0 | t_m | t_0 | t_m | |
| H-Ja | 400 | 457 | 710 | 785 | |
| H-Ja fine ($d < 20 \mu\text{m}$) | 400 | 457 | 705 | 785 | covered crucible |
| H-Ja coarse ($d > 60 \mu\text{m}$) | 395 | 456 | 708 | 785 | $\emptyset = 10 \text{ deg min}^{-1}$ weight $\sim 0.5\text{--}1 \text{ g}$ |
| Na-Ja | 403 | 470 | 730 | 790 | covered crucible |
| Na-Ja fine | 403 | 470 | 734 | 790 | $\emptyset = 10 \text{ deg min}^{-1}$ |
| Na-Ja coarse | 402 | 470 | 735 | 800 | weight $\sim 0.5\text{--}1 \text{ g}$ |
| H-Ja | 399 | 445 | 662 | 721 | Perkin-Elmer 1700 |
| | $\Delta H(\text{I}) = 224.0$ | | $\Delta H(\text{II}) = 312.5$ | | $\emptyset = 20 \text{ deg min}^{-1}$ |
| Na-Ja | 419 | 449 | 665 | 713 | |
| | $\Delta H(\text{I}) = 250.6$ | | $\Delta H(\text{II}) = 255.4$ | | |
| H-Ja | 330 | 450 | 510 | 600 | multiple crucible $\emptyset = 5 \text{ deg min}^{-1}$ |
| K-Ja | 380 | 462 | 750 | 812 | covered crucible $\emptyset = 10 \text{ deg min}^{-1}$ |

$t_{0,m}$ = onset temp., temp of maximum, $^{\circ}\text{C}$; ΔH = reaction enthalpy, kJ mol^{-1}

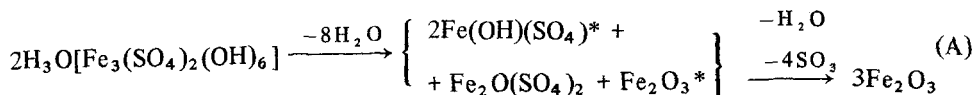
starting material. The losses of constitutional water molecules and of SO_3 occur at the same temperatures (Fig. 2, Table 2).

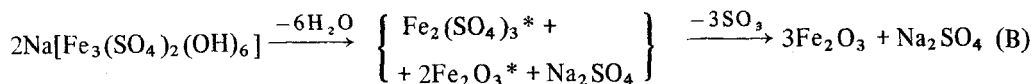
The partial pressure of the gaseous decomposition products determined by the crucible type (labyrinth crucible $\sim 0.1 \text{ MPa}$, covered $\sim 20 \text{ kPa}$, multiplate type $\sim 1 \text{ kPa}$) influences the position of the first peak only slightly, whereas the second one is shifted much more (by 150 deg).

Figure 2 shows the TG curves too. They allow the calculation of the activation energy E_{exp} through solution of the equation of Coats and Redfern [7] ($\ln g(\alpha) - 2 \ln T$ vs. $1/T$). Optimum results were obtained when diffusion equations D2 or D3 for $g(\alpha)$ were used (Table 3).

The shape of the TG curves when quasi-isothermal and quasi-isobaric conditions were used (Q-test) indicated crust formation during the decomposition process [8].

The mechanism presupposes the formation of $\text{Fe}(\text{OH})(\text{SO}_4)$, $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}_2\text{O}(\text{SO}_4)_2$, probably according to the schemes:





A scheme analogous to (B) may be accepted for K-Ja. Compounds denoted by * were found by X-ray examination. The earlier samples of H-Ja showed the first reaction to be divided into two steps [9], but the new samples investigated in this paper did not exhibit this division.

Table 3 Activation energies of decomposition reactions

| Jarosite | $E_{\text{exp.}}, \text{kJ mol}^{-1}$ | | Type of crucible |
|----------|---------------------------------------|----------|--------------------|
| | step I | step II | |
| H-Ja | 165 ± 15 | 350 ± 24 | labyrinth |
| H-Ja | 145 ± 15 | 305 ± 30 | multiplate |
| H-Ja | 170 ± 8 | 345 ± 30 | covered with a lid |
| Na-Ja | 220 ± 18 | 360 ± 30 | labyrinth |
| Na-Ja | 210 ± 20 | 360 ± 28 | with a lid |

When zinc oxide was mixed with the jarosites or prefired jarosites, to produce Zn ferrite (pigment with spinel structure), the DTA curves shown in Fig. 3 were obtained. The decomposition effect near 700° is compensated by the exothermic effect of ferrite formation. When prefired jarosite was used, the exothermic peak was higher. The conductometric method [10] gave the initial temperatures of this reaction as 580, 620, 620 and 600° for curves 6, 5, 4 and 2 in Fig. 3. The endothermic effect above 900° probably relates to the growth of ferrite grains. The X-ray

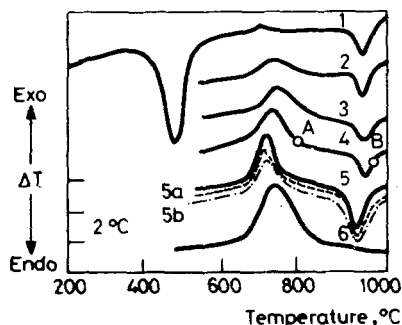


Fig. 3 DTA curves of the reaction $\text{Fe}_2\text{O}_3 + \text{ZnO}$.
 Source of Fe_2O_3 used: 1 - H-jarosite, 2-5 - H-jarosite prefired to 650° (10 min.), 700° (10 min.), 700° (0.5 hour) or 700° (1.5 hour), 6 - Fe_2O_3 Fepren DR 63

Table 4 Values of activation energy for reactions of prefired jarosites with ZnO

| ZnO + jarosite | $E_{\text{exp.}}$, kJ mol ⁻¹ |
|---|--|
| ZnO + H-Ja, prefired to 700 °C, 10 min. | 250 ± 15 |
| ZnO + H-Ja, prefired to 700 °C, 1.5 hour | 285 ± 26 |
| ZnO + Na-Ja, prefired to 700 °C, 10 min. | 260 ± 12 |
| ZnO + Na-Ja, prefired to 700 °C, 1.5 hour | 295 ± 25 |

diffraction diagram of the reaction product at point A in Fig. 3 indicated nearly amorphous material, while calcinate B gave intense diffraction peaks of Zn ferrite. Variation of the particle size fraction (Fig. 3, curve 5a: H-Ja fraction < 20 µm; curve 5b: particle fraction 60 µm; curve 5: standard H-Ja material) did not influence the ferrite formation.

The values of $E_{\text{exp.}}$ calculated from analyses of uncreated ZnO for the reaction of prefired jarosites with ZnO supplement the values reported in [9] (Table 4).

The calculations were carried out in the same way as for the values of $E_{\text{exp.}}$ for decomposition reactions. For $g(\alpha)$, the best results were obtained when diffusion mechanism D2 (or D3) was used.

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Zusammenfassung — Die Zersetzung von Hydronium-jarosit verläuft in zwei Stufen: (1) Abgabe von 8 Mol Wasser, (2) simultane Abspaltung von 1 Mol Wasser + 4 Mol SO₃/2 Mol Jarosit. Als Zwischenprodukte werden Fe(OH)(SO₄) und Fe₂O(SO₄)₂ vermutet.

Bei der thermischen Zersetzung von Na- und K-Jarosit tritt nur Fe₂(SO₄)₃ als Zwischenprodukt auf. Die Zersetzungstemperaturen werden durch die Tiegelform erheblich beeinflusst (über den Partialdruck der gasförmigen Zersetzungsprodukte). Die Teilchengrößenverteilung des Ausgangs-Jarosits hat keinen Einfluss auf die Temperaturen der Zersetzungsschritte des Jarosits und der Reaktion mit ZnO.

Aus den Ergebnissen der TG-Messungen werden experimentelle Aktivierungsenergien für die Zersetzungsreaktionen der Jarosite und ihre Umsetzung mit ZnO berechnet.

Резюме — Разложение оксоний-язозита происходит в двух температурных областях. В первой происходит потеря 8 молей воды из двух молей ярозита, а во второй — происходит одновременное выделение одного моля воды и 4 молей трехоксида серы. Предположено образование на этих стадиях двух промежуточных продуктов $\text{Fe}(\text{OH})\text{SO}_4$ и $\text{Fe}_2\text{O}(\text{SO}_4)_2$. При термической обработке ярозита натрия или калия единственным промежуточным продуктом является $\text{Fe}_2(\text{SO}_4)_3$. Температуры разложения, как показали результаты определения парциального давления газообразных продуктов, в значительной мере затрагиваются типом тигля. Размер частиц исходного ярозита не оказывает влияния на температурный интервал реакций разложения и на реакцию его с оксидом цинка. Оценка результатов ТГ измерений проведена расчетом экспериментальных энергий активации отдельных стадий разложения и реакции его с оксидом цинка.