

IRON(III) OXIDE FORMED BY DECOMPOSITION OF SODIUM JAROSITE AS A RAW MATERIAL FOR CERAMIC PIGMENTS OF SPINEL TYPE

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Iron(III) oxide prepared by the pre firing of jarosite compounds is used for the synthesis of spinel pigments, e.g. $ZnFe_{1-x}Cr_{1+x}O_4$. The reactivity of this iron(III) oxide towards zinc oxide decreases as the temperature and duration of the precalcination are increased. The conditions of jarosite compound decomposition significantly influence the colour of the ceramic pigment of Zn-Fe-Cr type too. As concerns the processing of jarosites for the production of H_2SO_4 and Fe_2O_3 , the optimal conditions of their thermal decomposition are determined.

A new hydrometallurgical method of Cu-Pb-Zn concentrate processing eliminates iron as a basic iron(III) sulphate called jarosite. The precipitation of iron in this way is convenient because of the good filtrability and the small content of coprecipitated elements. Depending on the alkali used, the Na^+ , K^+ , NH_4^+ or H_3O^+ salt may be obtained, generally with the formula $M^+[Fe_3(SO_4)_2(OH)_6]^-$. Efficient processing of this waste jarosite precipitate for H_2SO_4 and iron(III) oxide pigment formation is a way to enhance the economic value of this hydrometallurgical process [1]. The mechanism and kinetics of thermal decomposition of jarosite compounds have been studied in several papers [2-6]. The present paper deals with the use of iron(III) oxide prepared in this way for the production of ceramic pigments of spinel type.

Experimental

A sample of Na jarosite from the factory in Bruntál was used. Analysis of this starting material was carried out for its contents of Fe_2O_3 and SO_3 after leaching in dilute H_2SO_4 and hot water: a Fe_2O_3 content of 48.4 wt.%

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(theor. 49.41%) was determined by firing to 1000° and leaching in water, while a SO₃ content of 25.1% (theor. 24.78%) was determined gravimetrically as BaSO₄. X-ray analysis showed only the diffraction maxima of jarosite. The specific surface area was 2.6 m².g⁻¹. The particle size distribution was reported in [3]; 50% of the particles were larger than 23 μm.

The jarosite samples were calcined in an electric muffle kiln under isothermal or dynamic (5 deg·min⁻¹) conditions in air atmosphere. Thermal analyses were carried out with a 1500D derivatograph, and granulometric analyses with a Joyce-Loebl Disc Centrifuge or with an SK Laser Micron Sizer (Japan).

Results and discussion

The thermal decomposition of Na jarosite proceeds in two steps [3]. The first reaction (I) involves the release of constitutional water and the forma-

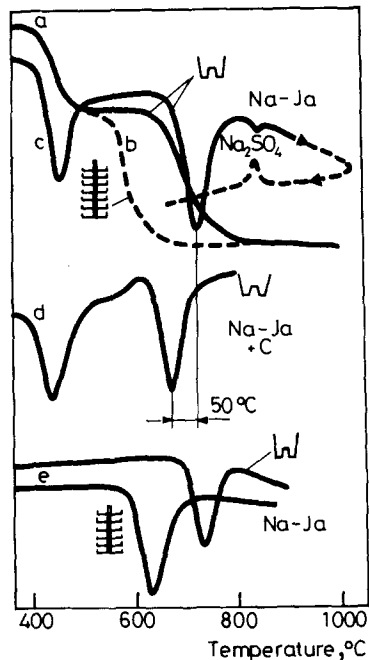


Fig. 1 TG, DTA curves of Na jarosite (NaJa) (a, b, c, e) and Na Ja + carbon (d)

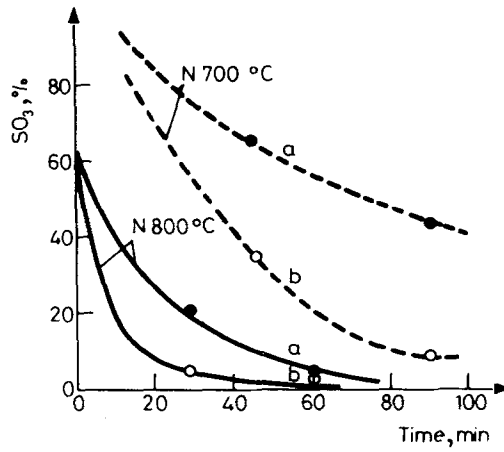


Fig 2 Residual $\text{SO}_3\%$ (except Na_2SO_4) in the calcimates (dynamic heating to 700 and 800°C for 0-90 min) a - conic crucible, b - plate

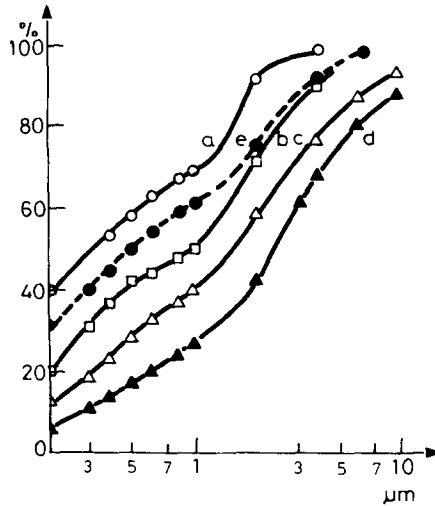


Fig. 3 Granulometric curves of NaJa prepared to 700-750-800°C for 30 min (a, b, c), or to 800°C for 60 min (d), sample d, ground in an agate mortar

tion of intermediate $\text{Fe}_2(\text{SO}_4)_3$, Fe_2O_3 and Na_2SO_4 . The existence of iron(III) sulphate and oxide was confirmed by X-ray examination. Na_2SO_4

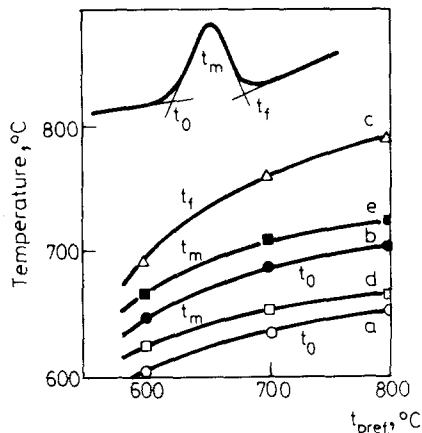


Fig. 4 Exothermic effect of ZnFe_2O_4 formation, samples prefired to t_{pref} , °C for 30 min (a, b, c), or for 60 min (d, e)

gives an exothermic effect in the DTA curve when cooling is applied (temp. range 850-870°). The second step (II) is connected with the release of SO_3 and SO_2 . Fe_2O_3 and Na_2SO_4 remain as products; the latter must be leached out in hot water. The losses on leaching are: after the first step 57.9% (theor. 62.9% Na_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$), and after the second step 22.9% (theor. 22.87% Na_2SO_4). The temperature of step II may be lowered when the decomposition of a thin layer of material is performed (lowering about 100 deg), or when milled carbon (5-10%) is added and a reducing atmosphere is formed (Fig. 1). However the second effect (analogy of [7]) is not so convenient when the gases are used for H_2SO_4 production. An increase of the calcination temperature (or holding time) causes a lowering of the SO_3 content (Fig. 2) and a very significant deterioration of the granulometric distribution (Fig. 3). The product of calcination (after leaching out of Na_2SO_4) must be milled; the laboratory grinding in an agate mortar yields a satisfactory distribution (Fig. 3, curve e). The reactivities of the iron(III) oxides formed were examined by means of DTA. As a measure of those reactivities, the temperatures of exothermic formation of ZnFe_2O_4 were used (Fig. 4). Increasing calcination temperature caused an increased t_0 and therefore a decreased reactivity. These results agree with application experiments. Iron(III) oxides were used as reaction component for synthesis of the industrial spinel pigment K 507 (Zn-Fe-Cr type). The colours of these pigments applied in a transparent glaze in the CIE Lab system show a loss

of colour purity with increase of the calcination temperature of prolongation of this process (Fig. 5).

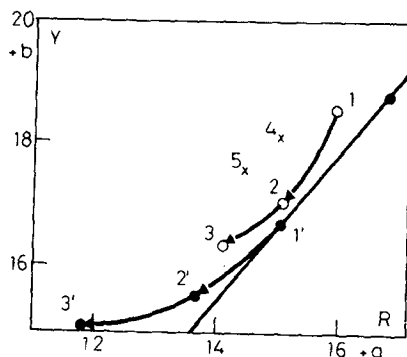


Fig. 5 Pigments in glaze, colour in CIE Lab system. 1, 2, 3 - jarosite prefired to 700-750-800°C/ for 30 min, 1', 2', 3' - 700-750-800°C for 60 min, 4, 5 - jarosite with carbon at 700°C for 30 and 60 min

Thus, the conditions of jarosite calcination must be selected with regard to the mode of application of the iron oxide as a product and for the side-production of H_2SO_4 . An optimal temperature range for nonisothermal firing is 700-750°, with a holding time of 1 hour.

References

- 1 V. Reichert, Proc. of Symposium Progressive Methods of Processing of Concentrated Polymetallic Ores, Jeseník, 1979, p. 117.
- 2 Z. Šolc and M. Trojan, Proc. Kommunikaty IV. Krajowe Seminarium im. St. Bretsznajdera, Plock, 1986, p. 15.
- 3 Z. Šolc, M. Trojan, D. Brandová and M. Kuchler, J. Thermal Anal., 33 (1988) 463.
- 4 Z. Šolc, M. Trojan and J. Jína, Thermanal 1988, Proc. p. B-28.
- 5 Z. Šolc, V. Balek, M. Trojan and M. Smíd, Thermanal, 1988, Proc. p. A-21.
- 6 J. Šubrt, T. Hanzlík, A. Solcová and V. Zapletal, Chem. prumysl, 36/61 (1986) 637.
- 7 B. Pacewska and J. Physiak, J. Thermal Anal., 33 (1988) 511.

Zusammenfassung — Mittels Vorbrennen von Jarositverbindungen erhaltenes Eisen(III)-oxid wird zur Herstellung von Spinellpigmenten, z.B. von $ZnFe_{1-x}Cr_{1+x}O_4$ verwendet. Die Reaktivität dieses Eisen(III)-oxides in der Reaktion mit Zinkoxid nimmt mit steigender Temperatur und Länge der Präkalzinierung ab. Die Bedingungen, unter denen die Zersetzung der Jarositverbindung stattfindet, bestimmen auch eindeutig den Farbton des Keramikpigmentes vom Typ Zn-Fe-Cr. Was die Verwendung dieser Jarosite für die Produktion von H_2SO_4 und Fe_2O_3 betrifft, wurden die optimalen Bedingungen für die Zersetzung ermittelt.