

## **THERMAL DECOMPOSITION OF MINERAL ZIRCON BY ALKALI METAL HYDROXIDES**

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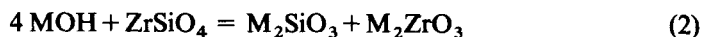
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Thermal decomposition of zircon mineral was studied in the presence of sodium and potassium hydroxides and in the presence of a waste mixture of hydroxides containing NaOH and KOH in a weight ratio of 2:3. The process was controlled in such a way that the decomposition products might contain the minimum possible amount of alkali and could thus be applied for the syntheses of zircon pigments without any further exacting treatment.

Zircon mineral is a very stable substance both thermally and chemically [1, 2] and is applied, *inter alia*, in ceramics. In these materials it serves as an opacifying agent, and its decomposition products can be transformed into zircon pigments [3, 4]. Due to the stability of the mineral, however, its decomposition is very difficult [2, 5]. The more modern methods make use of high temperatures [5] and have high demands with respect to construction materials and energy consumption. Therefore, it is at present again becoming topical to return to "classical", less energy-demanding ways of decomposition of zircon with alkali. Especially promising are the methods [4] utilizing some alkali wastes, e.g. the hardening bath wastes from the machine industry which are dealt with in this report.

### **Experimental**

In this report we describe the decomposition of Australian zircon mineral containing 96%  $ZrSiO_4$ , finely ground, most particles (more than 90% by wt.) being within the limits from 1 to 4  $\mu m$ , with a specific surface of 0.65  $m^2/g$ . With regard to the application of the decomposition products which was followed in our laboratory, it was our purpose to obtain a product corresponding only to alkali metal silicozirconate (1), and not to a mixture of alkali metal silicate and zirconate (2):



Verification experiments at 600–900° showed the optimum (for this purpose) molar ratio of hydroxide to zircon to be 2.0 (calculated on dry MOH) and corresponding to Eq. (1). Hence, with this ratio we prepared the individual starting mixtures of hydroxide and zircon for TA and calcination experiments. The same ratio was also chosen in the case of application of the waste hydroxide mixture represented by a hardening bath discarded after repeated application in the machine industry and containing NaOH and KOH in the weight ratio of 2:3. The TA of the starting mixtures were carried out with a derivatograph Q-1500 apparatus. The subsequent calcinations were performed in an electric furnace with programmable heating: either for the same period at various temperatures or at several chosen temperatures (time-dependence). The decomposition products were identified and analysed by IMA: X-ray diffraction analysis, IR spectroscopy, and the AAS method. The degree of decomposition of the zircon was determined by the extraction experiments developed in our laboratory [6], a gravimetric determination of the zircon content besides the other zirconium components.

### Results and discussion

The thermal analyses (5 deg/min, an open Pt crucible) showed that the first endothermic process consists in the release of the moisture present in the hydroxides. In the case of KOH, this corresponded to 9.5% by wt. of the starting mixture (22% by wt. of the KOH), the respective temperature interval being 150–390°. For NaOH, the respective values were 6.5 and 18.4% in the interval 100–240°, and for the hydroxide mixture (denoted as KOH—NaOH) 8.3 and 20.5% at 150–390°; in the last case, a certain amount of NaHCO<sub>3</sub> present in the NaOH also made itself felt, being decomposed in another endothermic process at 240–360°. The DTA curve indicated the melting of NaOH and KOH at about 320 and 380°, respectively, and a modification transformation of KOH at 248°. Zircon is decomposed above 400° with release of the constitutional water according to Eq. (1). In the case of NaOH, this process takes place in the interval from 380 to 560°, the decisive part of the water being released, and the reaction proceeding relatively quickly at 500–560°; for KOH, the respective intervals are 400–650° and 550–650°, and for KOH—NaOH they are 350–540° and 480–540°. The release of the constitutional water itself represents a distinctly endothermic process, whereas the formation of alkali metal silicozirconate is exothermic. These two processes are mutually almost overlapping, and hence the overall energy balance of decomposition reaction (1) is slightly exothermic. Therefore, the DTA curves have a complex course in these temperature regions and confirm this idea. When reaction (1) is finished (TA 800°), the DTA curves show no more energy changes and the

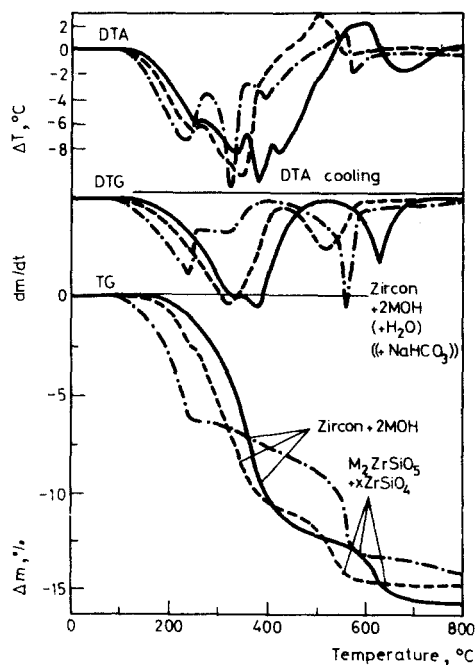


Fig. 1 Thermal curves of starting mixtures—zircon + 2 MOH

sample weight (TG) is almost steady, too. The sample corresponds mainly to  $M_2ZrSiO_5$ , which was confirmed by the IMA methods and by a certain content of undecomposed zircon. After completed TA, the samples were submitted to acid extraction (6), and the zircon content was found to be 12.3% (for KOH), 38.8% (NaOH), and 19.0% (KOH—NaOH).

Under isothermal conditions in an electric furnace, the decomposition proceeds with higher yields. After a 1-hour calcination at the respective temperature (Fig. 2),

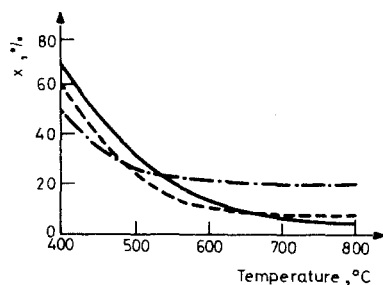


Fig. 2 The dependence of the undecomposed zircon portion ( $x$ ) on the calcination temperature (calc. time 1 h)

20% undecomposed residue remained at 600°, i.e. 80% decomposition took place. With KOH this residue was only about 10% and was further decreased with increasing temperature (4% at 800°, i.e. 96% decomposition). As already indicated by the TA, the application of the hydroxide mixture KOH—NaOH (3 : 2) combines the advantages of application of the individual hydroxides, i.e. the KOH component allows a higher decomposition degree and the NaOH component decreases the decomposition temperature and accelerates its course (a faster approach to equilibrium—Fig. 3). For a higher yield of the decomposition, it is more advantageous if the KOH component predominates in the mixture (e.g. the ratio 3 : 2 is used). This fact further increases the technological importance of the application of the above-mentioned waste hydroxide mixture. Its application at 600° resulted in decomposition of 80% (20% residue) and 94% (6%) of the zircon after 0.5 and 1.5 h, respectively.

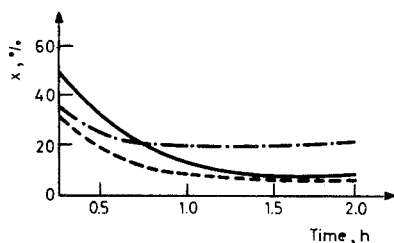


Fig. 3 The dependence of the undecomposed zircon portion ( $x$ ) on the calcination time at 600 °C

## References

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**Zusammenfassung** — Es wurde die thermische Zersetzung eines Zirkonminerals in Gegenwart von Natrium- und Kaliumhydroxid sowie in Gegenwart einer Altlaugung mit einem Gehalt an NaOH und KOH im Verhältnis zwei zu drei untersucht. Der Prozeß wird derart gesteuert, daß die Zersetzungsprodukte einen möglichst geringen Anteil an Laugung besitzen und so ohne weitere arbeitsaufwändige Behandlungen zur Synthese von Zirkonpigmenten verwendet werden können.

**Резюме** — Термическое разложение циркониевого минерала изучено в присутствии гидроокисей натрия и калия, а также в присутствии отработанных смесей гидроокисей натрия и калия в весовом соотношении 2 : 3. Процесс контролировался таким образом, что продукты разложения могли содержать только минимально возможное количество щелочей и, следовательно, такой метод может быть использован для получения циркониевых пигментов без какой-либо дальнейшей обработки.