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Technical note

Decomposition of sodium zincate in alkaline solution by dilution

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ABSTRACT

The decomposition of sodium zincate, $NaZn(OH)_3$, in the alkaline solution (Na_2O–ZnO–H_2O equilibrium system) containing 30–34% Na_2O is complex because of the temperature dependence of the solid precipitate which occurred. In this paper, the sodium zincate decomposition in the alkali solution containing 32.43% Na_2O and 22.93% ZnO is investigated by assessing the effects of temperature, dilution factor and time on the decomposition rate (R) of $NaZn(OH)_3$. The results show that ZnO precipitates when the saturated $NaZn(OH)_3$ solution at 100 °C is subjected to water dilution and subsequent cooling to 75, 50 and 25 °C. The decomposition kinetics at 75 °C can be described by the equation, $R = 1 - e^{-1.1t^{0.3}}$, where t is the reaction time. ZnO crystal obtained is rod-shaped and becomes coarser at higher temperatures and lower dilution times. The decomposition rate of $NaZn(OH)_3$ increases with dilution temperature, stirring time and dilution factors. Sodium zincate decomposition and recycling of alkaline solution can be illustrated using the Na_2O–ZnO–H_2O equilibrium phase diagram, which are similar to those in alumina production. The results are beneficial to the extraction of zinc from its oxide ores leached with alkaline solution.

1. Introduction

Zinc oxide ores have received increasing attention due to the decreased sphalerite ores for zinc production (De Wet and Singleton, 2008; Jiang, 2004; Yuan et al., 2010). However, it is difficult to treat zinc oxide ores due to the presence of multiple minerals including carbonate (smithsonite) and silicate (hemimorphite) (Feng and Yang, 2007; Navidi Kashani and Rashchi, 2008). Alkaline leaching has proved effective for the treatment of zinc oxide ores because the metal can be leached in the form of $Zn(OH)_4^{2-}$ in strong alkaline solution (pH > 12) (Frenay, 1985; Ikenobu, 2000; Shirin et al., 2006; Thedford et al., 1954; Zhang and Muhammed, 2001). Over 85% of Zn can be leached from the smithsonite-bearing ore when the leaching operation is conducted above 95 °C using 5 mol/L NaOH (Zhao and Stanforth, 2000). On the other hand, alkaline leaching of refractory zinc silicate (hemimorphite) with 5 mol/L NaOH and mechanical agitation could extract 73% of Zn at 85 °C (Chen et al., 2009) and 95% of Zn at 110 °C (Zhao et al., 2009). These studies clearly demonstrate that leaching temperature and alkali concentration have great effects on the leaching process.

In order to reveal the mechanism of alkaline leaching of zinc oxide ore, zinc oxide solubility in sodium hydroxide solution from 25 to 100 °C was measured in our previous work (Chen et al., 2012). It was found that the equilibrium concentration of zinc oxide first increases and then decreases with increasing concentration of Na_2O, suggesting the same changing tendency as that in alumina production. The variation in the concentration of zinc oxide leads to a maximum value, forming a "peak" point indicating the phase change from ZnO to $NaZn(OH)_3$ that controls the solubility. When the concentration of Na_2O is less than that of the "peak" point at different temperatures, the solubility of ZnO has the same variation tendency. Conversely, the solubility is different when the concentration of Na_2O is more than that of the "peak" point at different temperatures. The solubility of $NaZn(OH)_3$ decreases with increasing alkali concentration at the same temperature, which shows that $NaZn(OH)_3$ in alkali solution may be decomposed by decreasing temperature and/or alkali concentration. Moreover, the concentration of the "peak" points is about 34% Na_2O/26% ZnO at 100 °C, 30% Na_2O/20% ZnO at 75 °C, 29% Na_2O/19% ZnO at 50 °C and 28% Na_2O/19% ZnO at 25 °C. The concentrations of Na_2O and ZnO at the three "peak" points in the temperature range from 25 to 75 °C are lower than that of 100 °C. The solid precipitate in the sodium zincate solution containing 30–34% Na_2O in the Na_2O–ZnO–H_2O system is ZnO at 100 °C but is $NaZn(OH)_3$ at 25–75 °C. The decomposition of equilibrated sodium zincate solution appears to be complex and should be studied in detail, which has not been reported yet.

It is well considered that the chemical properties of zinc and aluminum are very similar and their oxides (ZnO and Al_2O_3) are amphoteric. Zinc and aluminum form metal cations (Zn^{2+} and Al^{3+}) in acid solution but anions ($ZnO_2^{2-}/Zn(OH)_3^-$ and $AlO_2^-/Al(OH)_4^-$) in alkaline solution. Alumina production has been carried out successfully for many years by the Bayer process, which is based on the solubility of Al_2O_3 in sodium hydroxide solution. Al_2O_3 can be extracted from ores into solution which can be decomposed to produce Al_2O_3 production by decreasing temperature and alkali concentration. Does zinc oxide production follow a similar process? In principle, the leaching solution may be decomposed to produce ZnO like Al_2O_3. It is shown from our former

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experiments that temperature and alkali concentration affect complexly/greatly the equilibrium process when the leaching solution contains more than 30–34% Na_2O (Chen et al., 2012).

The main aim of this study is to determine the decomposition of the equilibrated sodium zincate solution containing 30–34% Na_2O in the Na_2O–ZnO–H_2O system. It demonstrates the effects of decomposing temperature, dilution factors and reaction time on the decomposition rate of $NaZn(OH)_3$ from the solution containing 32.43% Na_2O and 22.93% ZnO. Alkali recycling is also investigated by comparing it with that in the Bayer process for alumina production. The zinc Bayer process is firstly used in the work. Compared with the Bayer process for alumina, the treatment of sodium zincate includes three steps (dissolution, dilution/decomposition and evaporation) but no seed is required for crystal. This may provide some theoretical experiments for a simple process of zinc oxide metallurgy.

2. Experimental

Sodium zincate solution was prepared by dissolving analytical grade sodium hydroxide (334.76 g) and zinc oxide (183.44 g) in 281.80 mL distilled water in a 1.0 L PTFE (polytetrafluoroethylene) beaker (as shown in Fig. 1) which was then placed in an oil bath with stirring for 48 h at 100 °C until the Na_2O–ZnO–H_2O system equilibrium was achieved. During the process, a slurry was formed, which later naturally separated to a clear solution and precipitated through gravity sedimentation after stirring was stopped. The clear solution was sodium zincate solution which was collected and used for dilution experiments.

The sodium zincate solution was diluted with 1–9 times weight distilled water to 100 g end quantity in a 150 mL plastic bottle (made in Shanghai Plastic Factory, China) until its temperature dropped to 75, 50 and 25 °C, respectively. The bottle was rapidly placed in a mechanical shaker (QHZ-12A model, made by Changzhou Experimental Instrument Co. Ltd. Factory, China) and stirred for given time periods at 145 r/min in each case. A small portion of the solution was sampled for analysis after centrifugation (Centrifuge, S5300 model, made by Shanghai Yide Industrial Development Co. Ltd., China). The concentrations of ZnO and Na_2O were determined by EDTA titration and neutralization titration. The decomposition rate (R) of sodium zincate was calculated by (Chen et al., 2012)

$$R = \frac{w_1 - nw_2}{w_1(1-w_2)} \times 100\% \quad (1)$$

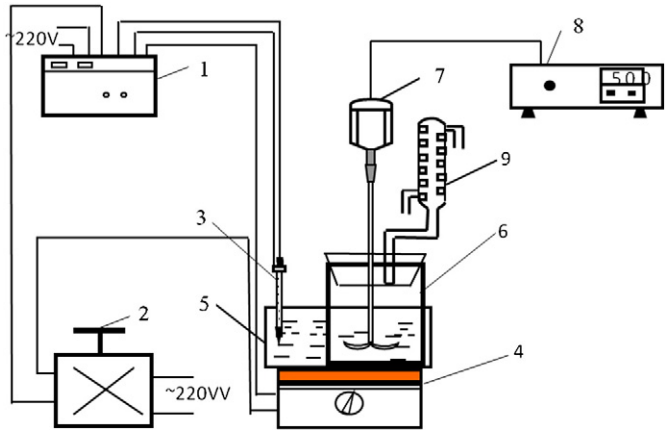

Fig. 1. Experimental apparatus for sodium zincate decomposition. 1—Power relay, 2—contact pressure controller, 3—mercury contact thermometer, 4—magnetic blender, 5—oil bath pot, 6—Teflon beaker, 7—agitator stir transformer, 8—blender motor, 9—governor, and 10—condenser tube.

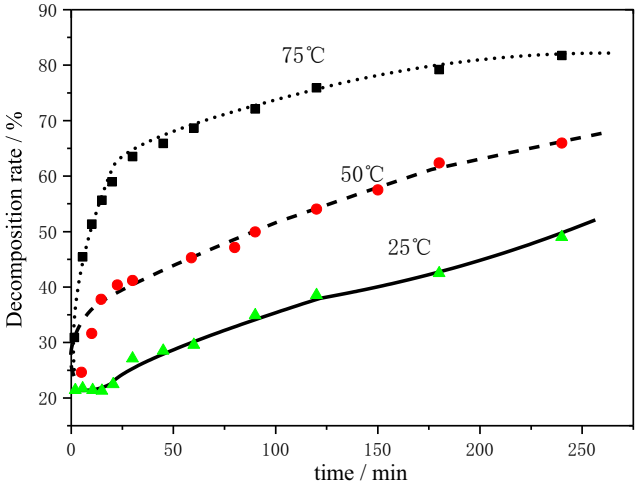

Fig. 2. Effect of temperature on decomposition rate of sodium zincate (n = 5).

where w_1 and w_2 are the ZnO contents in the original clear solution and in the centrifuged solution, respectively.

3. Results and discussion

3.1. Effect of temperature

Fig. 2 shows the effect of temperature on the decomposition rate of sodium zincate in the alkaline solution diluted 5 times at various temperatures. It indicates that the decomposition rate increases with the decomposition temperature. For example, the decomposition rates of sodium zincate at 75, 50 and 25 °C after stirring for 30 min are 62.6, 44.4 and 22.5%, respectively. The rates increase to 81.1, 65.9, 49.0% at 75, 50, 25 °C after stirring for 240 min, respectively. Supersaturation slightly affects the formation and growth of nucleation because of the same solubility which is independent of temperature when the concentration of Na_2O is lower than 28% after diluting 5 times (Chen et al., 2012). However, the formation and growth of nucleation takes place more quickly at higher decomposing temperatures (Li, 2008), leading to the higher decomposition rate. This shows that there exists a changing reaction rate.

Further understanding of the decomposition can be achieved by determining the decomposition kinetics. The following equation is used to describe the relationship between the decomposition rate and time (Li, 2008; Uekawa et al., 2004):

$$R = 1 - e^{-kt^n} \quad (2)$$

where k is the rate constant on the formation of new nucleation and its growth and n is an index, whose values were obtained for the decomposition listed in Table 1.

It is observed from Table 1 that the values of k increased with the decomposition temperature. It also shows that more sodium zincate decomposes at higher temperatures. 75 °C is thus a reasonable temperature for decomposition.

Table 1
Values of k and λ by fitting from the kinetics equation in Eq. (2).

Temperature/°C	75	50	25
k/s^{-1}	1.10	0.90	0.81
λ	0.29	0.28	0.27