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Measurements of zinc oxide solubility in sodium hydroxide solution from 25 to 100 °C

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Abstract: The solubility of zinc oxide in sodium hydroxide solution was measured in a closed polytetrafluoroethylene vessel from 25 to 100 °C. The ZnO solubility was determined by employing the method of isothermal solution saturation. The results show that only ZnO solid exists in the equilibrium state in the low concentration alkali regions, and the solubility of zinc oxide is almost invariable with temperature. With the increase of alkali concentration, equilibrium solid turns from ZnO to $NaZn(OH)_3$ suddenly, this mutation is called invariant point. The alkali concentration of the invariant points increases with increasing temperature, but the solubility of $NaZn(OH)_3$ decreases with increasing alkali concentration at the same temperature. At the same Na_2O concentration, the higher the temperature is, the higher the solubility of $NaZn(OH)_3$ is.

Key words: ZnO solubility; sodium hydroxide solution; $Na_2O-ZnO-H_2O$ system; equilibrium phase diagram

1 Introduction

As sphalerite mines are becoming exhausted, researchers have diverted attention to zinc oxide ores. It is more necessary to extract zinc from zinc oxide ores [1−4]. There is a lot of gangue in the zinc oxide ores. Some metals, such as Mg, Ca and Fe, are leached if the ores are treated with acid leaching, and the cost is high. But the cost can be cut if zinc oxide ores are treated by alkali [5]. Moreover, ZnO can react with NaOH to produce $ZnOH^+$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ at pH=6−14. When the alkaline concentration is higher (pH>12), $NaZn(OH)_3$ or $Na_2Zn(OH)_4$ is produced as:

$$NaOH+ZnO+H_2O=\!=NaZn(OH)_3$$

$$2NaOH+ZnO+H_2O=\!=Na_2Zn(OH)_4$$

$NaZn(OH)_3$ or $Na_2Zn(OH)_4$ has certain solubility in the alkaline solution. Many experts have researched the leaching of zinc oxide ores with alkaline. ZHAO and STANFORTH [6] and FENG et al [7] obtained more than 85% Zn when the leaching operation was conducted with 5 mol/L NaOH above 95 °C. In the previous studies, it was found that alkali leaching can obtain 73% Zn at 85 °C and 90% Zn at 110 °C with 4.5 mol/L NaOH solution [8,9].

It is increasingly popular to treat zinc oxide ores with alkali. For alkaline leaching, leaching temperature and alkali concentration have great effect on zinc extraction. So, it is necessary to investigate the solubility of ZnO in the NaOH solution from 25 to 100 °C [10,11]. But there are few researches on it except the report by URAZOV et al [12]. It was found that ZnO solubility was higher at 75 °C than that at 25 °C when Na_2O concentration was below 25%. According to the results, zinc oxide or zinc hydroxide could be precipitated by decreasing temperature. Therefore, it would be an appropriate method to extract zinc from zinc oxide ores with alkali leaching. However, our previous studies showed that there was no ZnO precipitation by decreasing temperature. Thus, it is important to re-measure the ZnO solubility in NaOH solution from 25 to 100 °C.

2 Experimental

2.1 Material

All the reagents used in this research are of analytical grade. Zn concentration was analyzed by EDTA titration and Na_2O concentration was analyzed by neutralization titration with H^+ in the solution. Solid was analyzed by chemical methods and characterized by

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X-ray powder diffraction analysis using Cu K_{α} radiation. The sodium zinc hydroxide solid obtained was verified by Schreinemaker's method [13,14].

2.2 Equipment and procedure

The ZnO solubility was determined by employing the method of isothermal solution saturation [13]. Experiments were carried out in a closed polytetrafluoroethylene (PTFE) vessel in a water bath below 75 °C, while at 100 °C it was in an oil bath. ZnO was added into 0.8 L alkaline solution. Different equilibrium time was taken at different alkali concentration and temperature. Thus, when the zinc content of the solution did not change for a long time (more than 12 h) and the solid was redundant (about more than 20 g) in the solid phase, the reaction of ZnO with alkali reached balance. The slurry was naturally separated through gravity sedimentation until the solution was clear.

Their content in the leaching solution was calculated by:

$$w_{\mathrm{m}}=\frac{C_{\mathrm{m}}\times V}{W}\times 100\%$$

where, w_{m} is the content of Na_2O or ZnO in the leaching solution; C_{m} is the concentration of Na_2O or ZnO in the leaching solution; V is the volume of the leaching solution and W is the mass of the leaching solution.

3 Results and discussion

3.1 Phase diagram of Na_2O−ZnO−H_2O system at 25 and 75 °C

The equilibrium data at 25 and 75 °C are plotted in Fig. 1. Points *A* and *D* represent solids ZnO and $NaZn(OH)_3$, respectively (as shown in Fig. 2). Points *O*, *B* and *C* are all located on the saturated liquid line. The solubility of ZnO in pure water at 30 °C is only 0.0016 mg/mL and can be considered to be 0. So, point *O* on the ordinate axis of the diagram represents the solubility of ZnO in pure water at 25 °C. Curves *OB* and *BC* represent the compositions of saturated ternary solutions that are in equilibrium with solids ZnO (*A*) and $NaZn(OH)_3$ (*D*)(containing 22.3% Na_2O and 58.3% ZnO), respectively. Point *B* is the intersection point of curves *OB* and *BC* and is called the invariant point. Two ingredients points for a sample are one point in the solid above curve *OB* and one point in liquor on the curve *OB*. Two different coupling lines of these two points would cross at point *A* (with 100% ZnO). Similarly, different

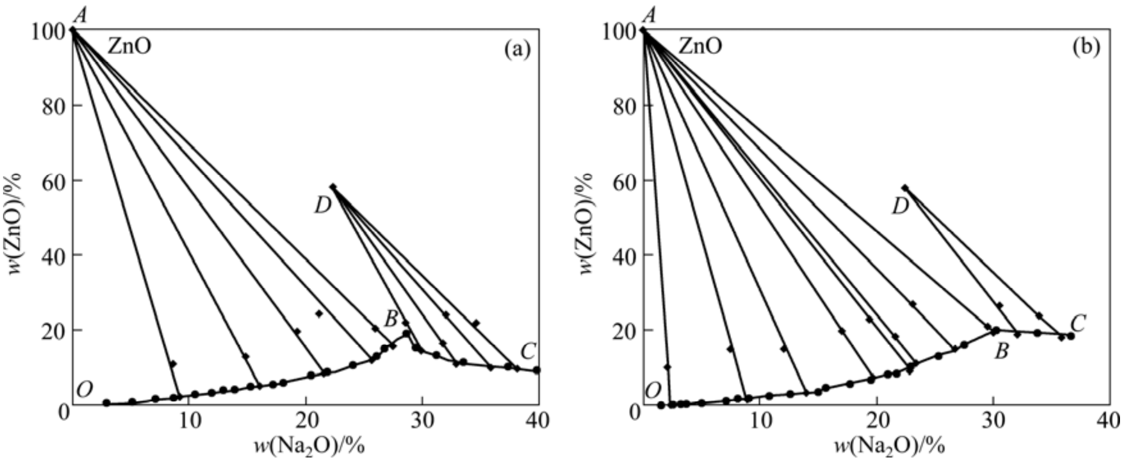

Fig. 1 Equilibrium diagram of Na_2O−ZnO−H_2O system at 25 °C (a) and 75°C (b)

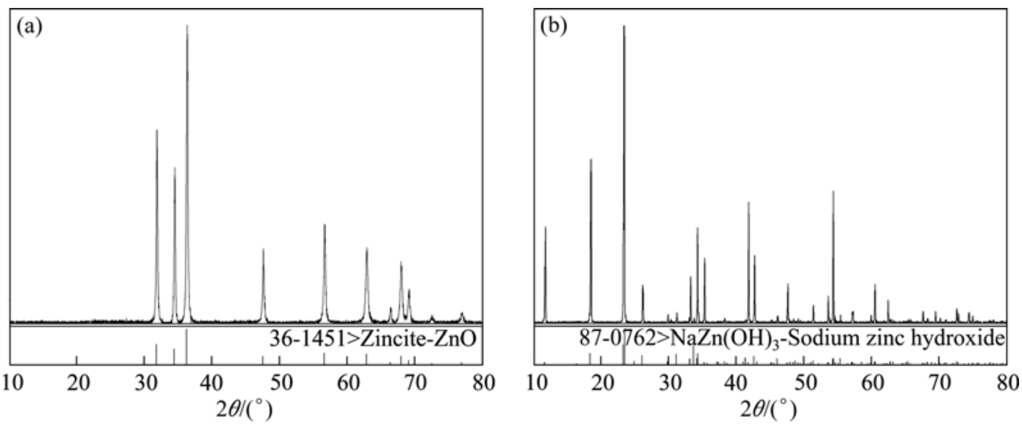

Fig. 2 XRD patterns of equilibrium solid phase of line *OB* (a) and line *BC* (b)

coupling lines of two ingredients of solid above curve *BC* and liquor on curve *BC* would cross near point *D*, which indicates that only one identical equilibrium solid point exists when Na_2O concentration is more than 28%.

The straight line connected ZnO or $NaZn(OH)_3$ (*D*) with water (origin) does not cut its corresponding saturation curve, which indicates that double salt is incongruently soluble in the ternary system at 25 °C. The dots of the straight line are the contents of equilibrium wet solid phase. Moreover, the higher the ZnO content of liquor is, the closer it is to *B* point.

There are the same results in the system at 75 °C.

3.2 Solubility

The solubility of zinc oxide is determined at different Na_2O concentration at 25, 50, 75 and 100 °C, respectively, and the results of the ternary phase diagrams of Na_2O−ZnO−H_2O system are shown in Fig. 3. The solubility of zinc oxide in 5% Na_2O solution increases slowly, and then increases faster in 5%−28% Na_2O solution at 25 °C, in 5%−29% Na_2O solution at 50 °C, in 5%−30% Na_2O solution at 75 °C and in 5%−34% Na_2O solution at 100 °C, respectively. The change tendency of the four solubilities of zinc oxide (Line *OB*) is almost similar at the four different temperatures. However, the four maximum values of zinc oxide solubility are different. After the solubility reaches the maximum, with further increase of alkali concentration, the solubility of $NaZn(OH)_3$ begins to decrease. The higher the temperature is, the higher the solubility of $NaZn(OH)_3$ is. It is similar to the solubility of zinc oxide in the KOH solution [15]. Thus, according to Bayer process of alumina, ZnO in the alkaline solution on the left part of equilibrium curve cannot be obtained but $NaZn(OH)_3$ in the alkaline solution on the right part of equilibrium curve can be obtained. Fortunately, ZnO can be obtained by diluting.

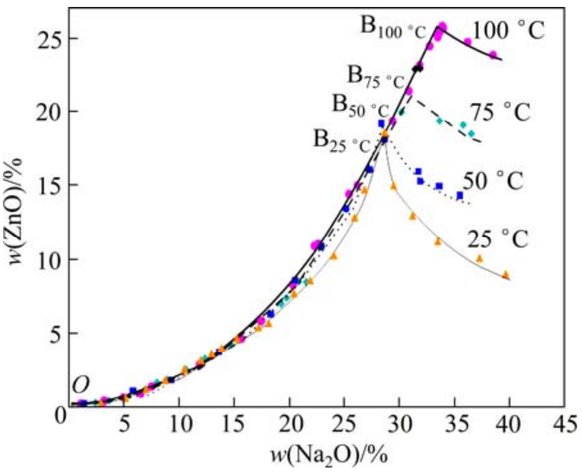

Fig. 3 Solubility of zinc in Na_2O−ZnO−H_2O system

However, the above results are different from the research by URAZOV et al [12], as shown in Fig. 4. The solubility of zinc oxide increases obviously with the increase of temperature and Na_2O concentration. The above results are similar to our previous work.

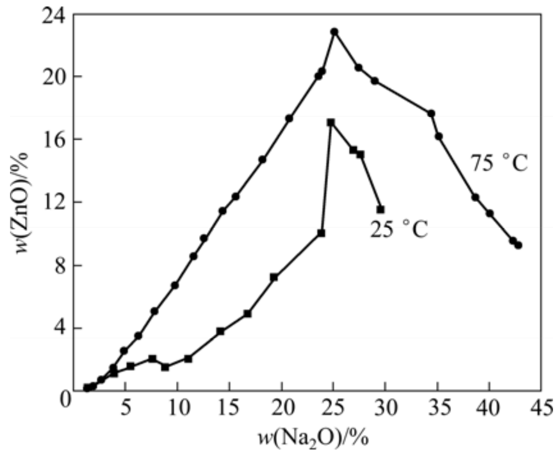

Fig. 4 Solubility of zinc oxide in Na_2O−ZnO−H_2O system by URAZOV et al

4 Conclusions

1) The equilibrium phase diagram of Na_2O−ZnO−H_2O system in the sodium hydroxide solution was revalued from 25 to 100 °C. The solubility of zinc oxide is different from the report by URAZOV et al while it is similar to that in the KOH solution. It is instructive to treat zinc oxide ores with sodium hydroxide.

2) The change tendency of the solubility of zinc oxide is similar at 25, 50, 75 and 100 °C, but the four maximum values of zinc oxide solubility are different, and that of $NaZn(OH)_3$ decreases with increasing alkali concentration. At the same Na_2O concentration, the higher the temperature is, the higher the solubility of $NaZn(OH)_3$ is.

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25~100 °C 下 ZnO 在 NaOH 溶液中溶解度测定

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摘 要：采用等温溶解饱和度法，在 25~100 °C 下于密闭的聚四氟乙烯容器内测定 ZnO 在 NaOH 溶液中的溶解度。结果表明：在低浓度 NaOH 溶液中，平衡体系中只有 ZnO 一种固相存在，此时氧化锌的溶解度基本上不随温度改变。随着 NaOH 浓度增高，平衡固相由 ZnO 突然转变为 $NaZn(OH)_3$。这个突变点叫不变点。不变点的 NaOH 浓度随着温度的升高而增加，但在同一温度下 $NaZn(OH)_3$ 的溶解度随 NaOH 浓度增加而减少。在同 Na_2O 浓度下，温度越高，$NaZn(OH)_3$ 的溶解度越高。

关键词：ZnO 溶解度；NaOH 溶液，Na_2O−ZnO−H_2O 体系；平衡相图

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