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Solubility investigations in the $NaOH-Na_3VO_4-Na_2CrO_4-Na_2CO_3-H_2O$ system at (40 and 80) °C

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ABSTRACT

To realize the effective separation of Na_3VO_4, Na_2CrO_4 and the impurity Na_2CO_3 in a newly developed vanadium production process using concentrated alkaline solution as reaction media, the equilibrium liquid phase solubility and solid phase compositions of the $NaOH-Na_3VO_4-Na_2CrO_4-Na_2CO_3-H_2O$ system at (40 and 80) °C were measured. The obtained solubility data were afterwards compared with quaternary $NaOH-Na_3VO_4-Na_2CrO_4-H_2O$ subsystem to investigate the salting-out effect of Na_3VO_4, Na_2CrO_4 and Na_2CO_3. Further, a strategy for effective separation of Na_3VO_4 and Na_2CrO_4 from the $NaOH-Na_3VO_4-Na_2CrO_4-Na_2CO_3-H_2O$ pentabasic system has been proposed on the basis of detailed analysis of crystallization zones.

1. Introduction

Vanadium is predominantly used as an alloying material in steel and iron industries for the production of high-strength low-alloy (HSLA) steels, accounting for more than 85% of global vanadium consumption, due to its distinct feature to increase the steel strength. With the fast development of global construction industries, the demand and market for vanadium products have been performing strong for more than a decade [1–3]. In addition, vanadium and related products have been utilized as titanium alloy additives, catalysts, electrolytes and have gained new research attention in the last few years as accumulating evidences suggest that vanadium could be used as therapeutic in cancer treatment [4–13].

Instead of primary ores, vanadium is usually extracted from metallurgical slag including converter and smelter slag, waste catalysts, oil fly ash and stone coal, among which vanadium-bearing slag accounts for 58% of the world's total production [14–16]. Meanwhile, the most popular vanadium slag extraction process is sodium salt roasting method mainly consists of the following typical operation units: sodium salt roasting, acid/water leaching, purification and precipitation [17–19]. Unfortunately, this process has inherent flaws including low vanadium extraction efficiency (average 65–85%), high operation temperature (850 °C), and release of hazardous substances including ammonia–nitrogen wastewater and aggressive gases (SO_2 and Cl_2). Moreover, the chrome spinel, which is generally associated with vanadium in the slag, is much more stable than vanadium spinel in thermodynamic consideration, and thus cannot be oxidized effectively unless the operation temperature is increased to above 1150 °C [20]. In this regard, the sodium salt roasting method is not able to extract chromium from vanadium slag synchronously, and therefore producing hazardous chromium containing tailings.

On the basis of cleaner production and industrial ecology principles, a novel technology named sub-molten salt method (SMS) has been developed by Institute of Process Engineering, Chinese Academy of Sciences for the recovery of vanadium and associated chromium from vanadium slag simultaneously [21,22]. In this new process, highly concentrated NaOH solution which is approximately 70–80 wt% is utilized to treat the vanadium slag, and the main reactions are listed as follows:

$$1/2FeO\cdot V_2O_3 + 3NaOH + 5/8O_2 \rightarrow 1/4Fe_2O_3 + 3/2H_2O + Na_3VO_4 \quad (1)$$

$$1/2FeO\cdot Cr_2O_3 + 2NaOH + 7/8O_2 \rightarrow 1/4Fe_2O_3 + H_2O + Na_2CrO_4 \quad (2)$$

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Vanadium and chromium are concurrently oxidized at 200 °C, which is significantly lower than that of the conventional method, and nearly 95% vanadium and 85% chromium recovery rates are achieved after reaction for 5 h. During the reaction, Na_2CO_3 is generated due to the reaction of NaOH and CO_2 in the air and others from the industrial grade NaOH feed material (0.3–2.5 wt%). Followed by dilution with water and filtration at 80 °C, a solution containing mainly NaOH, Na_3VO_4, Na_2CrO_4 and Na_2CO_3 is obtained at 250–300 g L^{-1} alkaline concentration.

Therefore, the investigation of Na_3VO_4 and Na_2CrO_4 solubility in Na_2CO_3 saturated NaOH solutions is thus of great importance for the design of effective separation method to obtain Na_3VO_4 and Na_2CrO_4 from the alkaline leaching solution. Due to the lack of relevant data in literature, solubility of the pentabasic $NaOH–Na_3VO_4–Na_2CrO_4–Na_2CO_3–H_2O$ system at (40 and 80) °C were examined and analyzed, the specific temperatures were chosen in consideration of the filtration temperature and economical efficiency of industrial operation at the same time.

2. Experimental

2.1. Apparatus and reagents

A HZ-9212S type thermostatic shaking water bath with an uncertainty of ± 0.1 °C and a HZ-9612K type thermostatic shaking air bath with an uncertainty of ± 0.1 °C were used to keep the samples which were contained in polypropylene bottles with a capacity of 250 mL to reach equilibrium at (40 and 80) °C, respectively. ICP-OES (PE Optima 5300DV, Perkin–Elmer) was used to determine the concentrations of sodium, vanadium and chromium in liquid phases and the solid phases were first dried in electrothermal air drying oven (DHG-9140A, Shanghai Yiheng Scientific Instrument Corporation) and then X-ray powder diffractometer PANalytical Empyrean was used for the solid phase identification.

The research was performed with analytical grade chemicals. Sodium hydroxide (NaOH, >96%), sodium chromate ($Na_2CrO_4 \cdot 4H_2O$, >99%) and anhydrous sodium carbonate (Na_2CO_3, >99.8%) were obtained from Sinopharm Chemical Reagent Company, and sodium vanadate ($Na_3VO_4 \cdot 3H_2O$, >99%) was provided by the Chengde Iron & Steel Company. High-purity Milli-Q water, with a resistivity of above 18.2 MΩ cm at ambient temperature, was used to prepare the series of supersaturated solutions and chemical analysis.

2.2. Experimental procedure

To guarantee the accuracy of the solubility data, the supersaturated solutions were prepared via two methods. One approach was based on the principle of excessive Na_3VO_4, Na_2CrO_4 and Na_2CO_3 crystallization from supersaturated NaOH solutions. First, according to the phase equilibrium composition, a series of appropriate concentration NaOH solutions which ranged from 1 to 700 g L^{-1} were loaded into glass beakers which positioned in a constant-temperature water bath at (60 or 95) °C, higher than the experimental equilibrium temperatures in order to reach supersaturation. Then sodium vanadate, sodium chromate and anhydrous sodium carbonate were added into the alkaline solutions with a 250 rpm stirring speed. The stirring was stopped when Na_3VO_4, Na_2CrO_4 and Na_2CO_3 salts could not dissolve any more as suggested by slurry being clearly formed. These slurries, 200 mL each, were then transferred into polyethylene bottles and sealed with polytetrafluoroethylene tape to prevent evaporation during equilibrating. The bottles were then placed in the thermostatic shaking bath maintained at temperatures of (40 and 80) °C and a constant shaking was maintained with a speed of 180 rpm to accelerate the equilibration and homogeneity of the slurries.

The second approach was based on the dissolution of Na_3VO_4, Na_2CrO_4 and Na_2CO_3 in NaOH solutions. First, the same as described in the above paragraph, NaOH solutions of predetermined concentrations were prepared and kept in the thermostatic shaking bath at (40 and 80) °C, respectively. Then small amounts of sodium vanadate, sodium chromate and anhydrous sodium carbonate salts were added into those NaOH solutions every day until the solution reached saturation. Sampling of the liquid phase and examining of the solid phase were performed every day before further addition of the salts into the solutions. The equilibrium state was considered to be achieved when the composition of liquid phase did not change with either time or further addition of salts, and vanadium-bearing, chromium-bearing and carbonate-bearing phases were presented in the solid phases simultaneously.

The equilibrium was assumed to be ultimately realized when the composition of the solutions prepared through the two mentioned different approaches above agreed with each other. Shaking was stopped once the system was found in an equilibrium state, and the samples were kept in the baths for 10 more days in order for the suspended precipitates to settle.

The density was determined by taking 1 mL equilibrium liquid phase sample using a sampling gun and then transferred to a pycnometer. Each data represents the average of at least three individual measurements with the precision of ± 0.0002 g cm^{-3}. Next, the pycnometer content was transferred quantitatively into a volumetric flask, followed by proper dilution with high purity water for the ion concentration determination. To prevent the saturation liquid from crystallization as the temperature changed during sampling, each sample tube was preheated to (40 or 80) °C. The concentrations of sodium, vanadium, and chromium were calculated by employing ICP-OES while CO_3^{2-} ion concentration was determined by titration using diluted hydrochloric acid in the presence of indicator methyl orange. The equilibrium solid phases were first dried at (40 or 80) °C for 24 h and then crystallography information was identified using X-ray diffraction with scanning range from 5° to 90°.

To guarantee the accuracy of analysis, each equilibrium system was sampled and analyzed at least three times, and the results hereafter were the average of multiple measurements with relative standard deviation values of less than 3%.

3. Results and discussion

3.1. $NaOH–Na_3VO_4–Na_2CrO_4–Na_2CO_3–H_2O$ system

The results of the pentabasic $NaOH–Na_3VO_4–Na_2CrO_4–Na_2CO_3–H_2O$ system at (40 and 80) °C were summarized in Table 1 and the presented data allowed us to plot Fig. 1. The major powder XRD pattern of the equilibrium solid phases obtained at 80 °C was examined to be $Na_3VO_4 \cdot 3H_2O$, Na_2CrO_4 and Na_2CO_3 in Fig. 2. Other solid samples at 80 °C had basically a same XRD diagram but only differences in peak strength with the presented one. And the solid phases obtained at 40 °C from XRD pattern analysis were similar to what found at 80 °C.

The curves in Fig. 1 clearly shows that the solubility of Na_3VO_4 and Na_2CO_3 are much lower than that of Na_2CrO_4 in the pentabasic system when the NaOH concentration is below 600 g L^{-1}, and the difference in solubility is more significant in relative low alkali region. For example, when the NaOH concentration is around 250 g L^{-1} at (40 and 80) °C, the concentration of Na_2CrO_4 is (401 and 399) g L^{-1}, while the solubility of Na_3VO_4 is (9.61 and 43.26) and Na_2CO_3 is (35.77 and 40.53) g L^{-1} respectively at the same alkali concentration. However, the solubility difference between Na_3VO_4, Na_2CO_3 and Na_2CrO_4 becomes less appreciable, which is