Fluid Phase Equilibria 360 (2013) 338–342

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Solubility investigations in the quaternary $NaOH–Na_3VO_4–Na_2CrO_4–H_2O$ system at 40 and 80 °C

Man Feng[a,b], Shili Zheng[a], Shaona Wang[a,*], Hao Du[a], Yi Zhang[a]

[a] National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, People's Republic of China
[b] University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, People's Republic of China

ARTICLE INFO

Article history:
Received 20 June 2013
Received in revised form
13 September 2013
Accepted 21 September 2013
Available online 29 September 2013

Keywords:
Na_3VO_4
Na_2CrO_4
Crystallization
Separation
Vanadium slag

ABSTRACT

In a new vanadium production process using concentrated alkaline solution as reaction media, the effective separation of Na_3VO_4 and Na_2CrO_4 plays an important role. The mutual salt solubility data in the $NaOH–Na_3VO_4–Na_2CrO_4–H_2O$ system at 40 and 80 °C therefore were measured and compared with ternary $NaOH–Na_3VO_4–H_2O$ and $NaOH–Na_2CrO_4–H_2O$ subsystems, respectively. With the crystallization areas discussed in detail, a strategy for effective separation of Na_3VO_4 and Na_2CrO_4 from the $NaOH–Na_3VO_4–Na_2CrO_4–H_2O$ quaternary system has been proposed.

1. Introduction

Vanadium is found in over 50 different minerals since it is the 22nd most abundant element in the earth's crust at a mean concentration of 150 g/t [1]. Usually, vanadium exists in its primary state with various minerals which include carnotite, roscoelite, vanadinite, mottramite and patronite as important sources of this metal [2]. Vanadium is widely used as additives, catalysts, electrolytes due to its excellent properties [1,3]. It has gained new research attention in recent years as accumulating evidences suggest that vanadium could be used as therapeutic [4–6]. However, about 87% of the vanadium is consumed as an alloying element: 1.5 M/T of V_2O_5 is required to produce 1 M/T of ferro-vanadium which introduced to the fabrication of steel and cast iron to improve the hardness and wear resistance of the material [7]. Hence, the vanadium consumption market is closely related to the development of steel and iron making industries. As the globally increased of steel production which generates larger volumes of vanadium bearing slag year by year, there will be a strong pricing and demand of vanadium in the future.

South Africa, Russia and China constitute majority of the reserves playing a dominant role in vanadium production [8]. Because of the low grade of vanadium in the processed ores (usually less than 2%) and the depletion of concentrated ore deposits all over the world [3], various types of sub-products, including the converter and smelter slag, spent catalysts, and oil fly ash, attract an increasing attention for the recovery of vanadium in industry as a result of a strong pressure to save the natural resources and protect the environment [9]. Meanwhile, recovering vanadium from the converter and smelter slag produced by the treatment of titanomagnetite in iron and steel industry is the most widely applied method [2,10], accounting for 58% of the world's total production [7]. The development of effective recovery methods will substantially increase the total extraction efficiency of vanadium from ores [11]. The representative process mainly consists of the following procedures: sodium salt roasting, acid/water leaching, solvent extraction, ion exchange and precipitation [12]. Roasting of vanadium slag with sodium salts is the currently most widely applied process [13]. But this process suffers from its low vanadium extraction efficiency (average 80–85%), high energy consumption, and discharge of environmentally hazardous substances including ammonia–nitrogen wastewater and toxic gases (SO_2 and Cl_2). With the increasing concerning of environment protection, the application of conventional technologies has been limited in China, and the classical process trigger the development of more efficient and environmental friendly vanadium extraction process [2].

Recently, focusing on the design of integrated recovery of vanadium and associated chromium (2400 mg/kg vanadium

* Corresponding author. Tel.: +86 10 82544856; fax: +86 10 82544856.
E-mail address: shnwang@home.ipe.ac.cn (S. Wang).

0378-3812/$ – see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.fluid.2013.09.050

slag) from vanadium slag simultaneously [14], an economical and effective production process was developed by Institute of Process Engineering, Chinese Academy of Sciences [15]. In this new vanadium extraction process, original vanadium slag was first treated with 80 wt% NaOH solution as reaction medium, and the main reactions involved in the process are as follows:

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

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

Compared to the traditional process, which typically operates at 800 °C, the liquid oxidation reaction temperature can be significantly reduced to 200 °C, achieving nearly 95% vanadium and 85% chromium recovery efficiency after reaction for 6 h. Followed by dissolution with water and filtering separation of the reaction slurry at 80 °C, a mixture of NaOH, Na_3VO_4, and Na_2CrO_4 solution was obtained. Consequently, it is necessary to study the equilibrium solubility of the quaternary NaOH–Na_3VO_4–Na_2CrO_4–H_2O system in order to separate Na_3VO_4 and Na_2CrO_4 from the leaching solution. 40 and 80 °C were finally chosen as the equilibrium temperatures in consideration of the filtering temperature and economical efficiency of industrial operation at the same time. Equilibrium data for the ternary NaOH–Na_3VO_4–H_2O and NaOH–Na_2CrO_4–H_2O subsystems have been published previously [16,17]. Due to the lack of relevant data of quaternary NaOH–Na_3VO_4–Na_2CrO_4–H_2O system at 40 and 80 °C in literatures, the design of an industrially applicable effective separation method is not yet able to be accomplished. In this regard, systematic examination of Na_3VO_4 and Na_2CrO_4 solubility in the NaOH–Na_3VO_4–Na_2CrO_4–H_2O quaternary system has been performed in this work, and the salting-out effect between Na_3VO_4 and Na_2CrO_4 has been discussed in detail. The obtained experimental data enable us to build a strategy method to separate Na_3VO_4 and Na_2CrO_4 from alkaline solutions.

2. Experimental

2.1. Apparatus and reagents

Polypropylene bottles with good heat resistance and chemical stability (capacity of 250 mL) were used for preparing the samples. These bottles were placed in a HZ-9212S type thermostatic shaking water bath with a precision of 0.1 °C and a HZ-9612K type thermostatic shaking air bath with a precision of 0.2 °C to reach equilibrium at 40 and 80 °C, respectively. The concentrations of sodium, vanadium, and chromium were determined using ICP-OES (PE Optima 5300DV, Perkin-Elmer). And the solid phases were first dried in electrothermal air drying oven (DHG-9140A, Shanghai Yiheng Scientific Instrument Corporation) and then examined by X-ray diffraction analysis (XRD, PW223/30 with Cu Kα radiation, 40 kV and 100 mA, Philips).

The chemicals used in this study were of analytical grade. Sodium hydroxide (NaOH) and sodium chromate ($Na_2CrO_4{\cdot}4H_2O$) were purchased from Sinopharm Chemical Reagent Company, and sodium vanadate ($Na_3VO_4{\cdot}3H_2O$) was provided by the Chengde Iron and Steel Company. The purities of sodium vanadate and sodium chromate are above 99%, and sodium hydroxide is above 96%. High-purity Milli-Q water, with a resistivity of above 18.2 MΩ cm at ambient temperature, was used for preparing the solutions.

2.2. Experimental procedure

The supersaturated solutions were prepared via two methods. One approach was based on the principle of Na_3VO_4 and Na_2CrO_4 crystallization from supersaturated NaOH solutions. First, alkaline solutions with predetermined NaOH concentrations were prepared in beakers positioned in a constant-temperature water bath at 60 and 95 °C, higher than the equilibrium temperatures in order to reach supersaturation. Then sodium vanadate and sodium chromate were added into the alkaline solutions while stirring with speed controlled to be 250 rpm. The stirring was stopped when Na_3VO_4 and Na_2CrO_4 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 samples were then placed in the thermostatic shaking bath maintained at temperatures of 40 and 80 °C and constant shaking with a speed of 180 rpm was maintained to accelerate the equilibration and homogeneity of the slurries.

The second approach was based on the dissolution of Na_3VO_4 and Na_2CrO_4 in NaOH solutions, and the experimental procedure was as follows. First, NaOH solutions with predetermined concentrations were prepared as described in the above paragraph, apart from the difference that the solutions were prepared at 40 and 80 °C, respectively. Then small amounts of sodium vanadate and sodium chromate salts were added into the NaOH solutions every day at constant temperature 40 and 80 °C until the solution reached saturation. Sampling of the liquid phase and examining of the solid phase were performed every day before further addition of sodium vanadate and sodium chromate salts to 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 both vanadium-bearing and chromium-bearing phase were presented in the solid phases simultaneously.

The solution composition of our samples prepared via the two mentioned different approaches above were compared constantly, and equilibrium was assumed to be realized when the solution compositions agree with each other. Once the system was in equilibrium state, the shaking was stopped, and the samples were kept in the baths for 10 more days in order for the suspended precipitates to settle.

The densities were measured by pycnometer test method. Each data represents the average of at least three individual measurements with the precision of ±0.0002 g cm^{-3}. Each equilibrium liquid phase sample of 1 mL was taken using a sampling gun and transferred into a volumetric flask, followed by dilution with high purity water for further analysis. To prevent the saturation liquid from crystallization as the temperature changed during sampling, the sample tubes were first heated to 40 and 80 °C, respectively. The concentrations of sodium, vanadium, and chromium were determined using ICP-OES. The equilibrium solid phases were first dried at 40 and 80 °C for 24 h and then grinded to powder in a mortar. The crystallography information was identified using X-ray diffraction with scanning range from 5° to 90°. To guarantee the accuracy of the analysis, each equilibrium system was sampled and analyzed at least three times, and the results hereafter were the average of multiple measurements with standard deviation of less than 3%.

3. Results and discussion

3.1. NaOH–Na_3VO_4–Na_2CrO_4–H_2O system

The equilibrium data for the quaternary NaOH–Na_3VO_4–Na_2CrO_4–H_2O system at 40 and 80 °C are summarized in Tables 1 and 2 and plotted in Fig. 1. And the major powder XRD pattern of the equilibrium solid phases obtained at 40 °C was