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Sodium stannate preparation from stannic oxide by a novel soda roasting–leaching process

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ABSTRACT

Sodium stannate is widely used in the electroplating and tin alloy industries. The traditional sodium stannate production processes suffer a variety of disadvantages including long flowsheet, high production cost and strict requirements for the equipment. In this study, a novel process for preparing sodium stannate is developed by roasting tin dioxide and sodium carbonate in CO/CO_2 mixed gas followed by leaching the intermediate products in a diluted sodium hydroxide solution. The effects of roasting and leaching parameters on the leaching efficiency of Sn were investigated. The Sn leaching efficiency reaches 85.6% under the optimal experimental conditions: roasting temperature of 875 °C, CO content of 15%, roasting time of 15 min, Na_2CO_3/SnO_2 mole ratio of 1.5, liquid-to-solid ratio of 4 cm^3/g, leaching temperature of 40 °C, leaching time of 60 min, and stirring speed of 300 rpm. Sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$) having a purity of 95.8% is successfully produced from cassiterite concentrates with a SnO_2 content of 76.4% through the new process, which is superior to the traditional approach for producing the industrial first-grade stannate.

1. Introduction

Sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$) is a raw material widely used in the electroplating (Vitkin, 1951), tin alloy production (Barry and Thwaites, 1983; Wright, 1982) and catalysts for organic synthesis (Soler et al., 2010; Zhang et al., 2011). Recently, the demand for sodium stannate has grown rapidly because the conventional flame retardant (Sb_2O_3) is gradually replaced by stannates (such as magnesium/zinc stannate) (Horrocks et al., 2012; Huang, 2000; Rashad and El-Shall, 2008), which are generally prepared from sodium stannate through hydrometallurgical processes (Huang et al., 2004; Wang et al., 2010). Hence, much effort has been spent developing an economical and efficient method for the production of highly pure sodium stannate.

Sodium stannate, as reported, has readily been generated by hydrothermal reactions in concentrated sodium hydroxide solutions using tin as the raw material. Sodium nitrate (Horn, 1978; Mciyhenney, 1929) or hydrogen peroxide must be used as an oxidant during the process (Su and Tang, 2012). Sodium stannate of acceptable quality can be obtained after filtration, purification and crystallization (Read and Marvel, 1928). However, this process has a few drawbacks, such as high production cost and long process flow, because metallic tin must be first produced by reduction smelting at high temperatures. A further disadvantage of the process is the emission of noxious gasses (NO_2 or NH_3), resulting in serious air pollution.

Several attempts were made to prepare sodium stannate using cassiterite concentrates as raw materials (Wang and Pu, 1987; Wright, 1982). In this process, the preprocessed cassiterite concentrates react with fused sodium hydroxide in an electric arc furnace, forming primary sodium stannate melts at high temperatures (generally higher than 800 °C). Then, the melts undergo cooling, crushing, leaching, purifying, filtering, crystallizing, drying, etc., before the highly purified sodium stannate is obtained (Little, 1930). However, excess sodium hydroxide used in this process causes severe equipment corrosion and environmental pollution.

Some secondary tin-containing resources, including tin plating slag, stanniferous alloy, steel scrap and electronic waste, have also been used for preparing sodium stannate (Barakat, 1998; Jha et al., 2012; Jun et al., 2004; Kékesi et al., 2000; Rimaszeki et al., 2012). However, multiple metallic elements, such as Cu, Pb, Sn, Ni, Fe, Zn and Pd, are commonly present in these materials, making it difficult to purify the products and remove these harmful elements (Deren, 1979; Zhang and Qiu, 2008).

In most cases, cassiterite concentrates seldom react with sodium carbonate under air atmosphere (Sun and Li, 1994). As a result, tungsten and tin can be separated from tin-bearing tungsten concentrates by roasting the material with sodium carbonate in air (Martins, 1996; Martins and Martins, 1997). On the contrary, it was reported that the

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gas-sensitivity of stannic oxide may vary substantially after being treated by the reducing gasses (CO, H_2, CH_4, etc.) (Hyodo et al., 2002; Sergent and Gélin, 2003).

Based on the above analysis, an exploratory experiment on the preparation of sodium stannate from cassiterite concentrates and sodium carbonate by controlling the roasting atmosphere has been carried out. The application of sodium carbonate was designed to replace sodium hydroxide, aiming at reducing the production cost and the security risks for the present sodium stannate production processes. It has showed that in a weakly reducing atmosphere stannic oxide reacted with sodium carbonate, forming sodium stannate (Zhang et al., 2012). Then, high-purity sodium stannate was obtained by leaching the roasted products with a very diluted sodium hydroxide solution.

In the present work, high-quality sodium stannate is prepared by reduction roasting of chemically pure tin dioxide and sodium carbonate under CO/CO_2 atmosphere followed by diluted sodium hydroxide leaching. The effects of the roasting and leaching parameters on the leaching efficiency of Sn were also investigated.

2. Experimental

2.1. Materials

Stannic oxide and sodium carbonate used in the study were analytical grade reagents with more than 99.5% purity.

The cassiterite concentrates used were taken from Yunnan, China. They were roasted at 900 °C for 120 min in advance and then leached with 25% HCl to remove the main impurity elements, including Fe, As, S, Pb, and Sb. It was found that cassiterite (SnO_2) seldom reacted with gangue during the roasting and was insoluble in hydrochloric acid (Li and Wei, 1996; Song, 2011; Wright, 1982). The chemical compositions of the original and pretreated cassiterite concentrates are given in Table 1.

The tested samples were pre-ground to a particle size passing through a 200 mesh screen (<0.074 mm). The gasses used for roasting, including CO, CO_2 and N_2, were more than 99.99% pure.

2.2. Methods

The experimental flowsheet is shown in Fig. 1. Stannic oxide and sodium carbonate were first mixed in a certain mole ratio. About 5.0 g mixture with 10% moisture was agglomerated to be a cylindric briquette, 10 mm in diameter under the pressure of 10 MPa to avoid blowing away the powder samples by the airflow. The green briquettes were dried in a drying oven at 105 °C for 4 h. Then, the experiments were carried out based on the procedures of roasting, leaching and sodium stannate preparation.

2.2.1. Roasting process

The dried briquettes were placed in a porcelain crucible and loaded into a heat resistant quartz glass tube. The samples were pushed to the roasting zone in an electrically heated horizontal tube furnace. Beforehand, the furnace was heated to a preset temperature. The roasting temperature was measured with a Pt–Rh thermocouple and controlled using a KSY Intelligent Temperature Controller (accuracy ± 5 °C). The experimental schematic diagram is illustrated in Fig. 2. Pure N_2 was directed to the quartz tube until the temperature reached a constant value. Next the N_2 was immediately replaced by the mixed CO/CO_2 gas. The content of CO in the CO/CO_2 mixture was adjusted by controlling the flowmeters. The inlet gas flow was fixed at 4.0 dm^3/min. After being roasted at given temperatures for certain time periods, the briquettes underwent a reverse flow cooling, contrary to the direction from the entrance of the tube furnace. The roasted briquettes were cooled to room temperature in pure N_2 atmosphere, and then discharged from the quartz tube followed by precise weighing and grinding until all particles passed through a 0.074 mm sieve. A computerized X-ray diffraction equipment (XRD, D/max 2550PC, Japan Rigaku Co., Ltd.) was used to determine phase compositions of the roasted products.

Table 1
Chemical compositions of the original and pretreated cassiterite concentrates (wt.%).

	Sn	Fe	SiO_2	CaO	S	Al_2O_3	Zn	As	Pb
Raw material	42.92	8.86	8.31	6.70	5.11	1.16	1.21	0.50	0.38
Pretreated	62.93	0.11	7.84	0.17	0.04	0.28	0.02	0.03	0.03

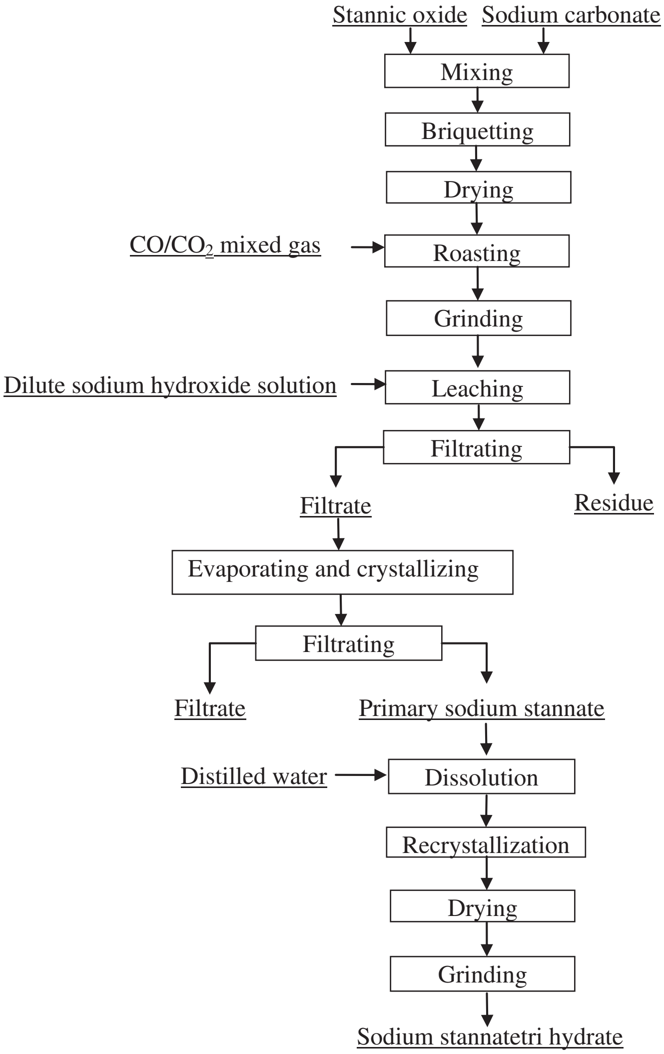

Fig. 1. The experimental flowsheet.

The preliminary research indicated that sodium stannate was generated during the roasting. It is inferred that the major chemical reaction involved in the roasting process is expressed as follows:

$$Na_2CO_3 + SnO_2 = Na_2SnO_3 + CO_2. \quad (1)$$

2.2.2. Leaching process

In each leaching test, 10.0 g of the ground roasted products was put into a beaker and leached with a highly-diluted sodium hydroxide solution in a water bath. Next, the leaching solution was filtered and prepared for the determination of Sn concentration using ICP-AES (ICP-AES, PS-6, American Baird Co., Ltd.).

Sodium stannate is water-soluble, while tin oxide or metallic tin is insoluble (Huang, 2000). Thus, it is possible to separate sodium stannate