Mechanochemically extracting tungsten through caustic processing of scheelite by controlling calcium dissolution

CrossMark

Min Chen, Zhao Li, Xuewei Li, Jun Qu, Qiwu Zhang *

School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei 430070, China

ARTICLE INFO

ABSTRACT

A novel process to extract tungsten from scheelite ($CaWO_4$) was developed by dry grinding with sodium hydroxide (NaOH) and controlling the calcium dissolution based on two methods. One was to wash the ground product composed of sodium tungstate (Na_2WO_4) and calcium hydroxide ($Ca(OH)_2$) in the solution of sodium salts instead of water. For example, W recovery was increased from 30% in water washing to 96% in a 0.1 M soda (Na_2CO_3) solution due to the formation of calcium carbonate ($CaCO_3$). Another was to add $Al(OH)_3$ further to the cogrinding of $CaWO_4$ and NaOH to produce Na_2WO_4 and katoite ($Ca_3Al_2(OH)_{12}$). Over 98% W recovery was simply obtained by only water washing the product due to the existence of insoluble $Ca_3Al_2(OH)_{12}$. Grinding time and $Al(OH)_3$ dosage were found to be key factors in affecting W recovery.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Tungsten, one of the most significant strategy resources and refractory metals, is widely used in several industrial applications due to the outstanding properties such as its high strength and excellent heat-resistance. Wolframite (($Fe, Mn)WO_4$) and scheelite ($CaWO_4$) are the main mineral resources. Currently, scheelite is playing an increasingly important role in tungsten industry because the mineral reserve of wolframite is getting depleted after gradual exploitation and utilization.

Among the metallurgical processes for extracting tungsten from the minerals, caustic one is usually used to treat wolframite and acidic one for treating scheelite concentrate of high grade. Hydrochloric acid is commonly used to decompose scheelite, forming tungstic acid, which is inclined to develop a layer over the solid particles to hinder the contract between HCl and the unreacted core, resulting in a low leaching rate [1–4]. Due to the problem of inverse reaction between Na_2WO_4 and $Ca(OH)_2$ to form $CaWO_4$ with the caustic process, several sodium salts of carbonate, silicate and phosphate were used in processing scheelite to avoid the generation of $Ca(OH)_2$. In the case of sodium carbonate roasting-leaching of scheelite, it was essential to operate at high temperatures (>500 °C) with excess soda [5,6], while CaO in the roasted mass would result in a loss of tungsten as a form of $CaWO_4$ during leaching [6]. Another case with soda was the digestion of scheelite by autoclaving, in which a 2.5–4 times stoichiometric amounts of soda addition and an operation temperature about 190–225 °C with a holding time of 2–4 h were inevitable to obtain a 90% tungsten recovery.

However, the excess soda was difficult to recover and would react with the $CaCO_3$ formed from the decomposition of $CaWO_4$, causing a waste in soda and an inefficiency in reaction [7]. As to the cases of using phosphate and silicate, similar problems as large amounts of reagents addition, operation at high temperature and the complex subsequent treatments for tungsten recovery and purification requires further investigations to solve [8–10]. Zhao et al. first reported a soda processing of scheelite together with sodium hydroxide addition through mechanical activation [11]. They continued their efforts by using sodium hydroxide to decompose scheelite [12–14] at a relatively lower operation temperature than that by soda processing. The process was successfully used for industrial application. Among many methods to increase W recovery, autoclaving process demonstrated a good application prospect [12]. The uses of large dosage of NaOH and high solid-liquid ratio were also important in raising W recovery. Other measurement as reactive extrusion was used to treat the samples with high solid-liquid ratio. Therefore, it is promising to develop an alternative process using less NaOH under an easy operation.

In recent years, much attention has been paid to the applications of mechanochemical methods to metallurgical processes [15–19]. Mechanochemical processing of several minerals of sulfate and carbonate with solid NaOH at a stoichiometric dosage were reported in our previous publications [20–22]. In the case of scheelite, although solid state reaction with NaOH mechanochemically to form soluble Na_2WO_4 could be expected, difficulty remained with low W recovery when washing the ground sample by water.

This work is aimed to study the caustic processing of scheelite by transforming the calcium into a water-insoluble compound with $Al(OH)_3$ addition by mechanochemical treatment, providing a novel

* Corresponding author.
E-mail address: Zhangqw@whut.edu.cn (Q. Zhang).

approach to directly extracting W from water washing. This approach allows a nearly stoichiometric use of NaOH to form Na_2WO_4, therefore an easy treatment for next step processing.

2. Experimental procedure

The scheelite sample used in this study was synthesized from Na_2WO_4 and calcium chloride ($CaCl_2$) solution by a precipitation reaction [23]. The reagents of NaOH, $Al(OH)_3$, Na_2CO_3, $Na_2SiO_3·9H_2O$, Na_2SO_4 and $Na_3PO_4·12H_2O$, provided by Sinopharm Chemical Reagent Co., Ltd., China, were analytical pure and used without any further purification.

The grinding experiments of scheelite with hydroxide additives were carried out under air condition in a planetary ball mill (Fritsch, Pulverisset-7, Germany), equipped with two zirconia pots (45 cm³ inner volume). Firstly, two grams of the mixture were added into the milling pot with 7 zirconia balls (15 mm in diameter). The mass ratio of ball to mixture was 35:1. Rotational speed of the mill was kept constant at 600 rpm with grinding time changed up to 150 min. The mill was set to operate for 5 min with another 5-min rest. Secondly, after the prescribed milling time, 0.2 g of the ground samples were dispersed in 50 ml solutions (0.1 M) of the four sodium salts as well as water. Agitated for 20 min, the solution was centrifuged at about 8400 ×g to recover the supernatant, followed by determination of water-soluble W by ultraviolet spectrometric method (Spectrophotometer UVmini-1240, Japan) and plasma-atomic emission spectroscopy (ICP-AES: Optima-3300SYS, Perkin Elmer, USA). Parallel experiments were performed to obtain the accurate results throughout the experiment stage. X-ray diffraction analysis (XRD, RU-200B/D/MAX-RB RU-200B, Japan) was carried out to identify the phases and compositions of the solid residues after washing, as well as the ground samples.

3. Results and discussion

3.1. Samples ground without $Al(OH)_3$

To investigate the mechanochemical reaction between $CaWO_4$ and NaOH alone, experiments were carried out at a molar ratio of 1:2.4 (= $CaWO_4$:NaOH). Fig. 1 shows the XRD pattern of the mixture ground for 1 h. The peaks of scheelite were not observed in the ground mixture but that of Na_2WO_4 became the main ones. Besides, the peaks of $Ca(OH)_2$ were also detected in the pattern of ground mixture, as well as that of $Na_2WO_4·2H_2O$. The water molecule might come from the moisture absorbed by unreacted NaOH. However, the phase of residual NaOH was not found in the pattern, inferring that it was in an amorphous
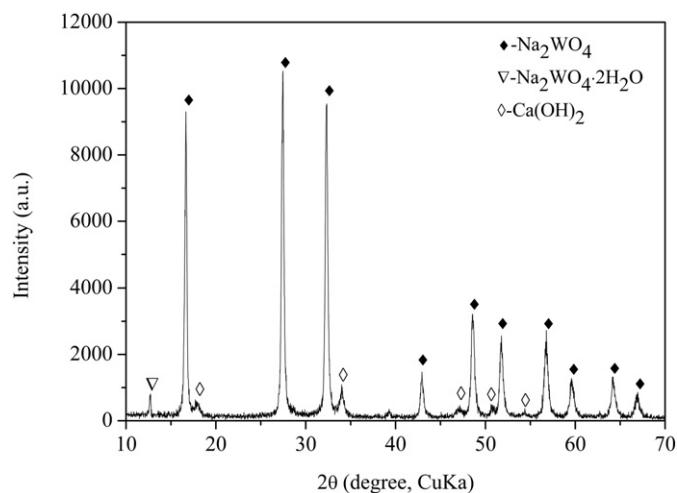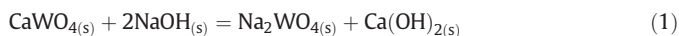
form. It was understood that the following reaction took place completely by the milling processing, during which $CaWO_4$ was totally transformed into Na_2WO_4.

$$CaWO_{4(s)} + 2NaOH_{(s)} = Na_2WO_{4(s)} + Ca(OH)_{2(s)} \qquad (1)$$

Subsequently, solutions of the four sodium salts at 0.1 M and water were used to extract tungsten from the ground mixture and the results are shown in Fig. 2. Compared with that only 30.2% of W dissolved in distilled water, the W recovery was increased to 63.1%, 85.8%, 90.5% and 96.7% by using the solutions of sulfate (Na_2SO_4), phosphate (Na_3PO_4), silicate (Na_2SiO_3) and carbonate (Na_2CO_3), respectively.

X-ray diffraction analyses of the solid residues after the extraction mentioned above were conducted to investigate the differences of W recovery among each solution. As shown in Fig. 3, only the peaks of $CaWO_4$ were observed in the pattern of residue in water, indicating that a majority of W was precipitated by Ca ion again, resulting in the low W recovery around 30%. On the contrary, the main phase in the pattern of the residue from Na_2CO_3 solution was $CaCO_3$, while the peak of $CaWO_4$ was hardly detected, which was exactly consistent with the high recovery of W in the solution. Similarly, main phase of $CaWO_4$ was found in the residue from Na_2SO_4 solution, as well as part of $CaSO_4·2H_2O$ [24], corresponding to the relatively low yield of W recovery. No evident existence of $CaWO_4$ phase in the residues from Na_3PO_4 and Na_2SiO_3 solutions resulted in the relatively high yields of W recovery. No remarkable phases were identified in the pattern of the residue from Na_2SiO_3 solution, suggesting that the $CaSiO_3$ might be in an amorphous state.

Besides, the solubility product constants of calcium compounds above [25] were as follows: $CaWO_4$ 8.7×10^{-9}, $CaCO_3$ 3.36×10^{-9}, $CaSiO_3$ 2.5×10^{-8}, $CaSO_4·2H_2O$ 3.14×10^{-5} and $Ca_{10}(PO_4)_6(OH)_2$ 2.35×10^{-59}. It was clear that the W recovery depended strongly on the solubility product constants of these calcium compounds. When the ground sample composed of Na_2WO_4 and $Ca(OH)_2$ was dispersed in water, as represented by Eq. (2), $Ca(OH)_2$ tended to react with Na_2WO_4 to form $CaWO_4$. When the ground sample was dispersed in the Na_2CO_3 solution, for example, there existed another tendency for $Ca(OH)_2$ to react with Na_2CO_3 to form $CaCO_3$ as represented by Eq. (4), which made the same sense for Na_3PO_4 as shown by Eq. (3). The higher the tendency to form $CaCO_3$ in the case of Na_2CO_3 solution was, the less the chance to form $CaWO_4$ was, therefore, the higher the W recovery was. On the contrary, the lower the tendency to form $CaSO_4$ in the case of Na_2SO_4 solution was, the higher the chance to

Fig. 1. XRD pattern of the product obtained from the reactant mixture with the molar ratio of $CaWO_4$:NaOH = 1:2.4 milled for 1 h.

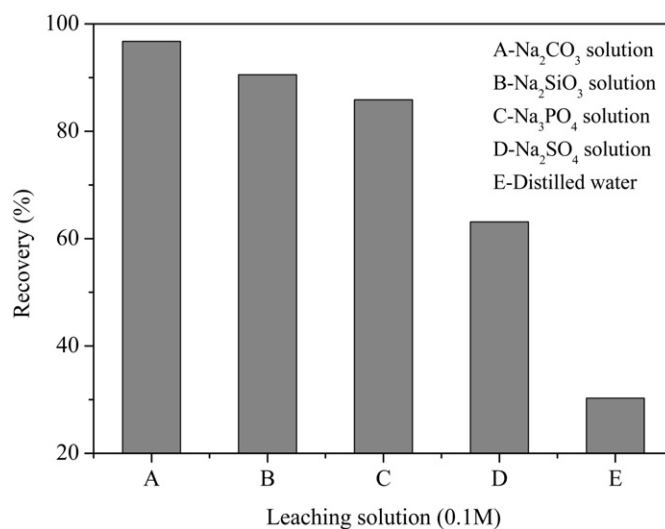**Fig. 2.** Recovery of W by treatment of the product obtained from the reactant mixture with the molar ratio of $CaWO_4$:NaOH = 1:2.4, using different leaching solutions.