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Ultrasound-assisted impurity removal from petroleum coke

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ABSTRACT

In the present study, iron and other impurities element leaching from petroleum coke in the presence of ultrasound were investigated. The parameters investigated were the different types of acid, leaching time, liquid–solid ratio, acid concentration, reaction temperature, ultrasound power and frequency. It has been found that the hydrochloric acid has the largest removal efficiency among the acids investigated. The maximum iron removal rate can be reached at the leaching time of 35 min, liquid–solid ratio of 10 ml/g, acid concentration of 12 wt%, reaction temperature of 50 °C, ultrasound power of 240 W and ultrasound frequency of 80 kHz. The removal efficiency increases considerably, compared to conventional stirring method. The mechanism of removal impurity from petroleum coke with ultrasound-assisted was analyzed through SEM results.

1. Introduction

Since conventional fossil fuels are drastically decreasing, effective utilization of solar energy has become vitally important. The solar energy is one of the sustainable and clean energy sources [1–3]. Currently more than 80% of commercial solar cells are made of silicon, particularly multi-crystalline silicon [4–6]. The rapidly growing of worldwide solar cells market requires a large quantity of silicon feedstock [7–10]. The process for obtaining solar-grade silicon (SoG-Si) is divided into two categories: *Siemens* process and metallurgical route [11,12]. The metallurgical route, five times more energy efficient than the conventional *Siemens* process [11,12], is a low cost, environment friendly method [7,13].

In SoG-Si production using metallurgical approach, metallurgical grade silicon (MG-Si) is purified by the combination of various metallurgical techniques [13], which contains slag refining [14,15], plasma refining [16,17], electron beam melting [18,19] and directional solidification [20,21]. The purity of MG-Si determines the following purifying process. It has been well known that the MG-Si is produced by reducing silica with carbon in arc furnace. The impurities of MG-Si come from the silica, the carbonaceous reductors and the electrodes of the arc furnace [22]. It is reported that the 99.5% high-purity silicon can be produced using the carbonaceous reductor with ash content of less than 0.5% [23].

Petroleum coke, a byproduct of the oil refining industry, is an ideal carbonaceous reductor due to its high calorific value and low price [24,25]. The common impurities of the petroleum coke have influence on the quality of the MG-Si. Therefore, removing impurities from petroleum coke is essential to increase purity of MG-Si.

We have reported that the petroleum coke can be purified by conventional acid leaching. However, it takes long time (6 h) and high temperature (70 °C) [26]. It has been documented that ultrasonic energy enhance chemical reaction rate because of cavitation bubbles [27]. This work reports the ultrasound-assisted acid leaching to removal iron from petroleum coke and its comparison with the conventional stirring method. Optimization of different operating parameters has also been investigated.

2. Material and methods

2.1. Materials and reagents

The petroleum coke in this investigation comes from Ningxia power Co., Ltd. The content of main impurities of the petroleum coke is given in Table 1. And the size of the petroleum coke is 106–75 μm. The reagents-grade chemicals and deionized water were used in the work.

2.2. Leaching tests

The experiments were performed with ultrasound assistance, using a digital ultrasonic cleaner (KQ-300VDE, Kunshan, China) which has three kinds of frequency (45 kHz, 80 kHz and 100 kHz). The digital ultrasonic cleaner with amount of water

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Table 1
ICP-OES analysis of concentration of main impurities in the petroleum coke.

Impurity	Fe	Al	Ca	P
Concentration (ppmw)	469	291	173	14

was firstly set to a given temperature. Then, a 500 ml beaker with 100 ml acid solution was placed in the digital ultrasonic cleaner. When the temperature of the acid solution was stable, the 10 g petroleum coke was added into the acid solution, and then the mixtures were simultaneously stirred at 300 rpm and sonicated at certain power. The factors investigated were the leaching time, liquid–solid ratio, acid concentration, reaction temperature and ultrasound power. All of the factors were investigated under three kinds of frequency (45 kHz, 80 kHz and 100 kHz). An amount of samples were taken out at the pre-determined time intervals, filtered immediately, rinsed three times with deionized water, and then dried at 90 °C for 40 min.

In order to study the effect of ultrasound on the purifying, the experiment was also performed without ultrasound assistance, and the other experimental processes and parameters were designed identically with the optimum conditions.

2.3. Analysis and characterization

The morphologies of the petroleum coke were observed using scanning electron microscopy (SSX-550, Shimadzu Japan). The elemental analysis of the petroleum coke was carried out by ICP-OES (Optima 2100 DV, PerkinElmer, USA). The iron removal efficiency of a process can be calculated using the equation:

$$\text{Iron removal efficiency }(\%) = \left(1 - \frac{\text{amount of iron in leaching solid samples}}{\text{amount of iron in petroleum coke}}\right) \times 100 \quad (1)$$

3. Results and discussion

3.1. Effects of different types of acids

The influence of acids ($H_2C_2O_4$, HNO_3, H_2SO_4 and HCl) on the impurity removal rate has been investigated at 30 °C with liquid–solid ratio of 10 ml/g for 60 min in the presence of ultrasound power of 210 W and frequency of 45 kHz. All kinds of acid concentrations were 10 wt%. Fig. 1 gives the impurities content of iron, aluminum, calcium and phosphorus using different acids. The lowest impurities content happened in the hydrochloric acid solution, while the highest happened in the oxalic acid solution. For example, the iron content of the petroleum coke decreased greatly from 469 to 92 ppm by hydrochloric acid; and 154 ppmw by oxalic acid, 127 ppmw by nitric acid and 130 ppmw by sulfuric acid. The chemical reaction using HNO_3, H_2SO_4 and HCl can be summarized as follows [28]:

$$6H^{+} + Fe_2O_3 \rightarrow 2Fe^{3+} + 3H_2O \quad (2)$$

The chemical reaction of $H_2C_2O_4$ can be summarized as follows [29]:

$$Fe_2O_3 + 3H_2C_2O_4 + H_2O \rightarrow 2FeC_2O_4 + 2H_2O + 2CO_2 \quad (3)$$

The higher impurities content in oxalic acid under ultrasonic treatment in comparison of hydrochloric acid, nitric acid and sulfuric acid may be due to chemical property of oxalic acid, which is weak acid. Therefore, the hydrochloric acid can be chosen as an ideal acid solution for all subsequent experiments.

3.2. Effect of leaching time

The effect of leaching time on the iron removal rate has been investigated under the following conditions: hydrochloric acid concentration of 10 wt%, liquid–solid ratio of 10 ml/g, reaction temperature of 30 °C and ultrasound power of 210 W. According to Fig. 2, the iron removal rate had a progressive increase with leaching time at initial phase within 35 min, and then is close to a stable value, meaning that the iron oxides on the surface of petroleum coke had been leaching out before 35 min. Therefore, the 35 min can be chosen as an optimal leaching time for all subsequent experiments. The iron removal rate increase with increasing ultrasonic frequency from 45 kHz to 80 kHz, but there was a slight increase in the iron removal rate with further increase in ultrasonic frequency of 100 kHz. At lower frequency, a long acoustic cycle exists, large bubbles are created. The consequence of larger bubbles is a more violent cavitation collapse [30]. But the amount of the cavitation bubbles is less than that at high frequency. Furthermore, the acoustic period is shorter at higher ultrasonic frequency, and then the pulsation and collapse of the bubbles occur more rapidly [31,32]. Therefore, a single cavitation bubble has small maximum diameter and releases less energy at high frequency. The energy of cativation bubbles at the 100 kHz is enough to clean the impurities of the particle surfaces. At the ultrasound frequency of 45 kHz, the removal rate of iron is lower than others,

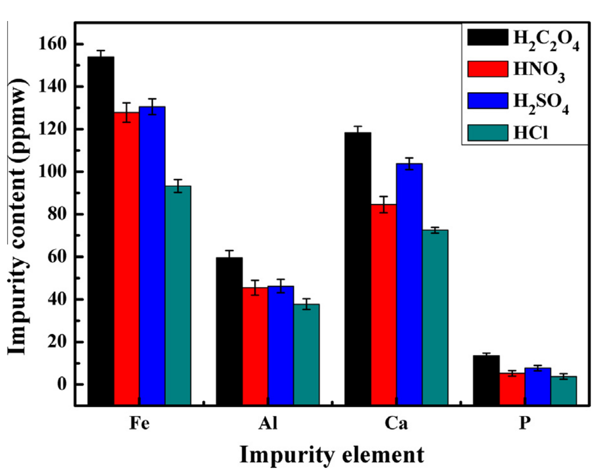

Fig. 1. Impurity content of petroleum coke leached in different acids.

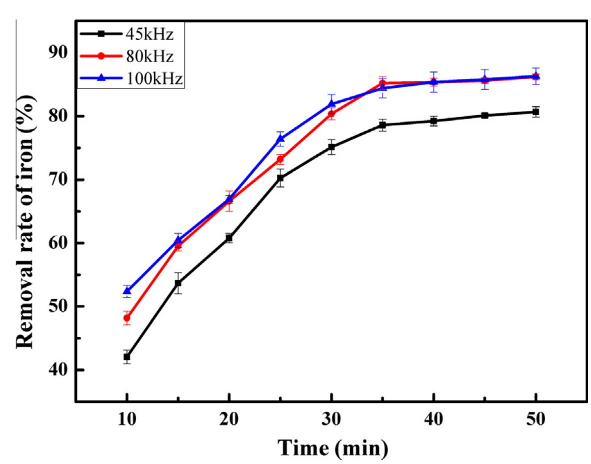

Fig. 2. Effect of leaching time on iron removal rate (the conditions of 10 wt% hydrochloric acid concentration, leaching temperature of 30 °C, liquid–solid ratio of 10 ml/g and ultrasound power of 210 W).