Hydrodesulfurization of Petroleum Coke

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Abstract

Properties of petroleum coke affect strongly the quality of anodes used in aluminum industry. A certain level of sulfur in anodes is necessary to reduce the reactivities; however, high levels of sulfur cause environmental problems. The demand for anode-quality coke with acceptable sulfur content is increasing faster than the available supply. Thus, the industry is searching for ways to reduce the sulfur content of cokes containing high levels of sulfur. There are different ways of desulfurizing green petroleum cokes such as solvent extraction, thermal desulfurization, and hydrodesulfurization. Solvent extraction can contaminate the coke. Thermal approach requires higher calcination temperatures leading to greater energy consumption and increases coke porosity. Hydrodesulfurization seems to be a viable option and was investigated in this study. The effect of water injection temperature and duration, water flow rate, and coke particle size on the hydrodesulfurization of green petroleum coke was studied. In addition, a number of calcination and thermal desulfurization experiments were carried out with the same green petroleum coke. Sulfur removal and weight loss results obtained in these experiments were compared. It was found that more sulfur can be removed at lower temperatures using hydrodesulfurization compared to thermal desulfurization. Hydrodesulfurized coke displayed a structure similar to the one calcined normally.

Keywords: Hydrodesulfurization, thermal desulfurization, petroleum coke, calcination, sulfur.

1. Introduction

The primary aluminum is produced using the Hall-Héroult process in which large amounts of carbon anodes are consumed. Anode quality is important due to its impact on cell operation, carbon and energy consumption, and environment. Properties of coke, one of the principal raw materials in anode production, influence significantly the anode quality. The rising demand for aluminum resulted in higher demand for green petroleum coke [1] while the availability of the good quality coke has been decreasing during recent years because of the significant increase in sour crude oil usage in refining industry due to economic reasons [2]. Sour crude oil leads to the production of high sulfur green coke, and aluminum industry uses such cokes by blending with low sulfur cokes [3]. Some amount of sulfur is needed in calcined coke to reduce anode reactivity [4]. However, using calcined coke with a sulfur content higher than necessary in carbon anodes would have a number of adverse effects on environment. The use of high-sulfur anode in electrolysis leads to an increase in emissions such as H_2S, COS, CS_2, and SO_2 [5]. High sulfur content in anodes may also cause sulfur removal during anode baking if the baking is continued above a certain temperature. This increases anode porosity and specific electrical resistivity and decreases anode baked density, leading to shortened anode life, increased energy and carbon consumption, and higher environmental emissions during electrolysis. Sulfur in anodes also results in a significant loss of current efficiency in the electrolysis cell [6-7].

According to the literature, the nature of sulfur in green petroleum coke is mostly organic, and thiophenes appear to be the most common forms of sulfur present in these cokes [8-10]. There are several methods for removing sulfur from petroleum coke. Solvent extraction uses chemical solvents [11]. This method is not suitable for the treatment of petroleum coke used in anode manufacturing since it contaminates the coke. In thermal desulfurization, coke has to be calcined at higher temperatures than that is normally used by the industry, which increases the energy consumption and results in a porous coke structure [12]. However, it was shown recently that the thermal desulfurization in a vertical shaft calciner at slow heating rates produces a coke that can possibly be used in blends at levels of 50% or lower [13]. Hydrodesulfurization is a widely used process by refineries to remove sulfur (S) from natural gas and refined petroleum products; but, it has not been applied yet to petroleum coke at industrial scale. In hydrodesulfurization, green petroleum coke is heated under a hydrogen or steam atmosphere, forming H_2S with sulfur present in coke [14-15]. More efficient contact between hydrogen and coke can improve the sulfur removal [16]. In this study, water vapor was directly injected onto the hot coke during calcination where coke comes in contact with water gas ($CO+H_2O$), volatiles, and H_2S (sulfur containing gas) [17].

This study was undertaken to investigate the simultaneous calcination and hydrodesulfurization of high-sulfur containing green coke and to determine if anode-grade coke could be produced. The effects of various experimental conditions (water injection temperature, water flow rate, etc.) on sulfur removal have been studied. The results are compared with those obtained from the calcination and thermal desulfurization experiments. The calcination and thermal desulfurization experiments were carried out at high heating rates, typically found in rotary kilns (40°C/min). The hydrodesulfurization experiments were carried out at low heating rates (slightly below 1°C/min (50°C/h)) representing the heating rates in a vertical shaft calciner since it can be realized only in such systems due to the need for good contact between gas and particles.

2. Methodology

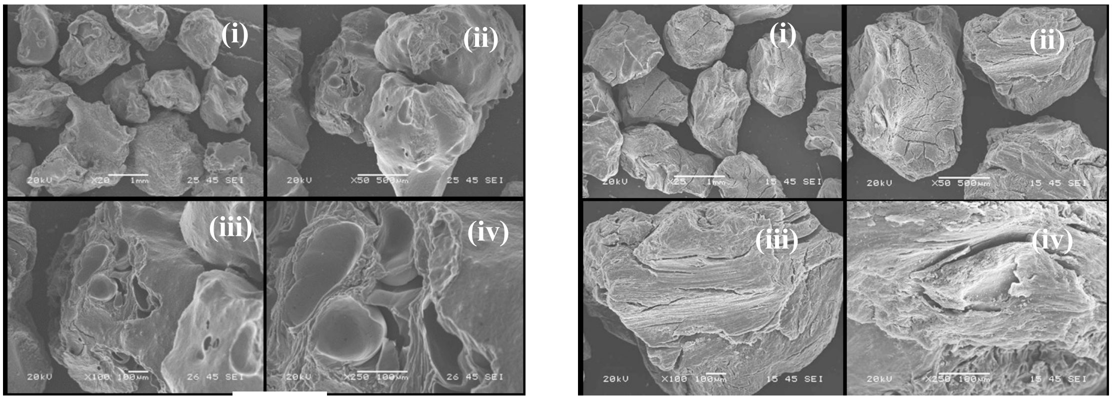
2.1. Material used

A number of different green sponge cokes were used in this study. The available properties of the green petroleum coke used for the hydrodesulfurization experiments are given in Table 1. A number of calcination and thermal desulfurization experiments were also carried out with the same coke to compare the results.

Table 1. Physical and chemical properties of green petroleum coke.

Elements (wt%)		**Impurities (ppm)**		**Proximate analysis (dry basis)**	
Carbon	88.17	Ni	122		
Sulfur	6.87	Fe	319	Volatile content (%)	12.8
Hydrogen	3.87	V	362	Ash content (%)	0.13
Nitrogen	0.97	Si	419	Fixed carbon (%)*	87.07
		Ca	19	Moisture content (%)	0.47
		Na	142		
		P	1	Real density (g/cm^3)	1.39

*by difference



(a) (b)

Figure 12. SEM micrographs of (a) CC-1080 and (b) HDS-60 at magnifications of (i) x20 (ii) x50 (iii) x100 (iv) x250.

4. Conclusions

In this project, an experimental study on the calcination, hydrodesulfurization, and thermal desulfurization of green petroleum coke was undertaken. Effects of different parameters on coke hydrodesulfurization such as water injection temperature and duration, water flow rate, and coke particle size were studied. Maximum sulfur removal was obtained when the water was injected to the coke sample at 850°C for 60 min. Since hydrogen required for the hydrodesulfurization is obtained through water shift reaction, part of the coke was consumed. Under the conditions given above, the coke loss (difference between the total weight loss and the weight loss due to volatiles) was acceptable (about 10%). Sulfur removal increased with increasing injection duration from 37 min to 60. However, further increase in injection duration reduced the percent sulfur removal at all water injection temperatures.

Sulfur is removed at lower temperatures by hydrodesulfurization compared to thermal desulfurization. To remove the same amount of sulfur, thermal desulfurization requires much higher temperatures, hence higher energy consumption, especially in a rotary calcination kiln. It should also be noted that hydrodesulfurization will increase the energy consumption in a vertical shaft calciner as well since water has to be vaporized before injection into the calciner or the cooling due to water injection in liquid form has to be compensated in the calciner itself. Further analysis is needed to compare the additional energy requirements for the two processes.

It would also be interesting to compare the hydrodesulfurized coke with the one calcined and thermally desulfurized in a shaft furnace since the work by Edwards [13] found that such cokes give better results than those calcined in a rotary kiln. Particle-gas contact is important for hydrodesulfurization, and thus tests need to be done in a vertical shaft calciner to determine the extent of sulfur removal under the conditions which are normally used in industry.

5. References

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