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Sulfuric Acid Leaching Process for Producing High Purity Graphite from 92.6% C to 98% C

Hien Tran Thi, Nga Do Hong

***Abstract*- Based on the characteristics of roasted graphite concentrate from Bao Ha, Lao Cai district, the present research a technology to increase the purity of the graphite carbon from 92.6% to 98%. Study was conducted on leaching agents, concentration of sulfuric acid, temperature, time, liquid/solid ratio affecting the process. The technological parameters chosen were: 10% concentration of sulfuric acid, reaction temperature room, reaction time 120 min, L/S=5. The results showed that the graphite content can be increased from 92.6% to 98%, which reaches the requirement for high purity graphite that used for manufacturing Mg-C breaks in steel mills.**

***Index Terms* — Graphite, high purity, chemical method, sulfuric acid.**

I. INTRODUCTION

Currently, there are many methods of refining graphite to achieved high purity. Summary, it can be divided into two methods: heat methods and chemical methods [1].

The heat method is to use very high temperature (4500 ^oC) to volatilized impurities contained in graphite concentrate. Graphite products obtained by this method can reach 99.9% C [2]. It is also possible by heating the graphite to 2500 ^oC under vacuum conditions, the impurities with low volatilization temperature were volatilized. Some studies also show that after treament the final product contained 98÷99 % carbon from graphite originated containing 85÷89 % carbon as a row material. These treatments included alkaline dissolution/acid leaching under 0.5 MPa pressure [3].

The chemical method for the removing of impurities through chemical reactions. Agents used to remove impurities include $NaOH/Na_2CO_3$, HF, HCl, H_2SO_4. The purity of the final product can reach 97÷98% carbon [4].

Original graphite ore from Bao Ha mine, Lao Cai district of Vietnam has graphite content from 10 % to 12%, the rest are impurities. After grinding - flotation can raise the content of ≥ 94% carbon (graphite concentrate grade 1) and ≥ 83% carbon (graphite concentrate grade 2) [5]. Graphite containing ≥ 94% carbon is used for manufacturing magnesium carbon bricks in steel mills, but graphite containing ≥ 83% carbon is not. Some researcher have showed that the purer graphite is, the longer the life of magnesium carbon bricks. Therefore, this study showed the results of removing impurities to the final graphite product can reach > 95% carbon from graphite containing ~ 83% carbon to 98% carbon by chemical method.

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II. EXPERIMENTAL

The research sample is 50 kg of graphite (< 0.144 mm) from Bao Ha mine, Lao Cai district of Vietnam, is roasted with alkaline, filtered, washed with water to remove residual alkaline, then dried at 105 ^oC. The chemical composition of graphite is showed in Table. 1.

Table. 1. Chemical composition (wt%) of Bao Ha graphite is roasted alkaline

C	V	Ash	Ash				
			Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO
92,6	1,26	5,85	26,19	41,69	18,47	4,33	4,58

Efficiency of removing of impurity (η) is calculated as follow:

$$\eta = \frac{M_{before} - M_{after}}{M_{before}}.100\%$$

Where M_{before} is weight of impurities quantity in the sample. By analyzing the carbon content of the sample, $M_{before} = m_{sample} - m_{sample}$ x% $carbon_{sample}$, (m_{sample} and % carbon of sample are weight and carbon content of sample). After drying the sample, m_{sample} is defined ±0.0001 g error.

M_{after} is weight of the impurities in the product. By analyzing the carbon content of the product, $M_{after} = m_{product} - m_{product}$ x% $carbon_{product}$, ($m_{product}$ and % carbon of product are weight and carbon content of product). After drying the sample, $m_{product}$ is defined with ±0.0001 g error.

In the experiments, the weight total of impurities is determined by either carbon analyze or followed the weight reduction as a formula: $M_{after} = M_{before} - (m_{sample} - m_{product})$.

III. RESULTS AND DISCUSSION

A. Affect of various leaching agents

Graphite concentrate after pretreatment with sodium hydroxite, leaching with water, then leaching with acid. In summary of [5]-[7], graphite leaching is good in sulfuric acid or chlorhydric acid. Therefore, the experiment was done with both of acids and find out which acid is the more suitable.

The experiment conditions:
- Sample: 100 gram
- Liquid/solid ratio: 5
- Room temperature
- Stirring speed: 200 rpm
- Time 30, 60, 90 and 120 min.

The concentrate of H_2SO_4 of 10% [5], [6]. Mole of H^+ of H_2SO_4 10% is equivalent with HCl 7,5%, the result of various leaching agents (see Fig. 1).

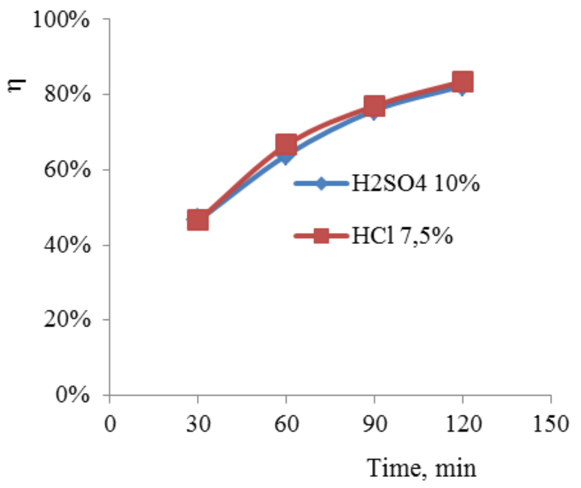

Fig. 1. Effect of various leaching agents on the removal of impurities.

The result showed that, when using chlorhydric acid as leaching agent to treat graphite, the removal of impurities was higher than when sulfuric acid was used but the difference was insignificant. The reason is that chlorhydric acid reacts with CaO to form soluble $CaCl_2$ and its content in the impurities is low. Sulfuric acid is inexpensive and its anticorrosion problems are easy to be solved. In addition, in term of economics, with the ratio of acid concentration which was used to experiment, the cost of various leaching agents for one ton of graphite 92% carbon content in Table. 2.

Table. 2. The cost of various leaching agents for one ton of graphite 92.6% carbon

Leaching agents	Amount of acid is used for one ton of graphit	Price (reference)	Cost (million VND)
H_2SO_4	510 kg (H_2SO_4 98%)	4.200 VND/kg	2,142
HCl	1041 kg (HCl 36%)	2.600 VND/kg	2,707

Thus, with the high effect of impurities removal and low cost, sulfuric acid was used as a leaching agent for the present process.

B. Effect of sulfuric acid concentration

The experiment conditions:
- Sample: 100 gram
- Liquid/solid ratio: 5
- Room temperature
- Stirring speed: 200 rpm
- Time: 120 min.
- Sulfuric acid concentration (%): 6; 8; 10; 12; 14.

Fig. 2 shows the sulfuric acid concentration effects on the removal of impurities of the graphite. Thus, with the concentration of 6%, after 120 minutes only 45.1% is reached. When raise the concentration from 6%-10%, the effect of the impurities removal increase rapidly. At the concentration 10%, the effect is 82.3%.

Continue raising the concentration from 12% to 14%, the removal of impurities goes up slowly. At the concentration of 14%, the effect is around 86%.

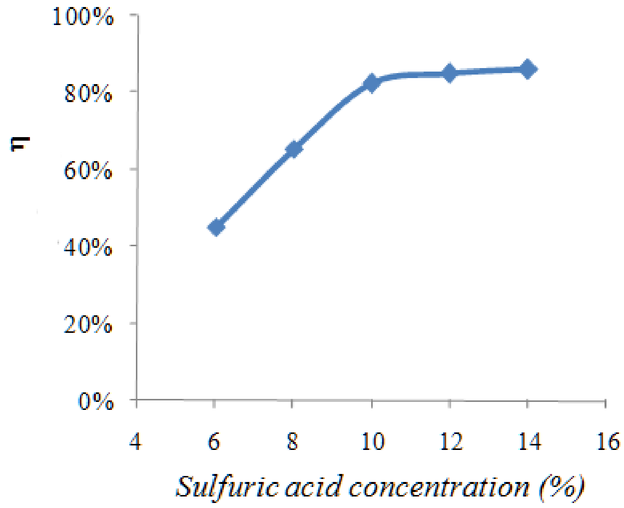

Fig. 2. Effect of acid concentration on the removal of impurities

The changing of the inpurities removal follows the concentration of liquor because the acid concentration is low, the amount of acid is not enough to join the chemical reactions, therefore, with invested time only small amount impurities is dissolved. When raise the acid concentration, the chemical reaction happened strongly that makes the major impurities are dissolved. However, the effect of remove impurities is limited. Whereby, the effect of remove impurities is 80-85% even the concentration still raising. That means in the graphite concentrate there is amount of impurities cannot be dissolved by H_2SO_4 (organic, SiO_2, CaO in the $CaSO_4$ form, etc.,) or impurities in between graphite scales that makes to difficult for reaction.

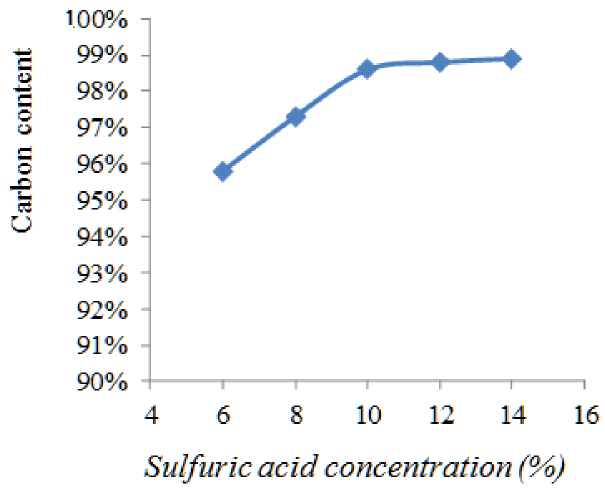

Fig. 3. Effect of the sulfuric acid concentration to the content of carbon in the product.

Fig. 3 shows the relative between the acid concentration and the content of carbon. The sulfuric acid concentration increase to 10% and the content of carbon increase to 99%, respectively. The sulfuric acid concentration increase to 14% the removal of impurities does not change significantly with an increase in concentration, which is an indication that the reaction mechanism change. The sulfuric acid concentration for the test was 10%.

C. Effect of temperature

The experiment conditions:
- Sample: 100 gram

- Liquid/solid ratio: 5
- Stirring speed: 200 rpm
- Time: 60 min.
- Sulfuric acid concentration: 10%
- Temperature: room temperature, 50 and 70°C

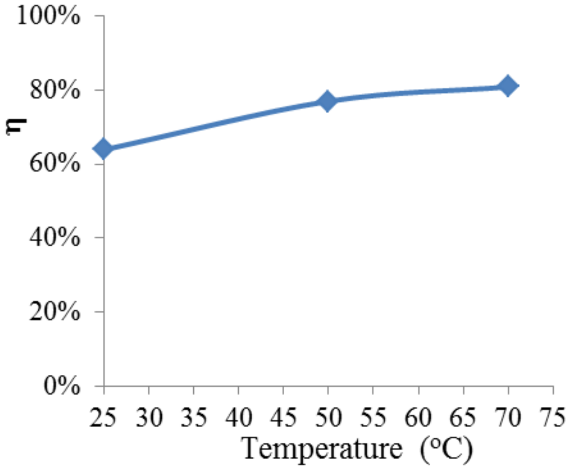

Fig.4. Effect of temperature on the removal of impurities from graphite

Fig. 4 shows that, effect of temperature on the removal of impurities from graphite is quite clearly. The increase of temperature, the removal of impurities increase but is insignificant at the range of 50-70°C. This phenomenon is because the reaction is transferred from the interface chemical reaction to diffusion. This needs further study.

On the other hand, if high temperature leaching will increase production cost, the test was experiment at room temperature.

D. Effect of leaching time

The experiment conditions:
- Sample: 100 gram
- Liquid/solid ratio: 5
- Stirring speed: 200 rpm
- Sulfuric acid concentration: 10%
- Room temperature
- Leaching time (min): 30, 60, 90, 120, 150, 180, 210 and 240.

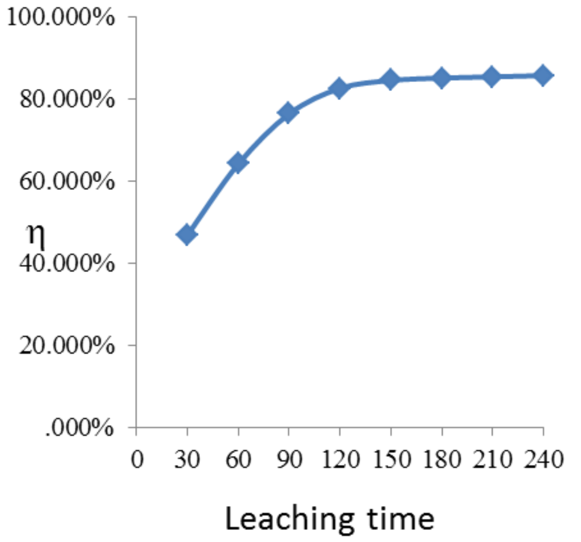

Fig.5. Effect of leaching time on the removal of impurities from graphite

Fig. 5 shows that, the increase of leaching time, the removal of impurities increase. The curve presents the relationship between the effected of leaching time on the removal of impurities is divided into three regions:

- Region 1: Leaching time from 30-120 minutes, effect of the removal of impurities increase rapidly.
- Region 2: Leaching time from 120-180 minutes, effect of the removal of impurities increase but slowly down.
- Region 3: Leaching time over 180 minutes, effect of the removal of impurities increase but insignificantly.

Therefore, the leaching time for test was 120 min. The final product is 98.6% carbon with (η) is 82.3%.

E. Effect of solid/liquid ratio

The experiment conditions:
- Sample: 100 gram
- Stirring speed: 200 rpm
- Sulfuric acid concentration: 10%
- Room temperature
- Leaching time: 120 min
- Liquid/solid ratio: 5

Graphite has specific gravity from 2.09÷2.26 g/cm^3 [8]. However, with flake natural graphite, the heap density is smaller. Therefore, the leaching of graphite concentrates requires a higher L/S ratio than normal leaching processes. According to the test results, it was very difficult to stirring when the L/S ratio was 1 or 2.

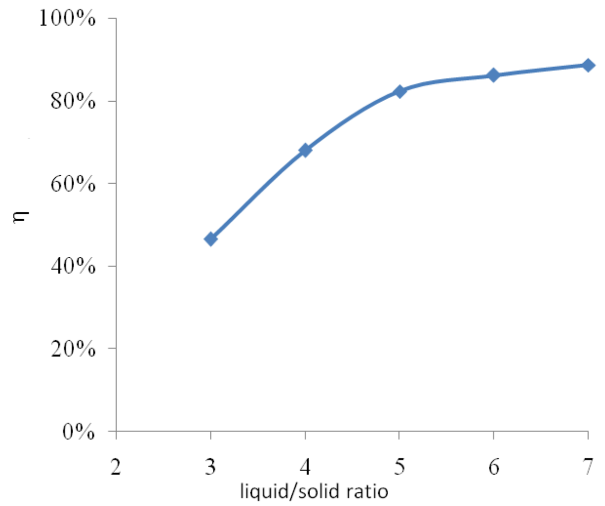

Fig.6. Effect of L/S ratio on the removal of impurities

Fig.6 indicates the effect of L/S ratio on the removal of impurities. With the increase of L/S, the removal of impurities increases. With L/S ratio was 5, the stirring of mixture was easy, but the increase of L/S to 7 is not required. The L/S ratio for test was 5.

Similar to the effect of L/S ratio on the removal of impurities, the carbon content of the product also increased rapidly when the L/S ratio increased to 5. The continue increase to 7, carbon content in product increases but insignificant. When L/S = 5, the final product reaches > 97% carbon (see Fig.7).

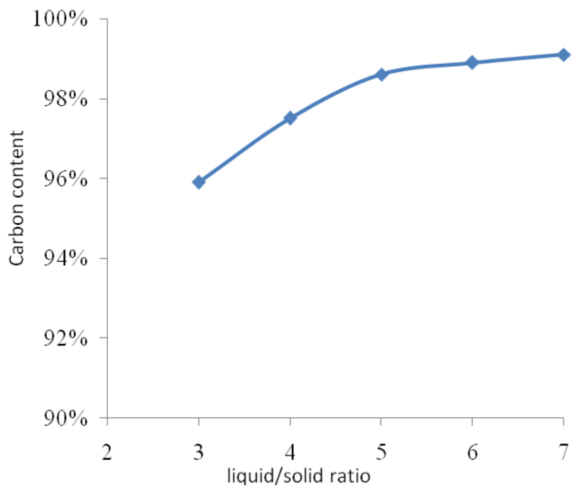

Fig.7 Effect of L/S ratio on carbon content of the final product

IV. CONCLUSIONS

Leaching process for producing high purity graphite from 92,6% carbon to 98% carbon was studied with many factors affecting, such as various leaching agents, sulfuric acid concentration, temperature, time and L/S ratio. Conclusions are as follows:

(1) Both sulfuric acid and chlorhydric acid are good leaching agents are capable of eliminating impurities in fine graphite ore. However, the cost of using H_2SO_4 is lower than that of HCl but the difference of effect of the impurities removal was insignificant. Hence, H_2SO_4 is chosen as leaching agent.

(2) Through various experiments, the technological parameters chosen were 10% concentrate of sulfuric acid, room temperature, reaction time 120 min, liquid to solid ratio 5.

(3) Under the above technical conditions, the final product reaches 98% carbon, the effect of the removal of impurities was 82.3%.

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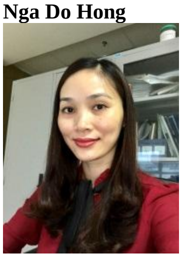

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