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Removal of Sulfur From Iron Ore with Physical and Chemical Methods

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Abstract - In this study, sulfur was removed from Kahramanmaras Elbistan iron ore, which has a high sulfur content, by application of microwave and chemical methods (H_2SO_4 / H_2O_2) together. Low-grade iron ore, with a high sulfur content, constitutes a significant bottleneck especially in technical applications. Various physical and chemical methods for removal of sulfur from a high sulfur content iron ore are applied. However, the sulfur removal process must be economical to be applicable reasonably. Therefore, both physical and chemical methods for removal of sulfur were investigated in this study. In the first part, iron ore was heated to a high temperature by microwave to decompose pyritic sulfur, which is one of the sulfur species in the ore (FeS_2), into sulfur dioxide (SO_2), ferrous sulfate ($FeSO_4$), and pyrrhotite (FeS). Then, the ore obtained by this process was extracted (leaching) with H_2SO_4/H_2O_2 solution at a determined concentration. The highest sulfur removal was obtained at 2.75 GHz and 900W microwave heating time of 210 sec and 0.03 N H_2SO_4/10% H_2O_2 treatment conditions at 60 min reaction time and ambient conditions. According to the obtained results, removal of sulfur content of the iron ore was not significantly affected at high microwave power, high H_2SO_4 and H_2O_2 concentration and high temperature conditions. By applying microwave and chemical methods (H_2SO_4/H_2O_2) together, sulfur content of iron ore was removed approximately by 84%.

Keywords: Iron ore; sulfur removal; physical and chemical methods.

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INTRODUCTION

World steel production is in continuous growth. Today, it is not even possible to imagine a life without steel. While the annual steel production in the world was 28 million tonnes in 1900, it reached 780 million tonnes at the end of the century. North America with a 14.5% share and Continental Europe, including the former Soviet Union and Eastern Block, with a 36% share became the steel producer blocks following Asia [1].

Problematic iron ore deposits containing silica, sulfur, copper, carbonate, alumina, titanium, phosphorus, and arsenic and directly affecting the cost, quality, and production in the sector are present in Turkey. These deposits with iron tenors between 20-54% are located in Malatya, Sivas, Erzincan, Bingöl, Kayseri, Kahramanmaraş, Balıkesir, Aydın, Ankara, and Kırşehir. Among these problematic deposits, 500-600 thousand tonnes are produced annually from siderite ore in Malatya-Hekimhan, containing 39% Fe and 4% Mn, and used in the sinter blend especially in İsdemir at the rates of 20%. Iron ore reserves determined following the studies conducted by the General Directorate of Mineral Research and Exploration are divided into 3 groups, based on the usage of iron and steel plants:

a) Workable iron ore reserve

These are the deposits, the exploration works limited to a certain extent and production of almost all of which have been made until today. Their ore tenors change between 51-62% Fe. Their current reserves are around 137 million tonnes in which 23 deposits are present.

b) Problematic iron ore reserve

The exploration works of this type of deposits have been performed, and the apparent probable reserve potential has been determined; however, the deposits were partially mined during certain periods since they contained some impurities which were undesired by integrated plants. Today, a significant part of these deposits are not active. Their ore tenors change between 19-54% Fe.

c) Potential iron ore reserve

Not enough exploration activities have been performed in Turkey, and a total of approximately 320 million tonnes of potential reserves has been determined in 27 fields. The tenors of these deposits change between 14-52% Fe. It is not possible to mine these deposits without determining the ore reserve and solving the technological problems for certain [2]. Almost all of the iron ore deposits in Turkey contain impurities in a range not approved by integrated plants. It is not possible to mine these deposits without determining the ore reserve and solving the technological problems for certain [2]. Sulfur, phosphorus, oxygen, hydrogen, and nitrogen are the dangerous impurities contained in steel. These are also known as interstitial atoms since they settle into interstitial spaces in the iron cage. The most important effects of these impurities on steel are ductility, impact resistance, and reduction of the resistance to corrosion. Oxygen and sulfur are also the source of non-metallic particles in steel, known as inclusion. These inclusions should be removed from steel as far as possible since they have dangerous effects on the properties of steel. Carbon is also a similar interstitial atom; however, it is generally not acknowledged as a dangerous impurity and its amount should be in accordance with the specification. However, new steel types that should contain carbon at a rate as low as possible have been developed nowadays. Sulfur is present in iron ore in the form of sulfatic, pyritic (FeS_2) and other sulfurous mineral salts. This is an unwanted content as stated in the iron-steel industry. It should be removed from the environment with physical and chemical methods at the ore stage or the pot stage. While sulfate sulfur can be easily removed from the environment with proper solvents, pyritic sulfur and sulfur in the form of mineral salts cannot be removed easily [3]. There are many methods for the removal of pyritic sulfur. However, the most effective method is the chemical method [4-8]. Furthermore, it is possible to transform pyritic sulfur into pyrrhotite (FeS) by exposing it to thermal decomposition (pyrolysis). This decomposition reaction is as follows [4]:

$$FeS_2 \rightarrow Fe_{(1-x)}S \rightarrow FeS \quad \text{or} \quad FeSO_4 \ (0<x<0,125)$$

With the decomposition of pyrite to pyrrhotite, elemental sulfur gas, pyrrhotite, and iron (II) sulfate are formed. Magnetic susceptibility of pyrrhotite is approximately a hundred times more than that of pyrite [5]. While elemental sulfur is removed at the gas phase, a part of pyrite in the environment is degraded to sulfate form. This facilitates the removal of a part of sulfur in the ore through dissolution. Microwave heating ensures selective and rapid heating. Pyrite is present at low rates compared to the iron and oxygen compounds in the ore. Ferromagnetic iron alloys such as magnetite provide rapid, effective and selective heating by absorbing microwave rays. Therefore, while pyrite reaches the decomposition temperature faster, energy loss is prevented [6-8]. Pyrite that undergoes no decomposition in the environment after microwave heating is oxidized to a structure that can be dissolved with proper solvents by oxidizing with H_2O_2.

Oxidation is shown as follows [4]:

$$H_2O_2 \rightarrow H_2O + {}^{1}\!/_{2}O_2$$

$$2\ FeS_2 + {}^{11}/_{2}\ O_2 \rightarrow Fe_2O_3 + 4SO_2$$

$$2\ FeS_2 + 7\ O_2 \rightarrow Fe_2(SO_4)_3 + SO_2$$

$$SO_2 + \frac{1}{2}\ O_2 \rightarrow SO_3$$

$$Fe_2O_3 + 3\ SO_3 \rightarrow Fe_2(SO_4)_3$$

The formed $FeSO_4$ compound can easily be dissolved with H_2SO_4 in water. Dissolution is provided as follows:

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

H_2SO_4 is known to increase the oxidation degree of H_2O_2 [4]. The effects of this interaction on the ore at room conditions (1 atm, 25 ^oC) are also examined. Parameters at room conditions are chosen to reduce the cost.

MATERIALS AND METHODS

The analysis of the raw iron ore is given in Table 1. Iron ore to be used in experiments was ground with a grinder and sifted through a sieve with 0.75 μm pores. The sifted sample was dried for 48 hours at room conditions. Approximately 40 g of the ore, prepared for the process, was taken to silica crucibles by being weighed at 0.001 g accuracy, and 5 different samples, prepared in this way, were treated in a home type microwave oven at 2.45 GHz frequency and 900 Watt for 30, 60, 90, 120, 180 and 240 sec. The treated ore was left to cool in a desiccator just after the microwave treatment.

For the process of sulfur removal with H_2O_2 solution, approximately 40 g of iron ore was weighed at 0.001 g accuracy and put in a 400 mL Erlenmeyer flask in a way that the "amount of ore (g)/volume of H_2O_2 solution (mL)" ratio will be approximately 1/5. During 60 min of the reaction time at room temperature, they were mixed with hydrogen peroxide solutions with 1%, 5% 10%, 20% and 30% concentrations throughout the reaction time. Afterwards, the treated ore samples, filtered with a rough filter paper, were dried for 6 hours under 160 mmHg of constant vacuum pressure and at 100 °C constant temperature.

For the process of sulfur removal with H_2SO_4 solution, approximately 40 g of ore was weighed at 0.001 g accuracy and put in 400 mL Erlenmeyer flask in a way that the "amount of ore (g)/volume of H_2SO_4 solution (mL)" ratio will be approximately 1/5 in specific sulfuric acid concentrations. For 60 min of the reaction time at room temperature, they were mixed with

H_2SO_4 solutions in 0.01 N, 0.03 N, 0.05 N, 0.07 N and 0.1 N concentrations throughout the reaction time. Afterwards, the treated samples, filtered with a rough filter paper, were washed 6 times with 20 mL of hot water and dried for 6 hours under 160 mmHg of constant vacuum pressure and at 100 °C constant temperature. The total sulfur and sulfate sulfur contents of the raw ore sample and treated ore samples were determined in accordance with TS 329 and TS 363 standards, respectively [9-10]. Since no organic sulfur was present in the sample, pyritic sulfur was calculated from the difference.

Table 1. The analysis of the raw iron ore (wt.%)

Fe	FeO	Al_2O_3	SiO_2	Na_2O	K_2O	P	S	Cu	S_{SOx}	$S_{pyritic}$
63,02	20,31	0,11	5,37	0,07	0,09	0,02	5,505	0,01	0,048	5,457

RESULTS AND DISCUSSION

The Effect of H_2SO_4 concentration

Upon increase of the sulfuric acid in the media during the leaching of the iron ore, removable sulfur amount firstly increases then decreases. This results from the porous nature of the ore. A high amount of sulfur exists inside the solution remaining as the hygroscopic moisture in the pores of the ore after the filtration. This content is crystallized after drying process and causes an increase in the sulfur rate of the ore. Therefore, dissolving effect of the leaching solution reduces in partially lower sulfuric acid concentrations. Thus, the residual solution following the leaching process bears low sulfur. As clear from Figures 1 and 2, sulfuric acid concentration is at optimum value around 0.03 N. High acid concentrations have a negative effect on the sulfur removal process. Furthermore, for the process costs, higher levels of acid concentrations negatively affect the sulfur removal process.

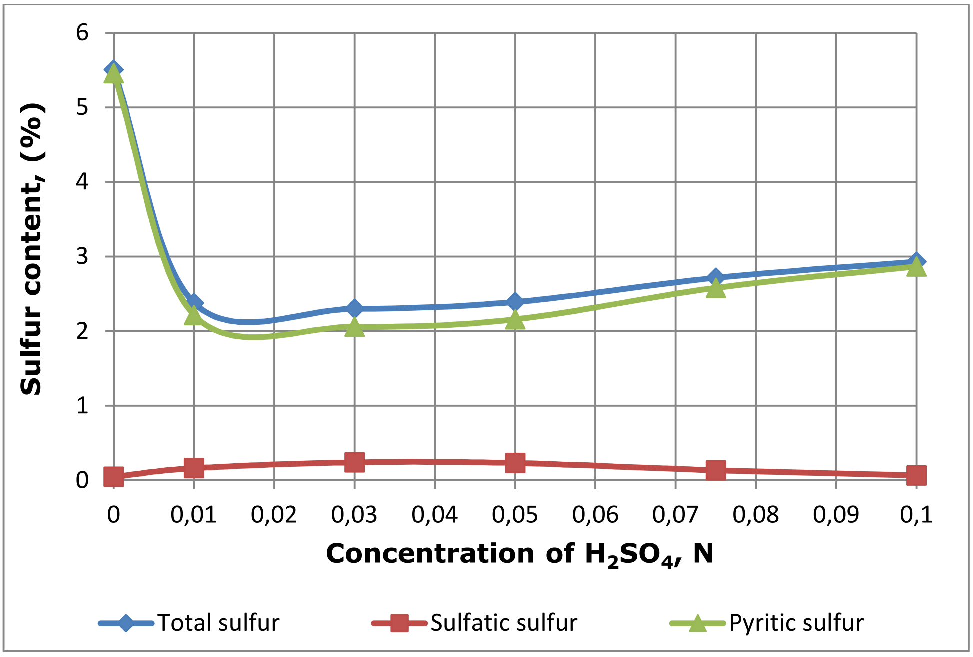

Figure 1. Effect of H_2SO_4 concentrations on sulfur content of the iron ore.

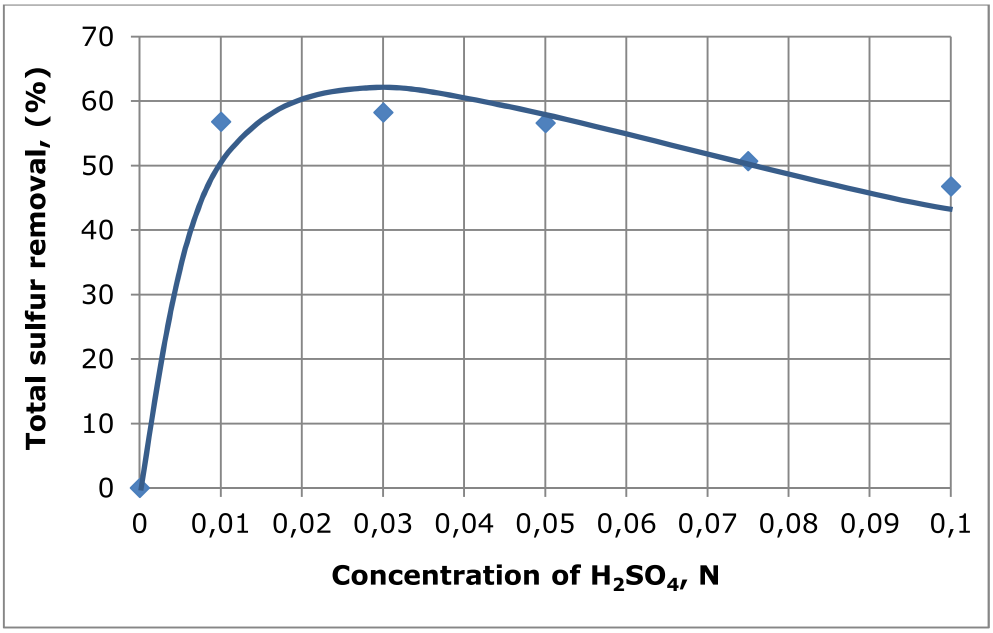

Figure 2. Effect of H_2SO_4 concentrations on total sulfur removal of the iron ore.

The Effect of H_2O_2 Concentration

In the leaching process of the iron core with hydrogen peroxide solution, pyritic sulfur and other sulfur compounds, highly available in the iron core, are oxidized to the sulfatic sulfur. In Figures 3 and 4, the most suitable H_2O_2 concentration for both total sulfur and sulfur types content and total sulfur removal is 10%. For high concentrations of H_2O_2, no significant change has occurred in the total sulfur and sulfur type contents. Moreover, some part of the sulfatic sulfur are attached to iron ions like $Fe_2(SO_4)_3$. This would cause loss of iron during leaching of H_2SO_4. Therefore, high concentrations of H_2O_2 were not preferred.

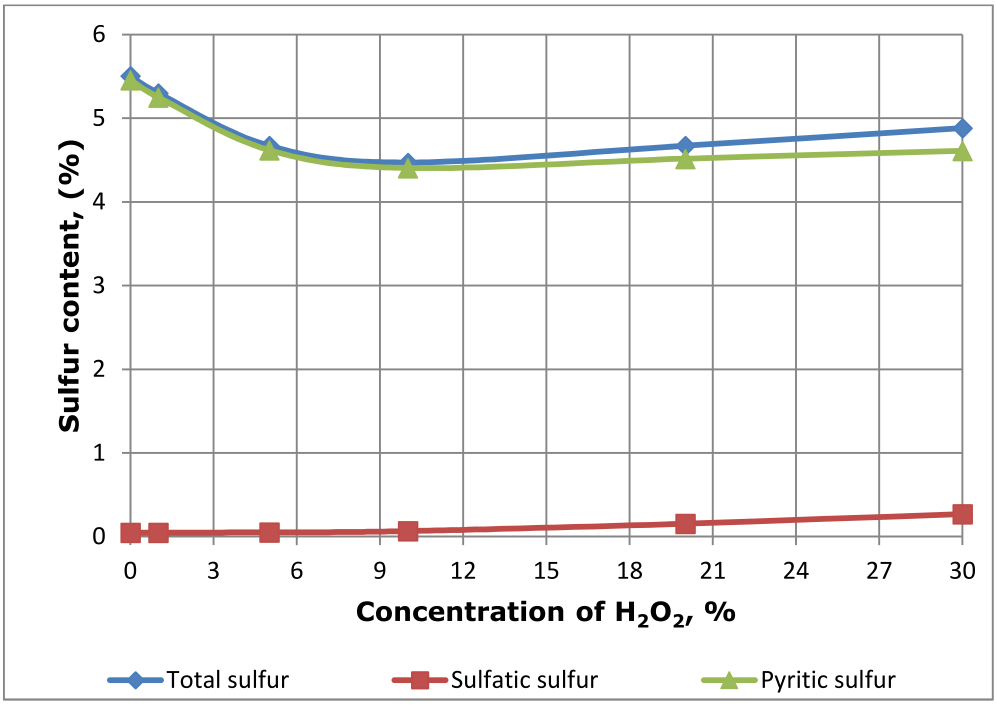

Figure 3. Effect of H_2O_2 concentrations on sulfur content of the iron ore.

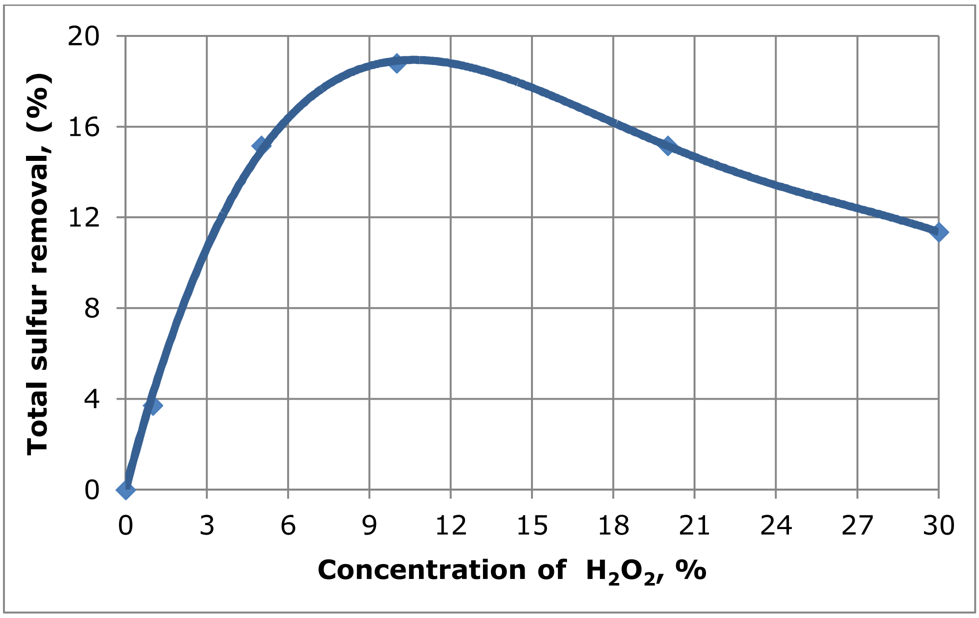

Figure 4. Effect of H_2O_2 concentrations on total sulfur removal of the iron ore.

The Effect of Heating by Microwave

A microwave oven of 2.75 GHz and 900 Watt was utilized to remove sulfur from the iron ore. The process of removing sulfur from the iron ore through the microwave method has allowed us to examine the effect of microwave rays in different durations on total sulfur and sulfur types. As stated above, a significant amount of pyritic sulfur is available in the iron ore. Therefore, pyrite and other sulfur compounds heat up very quickly via the microwave rays. Due to the liberated heat during this process, temperature goes up and thus decomposition of pyrite accelerates. Because the system used for the sulfur removal from the iron ore via microwave method is open to the atmosphere, significant part of the sulfur is oxidized and goes away as SO_2 and other sulfur oxide compounds. As clear from Figure 5 and 6, the most suitable microwave heating span is 210 s for both total sulfur and sulfur types content and also the total sulfur removal. Increasing the time over 210 s has not changed the total sulfur and sulfur types content significantly. Since the pyritic sulfur is decomposed until approximately 210 s, not a significant change has occurred in total sulfur removal in high microwave heating times.

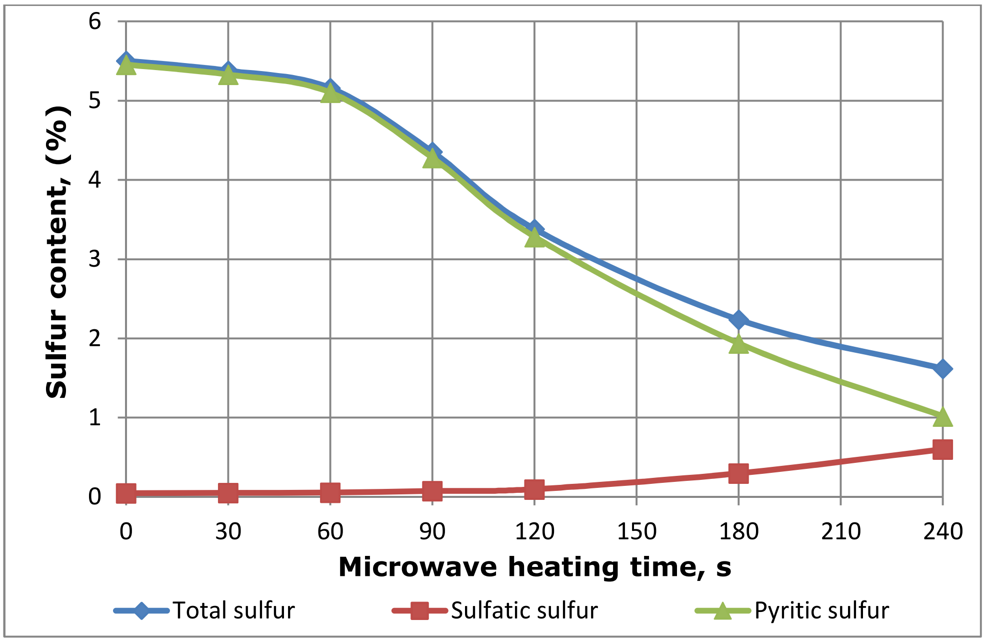

Figure 5. Effect of microwave heating time on sulfur content of the iron ore.

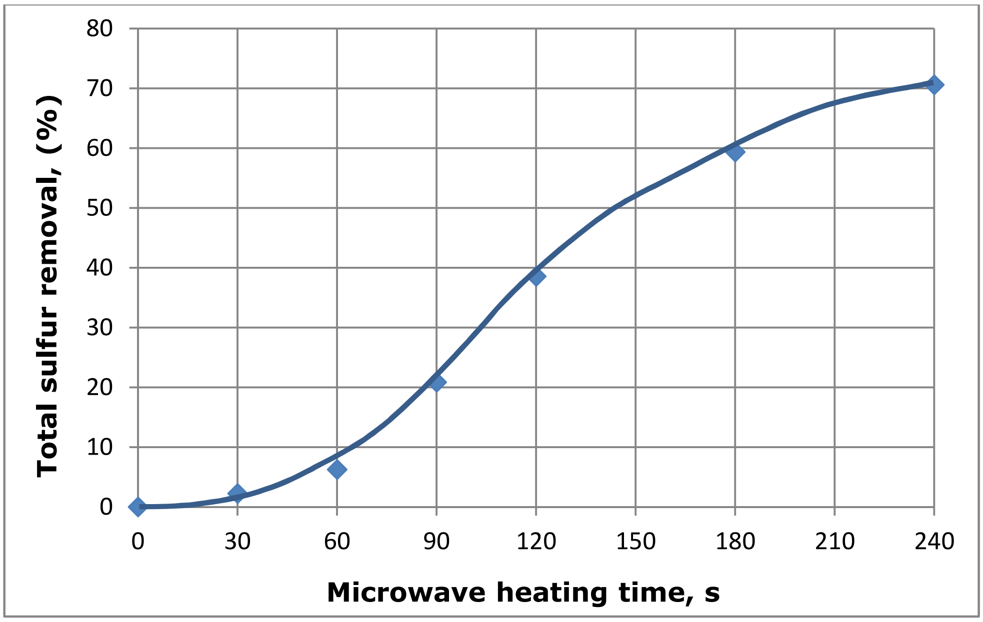

Figure 6. Effect of microwave heating time on total sulfur removal of the iron ore.

According to the results obtained, the optimum process parameters were briefly determined as 210 sec of heating with a microwave at 2.75 GHz and 900 W, H_2SO_4 concentration; 0.03 N, H_2O_2 concentration; and 10% in the removal of sulfur from iron ore with physical and chemical methods.

Following the treatment of the ore, pre-treated with a microwave at 2.75 GHz and 900 Watt, with 0.03 N H_2SO_4 and 10% H_2O_2 solutions at room conditions for 1 hour, the total sulfur content of iron ore was reduced from 5.505% to 0.894%, pyritic sulfur content was reduced from 5.457% to 0.894% and sulfate sulfur was removed completely. Since no organic sulfur is present in the iron ore sample, the total sulfur content is equal to the sum of sulfate and pyritic sulfur. Since no sulfate sulfur is present in the treated sample, the total sulfur is equal to pyritic sulfur. Therefore, the total sulfur and pyritic sulfur contents of the treated sample are the same (0.894%). At the end of these processes, the total sulfur content of the raw iron ore was removed at the rate of approximately 84%. It is considered that the rate of sulfur removal from raw iron ore can be increased and the cost of the process can be reduced with a study in which the power, frequency and heating rate of the microwave based on these parameters change.

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Türkçe Öz ve Anahtar Kelimeler

Fiziksel ve Kimyasal Yöntemlerle Demir Cevherinden Kükürdün Uzaklaştırılması

Buğra ÇAVUŞOĞLU, Hüseyin KARACA

Öz: Bu çalışmada kükürt, yüksek kükürt içeriğine sahip Kahramanmaraş Elbistan demir cevherinden mikrodalga ve kimyasal yöntemlerle (H_2SO_4 /H_2O_2) uzaklaştırılmıştır. Düşük kaliteli demir cevherinde yüksek kükürt içeriği vardır, özellikle teknik uygulamalarda bir darboğaz yaratmaktadır. Yüksek kükürtiçerikli demir cevherinden kükürdün giderilmesi için çeşitli yöntemler uygulanmıştır. Ancak, kükürt giderme sürecinin makul bir şekilde uygulanabilmesi için ekonomik olması gerekir. Bu nedenle, kükürt giderme için fiziksel ve kimyasal yöntemler incelenmiştir. İlk kısımda, demir cevheri pirit kükürdünü (FeS_2, cevherde bulunan kükürt türlerinden biridir) mikrodalga ile yüksek sıcaklığa ısıtılıp kükürt dioksit (SO_2), demir(II) sülfat ($FeSO_4$) ve pirotit (FeS) elde edilmiştir. Bunun ardından H_2SO_4 / H_2O_2 çözeltisi ile soz konusu cevher örneği belirlenen derişimlerde ekstrakte edilmiştir (liçing). En yüksek kükürt giderme performansı 2,75 GHz ve 900 W ısıtma ile (210 saniye) elde edilmiştir, kimyasal yöntemde ise 0,03 N H_2SO_4 / %10 H_2O_2 karışımı 60 dakika süreyle ve oda şartlarında kullanılmıştır Elde edilen sonuçlara göre, demir cevherinden kükürt gidermesinde yüksek mikrodalga gücü, yüksek H_2SO_4 ve H_2O_2 derişimi ve yüksek sıcaklık parametreleri belirgin bir şekilde etkili olmamıştır. Mikrodalga ve kimyasal yöntem (H_2SO_4 / H_2O_2) beraber kullanıldığında demirin kükürt içeriği yaklaşık %84 oranında giderilmiştir.

Anahtar kelimeler: Demir cevheri; kükürt giderme; fiziksel ve kimyasal yöntemler.

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