

DEVELOPMENT OF A METHOD FOR DETERMINATION OF METALLIC IRON CONTENT WITHIN HOT BRIQUETTE IRON (HBI) FOR STEELMAKING

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Abstract

The growing use of metallic iron in metallurgy and industrial chemical applications requires a fast, easy and cheap method for the determination of metallic iron, not merely in recyclable materials, such as iron pellets, reduced iron mill scale dust, electric arc furnace dust and pig iron, but from hot briquette iron (HBI) as well. This study investigates a new method for determination of metallic iron within HBI used for steel-making materials. The effects of reaction time, temperature, and stirring rate were studied. The concentration of iron was determined via Atomic Absorption Spectroscopy (AAS). After the optimization study, high-purity metallic iron powder (Sigma-Aldrich, PubChem Substance ID 24855469) was used to compare efficiencies and identify the optimum conditions; The present study was matched with international standard methods (BS ISO 5416:2006, IS 15774:2007). Results were consistent with certified values and metallic iron content could be determined within the 95% confidence level. The proposed method is easy, straightforward, and cheap.

Keywords: Hot Briquette iron; Metallic iron; Cementation; Analysis.

1. Introduction

The iron and steel industry is one of the most important business areas around the world [1]. Today, the steel products are generally produced from ferrous raw materials including ore, pellets, sinter, sponge iron and other direct reduced iron (DRI), pig iron, recycled iron and steel scrap, and a variety of waste products [1-3]. In 2013, total world crude steel production was of 1.6 billion tonnes (mmt) and the use of electric arc furnaces in this crude steel production is about 30% [4,5]. However, in Turkey, 71% of the total steel production is carried out by electric arc furnaces. This percentage is even higher in Turkey where two thirds of the steel produced is manufactured through the scrap. Further, Turkish steel producers are the main scrap consumers due to the insufficient domestic resources. Metallic iron production by using domestic resources is vital for Turkish iron and steel industry [6,7].

Numerous studies has been concentrated on new processes in the literature regarding the effort toward development of alternative direct reduced iron-making processes, alternative pig-iron-making processes and direct smelting reduction [1,6,7]. Additionally, composition of sample (i.e. metallic iron and total iron content) is more important for production process. So, the relation of between input and output of process, mass balance, economic value and mass quality should be calculated by producer

[1,2]. The literature contains several international standards for the analysis of all iron amounts in associated resources (i.e. iron ore, scrap, slag etc.). Generally these methods are related to titration [8,9], and precipitation [10]. However, two international standard methods were published by BS-ISO (British standard-International Standard) and IS (Indian standard) in 2006 and 2007 for determination of metallic iron content in HBI, respectively. Until 2006, several commercial and university laboratories were used household method, but they have found different metallic iron result in same sample (e.g. HBI or DRI) [1].

There are several house-hold methods on the determination of metallic iron via gravimetric method, which was applied with a magnetic collection, or mercuric chloride so as to extract metallic iron from sample. It is known that these methods have many advantages including ease of operation and low energy consumption. Nevertheless, these are bad separation efficiency and consequently might result in moderately low analysis result when applied to HBI sample [2, 11].

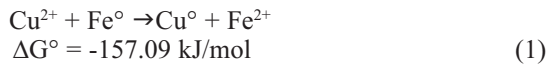
The application of BS ISO 5416:2006 and IS 15774:2007 should be used for determination of metallic iron content in HBI. However, these multi-steps dissolution procedures require highly skilled chemists and the use of bromine and mercury chloride for analysis of metallic iron content but the handling of such hazardous chemicals can be dangerous and

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demands practically continuous operator's attention.

It is known that the cementation of copper generally was carried out by iron in the industry, because it is cheap and readily available. Using this approach, a new method was designed for the determination of metallic iron by cementation method with copper. As can be seen the equation 1, metallic iron reduce Cu^{2+} to Cu^0 and becomes Fe^{2+} ions in the solution [11,12].



After the cementation reaction was carried out, the metallic iron content can be determined with spectrometric methods (AAS or ICP).

The main purpose of this study was to investigate the parameters on an effective metallic iron determination method from certificated HBI sample. Furthermore, comparisons of the optimum conditions were conducted on standard reference material. The present study was matched with international standard methods [13,14].

2. Materials and Methods

The certified HBI was supplied from Bureau Veritas test office in Istanbul. The chemical composition and X-ray diffraction (XRD) patterns (PANalytical PW3040/60, Netherlands) are presented in Table 1 and Fig. 1, respectively.

Table 1. The chemical analysis of certified HBI (BS ISO 5416:2006).

Certificated HBI	w/w, %
Fe_T	91.58
$\text{Fe}_{(\text{Me})}$	86.46
Metallization degree	94.41
C	1.37
S	0.02
P	0.02
SiO_2	4.66
CaO	1.04
Others	1.31

As seen in Fig. 1, metallic iron and SiO_2 were the major phases in the HBI. The particle size -65+80 mesh (-212+180 μm) HBI was used in the experiments [14]. In general, the solubility of iron displays a decreasing trend with increasing particle size in lixiviant system. This inverse relationship, which provides the direct correlation between particle size and iron solubility, is in accordance with previous studies in the literature [15,16].

All chemical reagents used in this study were of analytical grade. Metallic iron content determination

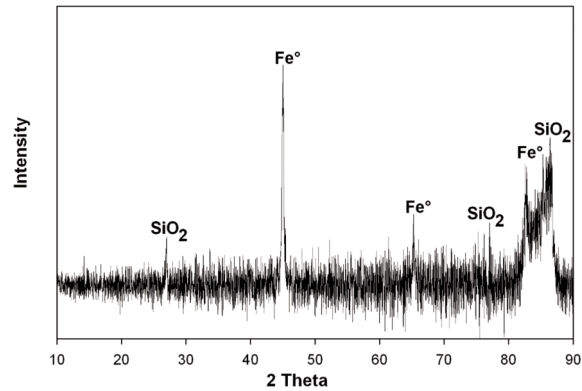


Figure 1. XRD pattern of HBI.

experiments were performed in a 250 mL capacity borosilicate glass beaker and continuously stirred with a magnetic stir-plate. The beaker was covered with watch glass to prevent evaporation losses. The beaker was heated in a temperature controlled silicon oil bath ($\pm 1^\circ\text{C}$). Each experiment used 0.5 g of HBI and 100 mL of 0.40 M copper sulfate solution (pH=3-4) while the effects of reaction temperature, reaction time and stirring speed on the metallic iron leaching were iteratively studied. The solid/liquid separation was performed with Whatman filter paper following each run. And then 10 mL HCl was added to adjust the solution pH to acidic region (pH \approx 1). After the leaching experiments, to determine of iron content, all samples were analyzed by AAS (Perkin Elmer AAnalyst 800, USA) using a standard protocol.

The fraction of metallic iron content was calculated using the following formula:

$$\text{Fraction, } X_{\text{Fe}} = \left[\frac{M_f}{W \times M_i} \right] \quad (2)$$

Here, W is the weight of the powder, M_i is the certificated value and M_f is the metal amount at the end of the experiment.

The solution pH value of the leaching solution (i.e. CuSO_4) is more important parameters for the determination of metallic iron content in HBI. It is known that ferric (trivalent iron) ions precipitated in the solution whose pH is above 2.5 while ferrous (divalent iron) ions start to precipitate about pH 7.00 (see equation 3 and 4) [11,12].



As expressed in equation 3 and 4, $\text{Fe}(\text{OH})_3$ exhibits a low solubility product constant than $\text{Fe}(\text{OH})_2$. After the sample was reacted with leaching solution, the solution pH was increased from 4.5 to ~ 7.0 .

The iron (II) can be precipitated in the solution when the leaching solution pH is high (acidic to basic area). Also, divalent iron can be converted trivalent



iron by increasing solution temperature and trivalent iron will be precipitated easily into solution approximately pH at 2.5 as $\text{Fe}(\text{OH})_3$. For these reasons, after reaction of the sample with CuSO_4 , the solution should be filtered immediately. The pH value of the filtrated solution should be adjusted to 1 with hydrochloric acid in order to avoid the precipitation of all iron hydroxide form [2]. Moreover, comparisons of the optimum conditions were conducted on standard reference material.

3. Results and Discussion

This process can be used to determination of metallic iron content in HBI by leaching with copper sulfate. Other iron compounds (e.g. iron oxides) were separated from the HBI by a simple electrochemical replacement technique. The metallic iron in the HBI was subsequently converted to aqueous $\text{Fe}(\text{II})$ ions.

3.1 Effect of temperature

The fraction of metallic iron content evaluated using a series of different temperatures (Fig. 2). In the experiments, 0.5 g HBI powder was performed by varying the temperature from 25 to 90°C with 100 mL CuSO_4 concentration of 0.40 M, time of 40 min and at 600 rpm. As shown in figure, the metallic iron content fraction increased with increasing temperature because the conversion of Fe^0 to Fe^{2+} is thermodynamically more favorable when the oxidizing-to-iron (II) ion ratio is high ($\Delta G^\circ = -157.09$ kJ/mol) [12]. Temperature was observed to play an important role in the leaching of metallic iron from the HBI. The dissolution efficiency increased as the reaction temperature was increased. For example, the temperature was increased from 30°C to 60°C, the dissolution of metallic iron also increased by approximately 20%, which indicates that the temperature plays a significant role for the leaching of

metallic iron from HBI. This trend is also in accordance with the previously published literature [11]. After above 80°C, there was no change in dissolution fraction of metallic iron. This is the reason why 60°C and 70°C was investigated in the following experimental series.

3.2 Effect of stirring speed

In this experiment, the effect of stirring speed on metallic iron dissolution fraction was investigated as a function of the shaking rate in the range of 0 to 600 rpm. Sample quantity (0.5 g HBI powder) and other parameters (100 mL CuSO_4 concentration of 0.40 M, for 40 min) were kept constant. Figure 3 displays the variation in metallic iron dissolution fraction with different stirring speeds. The stirring was an important parameter affecting the dissolution of metallic iron from HBI. Without stirring, a fraction of metallic iron 0.40 was obtained at 70°C, although the similar fraction of metallic iron was achieved using 100 rpm stirring at 60°C. This finding indicates that dissolution of metallic iron in HBI is affected by diffusion-controlled kinetic factors. This trend is also in accordance with the previously published literature [2, 11, 15]. By increasing the stirring speed from 300 to 600 rpm it was possible to increase fraction of metallic iron of ~12%. The more rapid the stirring speed, the greater the obtained fraction of iron. For example, at 60°C a fraction of metallic iron 0.55 was observed at a shaking rate of 200 rpm, whereas the fraction of metallic iron increased to 0.70 with a shaking rate of 400 rpm. This difference can be attributed to the fact that the probability of contact between the metallic iron atoms and copper ions present in the solution increases with increasing stirring rate, which results in higher efficiencies [17]. The maximum agitation rate (600 rpm) was selected for the subsequent experiments. The stirring of the leaching solution is important, because no stirring

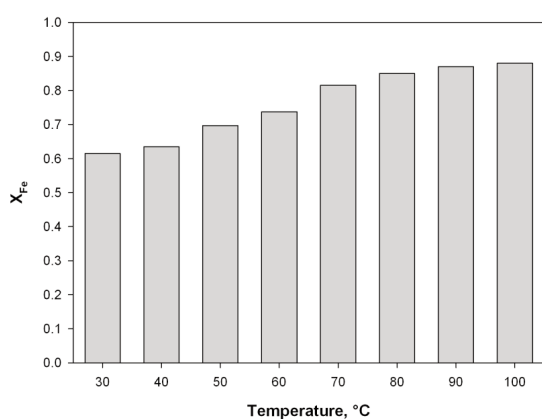


Figure 2. Effect of leaching temperature on HBI (0.5 g HBI, 100 mL of 0.4 M CuSO_4 , 40 min, 600 rpm).

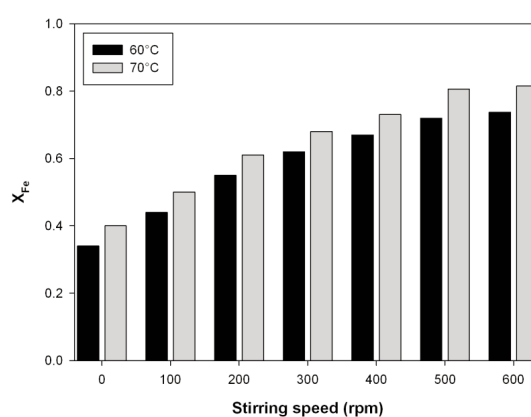


Figure 3. Effect of stirring speed on HBI (0.5 g HBI, 100 mL of 0.4 M CuSO_4 , 40 min).



may lead the metallic Cu particles to covered metallic iron and this plated metallic iron particles passives the metal particles hindering further dissolution.

3.3 Effect of time

In this experimental series, the effect of contact time on metallic iron dissolution fraction was studied in the range of 15 to 150 min. Sample quantity (0.5 g HBI powder) and other parameters (100 mL CuSO_4 concentration of 0.40 M at 60°C and 70°C, at 600 rpm) were kept constant. The figure 4 shows that increasing the contact time has a positive effect on dissolution fraction of metallic iron. The figure indicates that the dissolution fraction of metallic iron reached equilibrium after 120 min at 70°C. This is an expected result because the dissolution of metallic iron in CuSO_4 solution process was thermodynamically favorable. This result is in agreement with a study by Xu et al., 2003 [2], who determined metallic iron content using copper sulfate solution as leaching solution described herein.

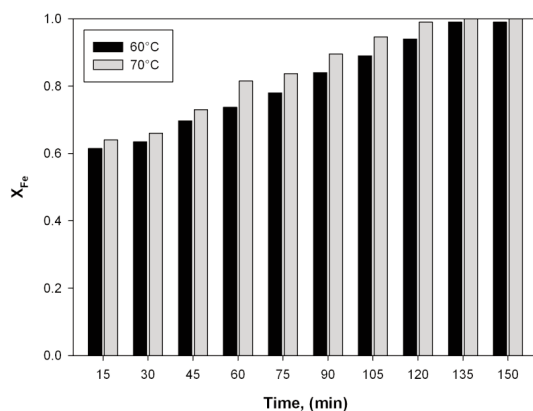


Figure 4. Effect of time on HBI (0.5 g HBI, 100 mL of 0.4 M CuSO_4 , 600 rpm).

3.4. Method accuracy and precision with SRM 2557 standard reference material

After the optimization study, high purity metallic iron powder (99.99 % Fe, Sigma-Aldrich, PubChem Substance ID 24855469) was used to validate the suitability and accuracy of the proposed method. Reference analyses results are shown in Table 2. Besides, the present study was matched with

Table 2. Comparison of the methods with certificated metallic iron (N=3).

Sigma- Aldrich, Standard	The present study Average experimental values, (%) ^A	BS ISO 5416:2006 method Average experimental values, (%) ^A	IS 15774:2007 Method Average experimental values, (%) ^A
Fe	99.98 ± 0.03	99.94 ± 0.07	99.92 ± 0.10

^AMean ± Standard Deviations (SD)

international standard methods (BS ISO 5416:2006, IS 15774:2007) [13,14].

Under optimized experimental conditions, metallic iron can be recovered to within the 95% confidence level in high purity metallic iron powder. Table 2 reveals SD that are lower than 0.010 for metallic iron, showing a good reproducibility during the entire analytical process. The reference results are generally in good agreement compared other international methods and with its certified values.

4. Conclusion

This study attended to determination of metallic iron content from steel-making material (e.g. HBI) via cementation (i.e. electrochemical replacement) technique. The main goal was to develop a method for determination of metallic iron content from steel-making material.

It is achieved that high accuracy and precision using hot briquette iron (HBI) and identified 0.5 g HBI powder was performed at 70°C with 100 mL CuSO_4 concentration of 0.40 M, time of 120 min and at 600 rpm.

(1) The present study for HBI is advantageous compared to the above methods because metallic iron can be selectively determinate from other iron oxides impurities.

(2) Additionally, presented a cheap method capable of determine at least 99% of the metallic iron present in any sample.

(3) The reference standard was used to compare efficiencies and results were consistent with certified values.

Therefore, it is proposed that the present study is applicable to the determination of metallic iron in various metallic iron contain samples. The present study is developed for determination metallic iron content from HBI. This result shows that the present study can be used in many laboratories such as steel-making industry, university and commercial laboratories etc.

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