CUKUROVA UNIVERSITY

INSTITUTE OF NATURAL AND APPLIED SCIENCES

MSc THESIS

Emre GÖZDAMLA

THE INVESTIGATION OF THE RECYCLABILITY OF THE IRON MINERALS IN THE BLAST FURNACE FLUE DUSTS

MINING ENGINEERING DEPARTMENT

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ABSTRACT

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In this study, the recyclability of the blast furnace flue dusts were investigated in terms of iron minerals. 3 different method were used as the reverse flotation process, the magnetic separation process, and the acid leaching process. In order to conduct chemical analyses the X-Ray Fluorescence device was used. The results were crosschecked by atomic absorption spectrometer. For the Fe element, the results were also crosschecked by volumetric analyses too. The concentrate which was acknowledged as the optimum were obtained from the reverse flotation process which was conducted by the help of reuse of the process water. For the concentrate, Fe grade was 52.61%, ash grade was 96.31%, weight was 22.10% of the weight of the feeding material, iron recovery was 68.41%, SiO_2 grade was 4.82%, [(CaO+ MgO)/(SiO_2+Al_2O_3)] ratio was 0.44, Zn grade was 0.81%, Pb grade was 0.37%, S grade was 0.08%, Mn grade was 0.64%, Cu grade was 0.04%, Ti grade was 0.12%, V grade was 0.02%, and Cr grade was 0.01%. On the other hand, P, As, and Ni grades were below the limits which the device measures. After the experiments, while the blast furnace flue dusts being recycled so as to be obtained concentrated iron minerals, it was observed that the reverse flotation process was more effective than the magnetic separation and the acid leaching processes in terms of being obtained concentrated iron minerals. At the same time, it was also observed that the acid leaching process was more effective than the magnetic separation and the reverse flotation processes in terms of the removal of the impurities. At the end of the study, because each one of these methods had different advantages and disadvantages, their being tried in a row was proposed.

Key Words: Iron ore, Flue dust, Recycling, Blast furnace

ÖZ

YÜKSEK LİSANS TEZİ

DEMİR ÇELİK YÜKSEK FIRINLARINDAKİ BACA TOZLARININ DEMİR MİNERALLERİNİN GERİ DÖNÜŞTÜRÜLEBİLİRLİĞİNİN ARAŞTIRILMASI

Emre Gözdamla

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Bu çalışmada yüksek fırın baca tozlarının geri dönüştürülebilirliği demir mineralleri açısından araştırılmıştır. Bu özelliği incelemek için ters yüzdürme işlemi, manyetik ayırma işlemi ve asit liç işlemi olarak 3 farklı yöntem kullanılmıştır. Kimyasal analizler için X-Ray Florösans cihazı kullanılmıştır. Daha sonra sonuçlara atomik absorbsiyon spektrometresi ile çapraz doğrulama yapılmıştır. Fe elementi için ayrıca volumetrik analiz ile de çapraz doğrulama yapılmıştır. Optimum olarak kabul edilen konsantre, işlem suyunun yeniden kullanılması yardımıyla ters flotasyon işleminden elde edilmiştir. Konsantre için Fe tenörü %52.61, kül tenörü %96.31, ağırlık besleme ağırlığının %22.10'u, demir (Fe) verimi %68.41, SiO_2 tenörü %4.82, [(CaO + MgO)/(SiO_2 + Al_2O_3)] oranı 0.44, Zn tenörü %0.81, Pb tenörü %0.37, S tenörü %0.08, Mn tenörü %0.64, Cu tenörü %0.04, Ti tenörü %0.12, V tenörü %0.02, ve Cr tenörü %0.01 olarak bulunmuştur. Öte yandan, P, As ve Ni tenörlerinin cihazın ölçüm limitlerinin altında olduğu gözlemlenmiştir. Deneylerden sonra, yüksek fırın baca tozları konsantre demir mineralleri elde edilecek şekilde geri dönüştürülürken, ters flotasyon işleminin, konsantre demir mineralleri elde edilmesi bakımından manyetik ayırma ve asit liç işlemlerinden daha etkili olduğu gözlemlenmiştir. Aynı zamanda, asit liçi işleminin, safsızlıkların giderilmesi bakımından manyetik ayırma ve ters flotasyon işlemlerinden daha etkili olduğu gözlemlenmiştir. Çalışmanın sonunda, her birinin farklı avantajları ve dezavantajları olduğu için, bu yöntemlerin üst üste denenmeleri önerilmiştir.

Anahtar Kelimeler: Demir cevheri, Baca tozu, Geri dönüşüm, Yüksek fırın

EXTENDED SUMMARY

In this study, the recyclability of the blast furnace flue dusts was investigated in terms of iron minerals. 3 different method were used as the reverse flotation process, the magnetic separation process, and the acid leaching process. In order to conduct chemical analyses the X-Ray Fluorescence device was used. The results were crosschecked by atomic absorption spectrometer. For the Fe element, the results were also crosschecked by volumetric analyses too. The feeding material of the study was the blast furnace flue dusts which were taken from Isdemir iron and steel making plant. For the feeding material, combustible grade was 36.28%, Fe grade was 30.97%, SiO_2 grade was 5.61%, Al_2O_3 grade was 1.89%, Zn grade was 1.22%, S grade was 0.61% S, K_2O grade was 0.5%, Cu grade was 0.02%, P grade was 0.03%, Cr grade was 0.008%, Pb grade was 0.57%, Mn grade was 0.36%, MgO grade was 2.52%, CaO grade was 1.88%, Ti grade was 0.13%, and V grade was 0.02%. Grades of Ni, As and Na_2O in the feeding material was below the limits which the device measures. After the qualitative mineral analysis which were conducted by X-Ray Diffraction device, when it was compared to the other iron minerals, it was observed that the flue dust contains hematite dominantly.

For the flotation process, simultaneously obtaining both iron containing part and unburned carbon containing part in a quite effective way was hardly possible because if it was desired to be obtained one of them in an effective way, it was needed to be used different reagents and the quality of the other one might be affected from this situation adversely. For example, if it was needed to be obtained carbonaceous parts as more qualified, pine oil might be needed to be used. Likewise, if it was needed to be obtained iron containing parts as more qualified, methyl isobutyl carbinol (MIBC) might be needed to be used. Due to this situation, reverse flotation process was implemented to the feeding material; namely, recycling of iron minerals in the flue dusts of the blast furnace in the Isdemir iron

and steel plant were primarily targeted per se. On the other hand, recyclability of coal minerals in these flue dusts was also investigated secondarily together with investigation of recyclability of iron minerals.

Besides, the reverse flotation process magnetic separation process and acid leaching process were also implemented to the feeding material. Magnetic separation process was implemented as high intensity wet magnetic separation and feeding material was tried to be beneficiated for 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 Tesla magnetic field intensities.

As a result of magnetic separation experiments performed with high field intensive wet magnetic separator, it was observed that the iron element tenor in concentrates which was obtained as magnetic part decreased as the magnetic field intensity increased. This suggests that with the increase in magnetic field intensity, other non-ferrous magnetic and non-ferrous contents may be attracted with iron. It was thought that the reasons for this situation may be that the sample was flocculated or the sample was not in the liberalization size. Also, since the magnetic field intensity was very high, it could have pulled the particles which showed very low magnetic properties together with the iron. The iron tenor for the magnetic field intensity of 0.25 Tesla was 41.29%. This value decreased to 40.39% at 0.50 Tesla magnetic field intensity. This value was 38.53% for 0.75 Tesla and 38.46% for 1.00 Tesla. This value decreased to 38.35% in 1.25 Tesla and 36.50% in 1.50 Tesla. In addition, it was observed that as the magnetic field intensity increased, iron element recovery (%) and ash recovery (%) increased. Iron recovery was 63.03% for 0.25 Tesla magnetic field intensity, 80.30% for 0.50 Tesla magnetic field intensity, 85.69% for 0.75 Tesla magnetic field intensity, 87.42% for 1.00 magnetic field intensity, 87.59% for 1.25 Tesla magnetic field intensity, 88.25% for 1.50 Tesla magnetic field for intensity. Ash grade was 68.72% for 0.25 Tesla magnetic field intensity, 71.26% for 0.50 Tesla magnetic field intensity, 71.29% for 0.75 Tesla magnetic field intensity, 71.56% for 1.00 Tesla magnetic field intensity, 72.24% for 1.25 Tesla magnetic field intensity,

73.45% for 1.50 Tesla magnetic field intensity. In addition, it was observed that the grades of the zinc elements decreased as the magnetic field intensity increased. Zinc element grade was 1.10% for 0.25 Tesla magnetic field intensity, 1.07% for 0.50 Tesla magnetic field intensity, 1.02% for 0.75 Tesla magnetic field intensity, 1.02% for 1.00 Tesla magnetic field intensity, 0.98% for 1.25 Tesla magnetic field intensity, 0.94% for 1.50 Tesla magnetic field intensity.

When the non-magnetic parts of the experiments with high field intensity wet magnetic separator was looked at, it was observed that as the magnetic field density increases, the combustible grades increased and the combustible efficiency decreased.

In acid leaching experiments, different parameters were tried as molar concentration, time, temperature, stirring speed. 90 minutes time, 6 molar medium, 300 rpm stirring speed, and 24 °C temperature were used as base point for the experiments. After that, related parameter was changed on it. In this way, the experiments were conducted. Experiments for 4, 5, 6, 7, and 8 molar concentrations, 30, 60, 90, 120, and 150 minute time intervals, 100, 200, 300, 400, and 500 rpm stirring speeds, and 24 ±5, 34 ±5, 44 ±5, 54 ±5, and 64 ±5 °C temperatures were implemented. Effect of time, effect of molar concentration, effect of stirring speed, effect of temperature were investigated separately.

The concentrate, which was acknowledged as the optimum, were obtained from the reverse flotation process which was conducted by the help of reuse of the process water. For the concentrate, Fe grade was 52.61%, ash grade was 96.31%, weight was 22.10%, iron recovery was 68.41%, SiO_2 grade was 4.82%, [(CaO+ MgO)/(SiO_2+Al_2O_3)] ratio was 0.44, Zn grade was 0.81%, Pb grade was 0.37%, S grade was 0.08%, Mn grade was 0.64%, Cu grade was 0.04%, Ti grade was 0.12%, V grade was 0.02%, Cr grade was 0.01%. On the other hand, P, As, and Ni grades were below the detection limits.

After the reverse flotation experiments, Fe grade was increased from 30.97% to 52.61% and Zn grade was decreased from 1.22% to 0.81%.

After the acid leaching experiments, the optimum result for acid leaching was obtained from the experiment which was conducted with 6 molar medium, 300 rpm stirring speed, 64 °C temperature, and 90 min. Although Zn grade was decreased to 0.04%, both excessive amount of Fe loss and excessive amount of weight loss were also observed. For example; for the optimum acid leaching result, the Fe grade decrease to 24.22%, and the remained weight from the feeding material was 50%. Due to this situation, as a result of the study, it was thought that the reverse flotation method was more effective than the acid leaching method and the magnetic separation method in terms of regaining of concentrated iron from the feeding material. On the other hand, in terms of Zn removal, the acid leaching method was more effective than the reverse flotation method. Because the tried methods had different advantages and disadvantages when they were compared with each other, at the end of the study, use of these methods in a row was proposed to be tried.

GENİŞLETİLMİŞ ÖZET

Bu çalışmada yüksek fırın baca tozları demir minerallerinin geri dönüştürülebilirliği açısından araştırılmıştır. Ters flotasyon yöntemi, manyetik ayırma yöntemi ve asit liçi yöntemi olmak üzere 3 farklı yöntem denenmiştir. Kimyasal analizler için X-Ray Florösans cihazı kullanılmıştır. Daha sonra sonuçlara atomik absorbsiyon spektrometresi ile çapraz doğrulama yapılmıştır. Fe elementi için ayrıca volumetrik analiz ile de çapraz doğrulama yapılmıştır. Bu çalışmanın besleme malzemesi olan demir-çelik yüksek fırını baca tozları Türkiye'nin en büyük iki demir-çelik üretim tesisinden birisi olan İsdemir'den elde edilmiştir. Besleme malzemesi olan baca tozlarının %36.28 yanmamış karbon, %30.97 Fe, %5.61 SiO_2, %1.89 AI_20_3, %1.22 Zn, % 0.61 S, %0.5 K_20, % 0.02 Cu, %0.03 P, %0.008 Cr, %0.57 Pb, %0.36 Mn, %2.52 MgO, %1.88 CaO, %0.13 Ti ve %0.02 V içerdikleri gözlemlenmiştir. Ni, As ve Na_2O tenörlerinin aletin ölçüm limitinin altında olduğu gözlemlenmiştir. XRD ile yapılan nitel mineral analizinden sonra diğer demir mineralleri ile karşılaştırıldığında baca tozunun baskın olarak hematit içerdiği gözlenmiştir.

Flotasyon prosesinde aynı anda hem demir içeren kısmı hem de yanmamış karbon içeren parçayı oldukça etkili bir şekilde elde etmek pek de mümkün değildi çünkü bunlardan birinin etkili bir şekilde elde edilmesi isteniyorsa, farklı reaktiflerin kullanılması gerekiyordu ve diğerinin kalitesi bu durumdan olumsuz etkileniyordu. Örneğin, karbon içeren kısımların (flotasyon prosesinde yüzdürülen kısmın) daha yüksek karbon tenörü ile elde edilmesi isteniyorsa, köpürtücü olarak çam yağı kullanılması gerekecekti. Benzer şekilde, demir mineralleri içeren kısmın daha yüksek demir tenörü ile elde edilmesi isteniyorsa, köpürtücü olarak metil izobütil karbinol (MIBC) kullanılması gerekecekti. Bu durum nedeniyle, ikisinden birisinin seçilmesi gerekiyordu. Bu yüzden, çalışmada demir mineralleri içeren kısmın (flotasyon sisteminde batan kısmın) tıpkı bir demir cevheri gibi geri dönüştürülebilirliğinin araştırılması tercih edilmiştir. Bu durumu incelemek için besleme malzemesine ters flotasyon işlemi uygulanmıştır. Diğer bir deyişle, çalışmada İsdemir demir ve çelik tesisindeki demir-çelik yüksek fırını baca tozlarındaki demir minerallerinin bir demir

cevherine benzer şekilde geri dönüştürülebilirliğinin incelenmesi öncelikli olarak hedeflenmiştir. Diğer taraftan, bu baca tozlarındaki karbon içeren minerallerin (kömürümsü minerallerin) geri dönüştürülebilirliği de demir minerallerinin geri dönüştürülebilirliğinin araştırılmasının yanında ikincil olarak incelenmiştir.

Ters flotasyon işleminin yanı sıra, yüksek alan şiddetli yaş manyetik ayırma işlemi de besleme malzemesi olan demir-çelik yüksek fırını baca tozu artıklarına uygulanmıştır. Yüksek alan şiddetli yaş manyetik ayırma işleminde yüksek alan şiddetli yaş manyetik ayırıcı yardımı ile besleme malzemesinin 0.25, 0.50, 0.75, 1.00, 1.25 ve 1.50 Tesla manyetik alan yoğunluklarında zenginleştirilebilirliği araştırıldı.

Yüksek alan şiddetli yaş manyetik ayırıcı ile yapılan manyetik ayırma deneylerinin sonucunda manyetik alan şiddeti arttıkça manyetik kısım olarak elde edilen konsantrelerdeki demir element tenörünün azaldığı gözlemlendi. Bu durum manyetik alan şiddetinin artmasıyla birlikte demir olmayan diğer manyetik içeriklerin ve manyetik olmayan içeriklerin demirle birlikte çekiliyor olabileceğine işaret ediyordu. Bu durumun nedenlerinin numunenin salkımlaşması ve/veya numunenin serbestleşme tane boyutunda olmaması olabileceği düşünüldü. Ayrıca manyetik alan şiddeti oldukça yüksek olduğu için çok az manyetik özellik gösteren partikülleri bile demir ile birlikte çekiyor olabilirdi. 0.25 Tesla manyetik alan yoğunluğu için demir tenörü %41.29 olarak bulunmuştur. Bu değer 0.50 Tesla manyetik alan yoğunluğunda %40.39'a düşmüştür. 0.75 Tesla için bu değer %38.53 olmuş ve 1.00 Tesla için %38.46 olarak bulunmuştur. Bulunan bu değer 1.25 Tesla'da %38.35'e ve 1.50 Tesla'da %36.50'ye düşmüştür. Bunun yanı sıra, manyetik alan yoğunluğu arttıkça demir element verimi ve kül veriminin arttığı da gözlemlendi. Demir verimi 0.25 Tesla manyetik alan yoğunluğu için %63.03, 0.50 Tesla manyetik alan yoğunluğu için %80.30, 0.75 Tesla manyetik alan yoğunluğu için %85.69, 1.00 manyetik alan yoğunluğu için %87.42, 1.25 Tesla manyetik alan yoğunluğu için %87.59, 1.50 Tesla manyetik alan yoğunluğu için ise %88.25 olarak bulunmuştur. Kül yüzdesi 0.25 Tesla manyetik alan yoğunluğu için %68.72, 0.50 Tesla manyetik alan yoğunluğu için %71.26, 0.75 Tesla manyetik alan yoğunluğu için %71.29, 1.00 manyetik alan yoğunluğu için %71.56, 1.25 Tesla manyetik alan yoğunluğu için %72.24, 1.50 Tesla

manyetik alan yoğunluğu için ise %73.45 olarak bulunmuştur. Bunun yanı sıra, manyetik alan şiddeti arttıkça çinko element yüzdesinin azaldığı da gözlemlenmiştir. Çinko element yüzdesi 0.25 Tesla manyetik alan yoğunluğu için %1.10, 0.50 Tesla manyetik alan yoğunluğu için %1.07, 0.75 Tesla manyetik alan yoğunluğu için %1.06, 1.00 manyetik alan yoğunluğu için %1.02, 1.25 Tesla manyetik alan yoğunluğu için %0.98, 1.50 Tesla manyetik alan yoğunluğu için ise %0.94 olarak bulunmuştur.

Yüksek alan şiddetli yaş manyetik ayırıcı ile yapılan deneylerin manyetik olmayan kısımlarına (artık kabul edilen kısımlarına) bakıldığında, manyetik alan yoğunluğu arttıkça yanabilir yüzde değerlerinin arttığı ve yanabilir verimin azaldığı görülmüştür.

Demir-çelik yüksek fırını baca tozu artıklarına uygulanan bir diğer işlem olan asit liç deneylerinde, molar konsantrasyon, zaman, sıcaklık, karıştırma hızı olarak farklı parametreler ile elde edilen sonuçlar incelendi. Deneyler için 90 dakika süre, 6 molar ortam, 300 rpm karıştırma hızı ve 24 °C sıcaklık standart parametreler olarak kullanıldı. Daha sonra üzerlerinde sadece ilgili parametreler değiştirilerek deneyler yapıldı. 4, 5, 6, 7, 8 molar konsantrasyonlar, 30, 60, 90, 120, 150 dakikalık zaman aralıkları, 100, 200, 300, 400, 500 rpm karıştırma hızları ve 24 ±5, 34 ±5, 44 ±5, 54 ±5, 64 ±5 °C sıcaklıklar asit liçi yöntemi yardımıyla besleme malzemesi üzerinde denendi. Zamanın etkisi, molar konsantrasyon değişiminin, karıştırma hızı değişiminin, ve sıcaklık değişimlerinin demir tenörüne ve başta çinko olmak üzere çeşitli safsızlıkların giderilmesi üzerine etkileri ayrı ayrı incelendi.

Optimum olarak kabul edilen flotasyon konsantresi, proses suyunun yeniden kullanılması vasıtasıyla gerçekleştirilen ters flotasyon işleminden elde edildi. Konsantre için Fe tenörü %52.61, kül yüzdesi % 96.31, ağırlık %22.10, demir element verimi %68.41, SiO_2 %4.82, [(CaO + MgO)/(SiO_2 + Al_2O_3)] oranı 0.44, Zn %0.81, Pb %0.37, S %0.08, Mn %0.64, Cu %0.04, Ti %0.12, V %0.02, Cr %0.01 olarak bulundu. Bunun yanı sıra P, As ve Ni değerlerinin cihazın ölçüm limitlerin altında olduğu gözlemlendi.

Ters flotasyon deneylerinden sonra Fe tenörünün besleme malzemesi tenörü olan %30.97'den %52.61'e yükseltilmiş olduğu ve en önemli safsızlıklardan biri olan Zn'nin %1.22'den %0.81'e kadar indirilmiş olduğu gözlemlendi.

Asit liç deneylerinden sonra, 6 molar ortam, 300 rpm karıştırma hızı, 64 °C sıcaklık ve 90 dakika ile gerçekleştirilen deneyden asit liçi prosesi için optimum kabul edilen sonuç elde edildi. Zn %0.04'e kadar düşürülmesine rağmen, hem aşırı miktarda Fe tenör kaybı hem de aşırı miktarda ağırlık kaybı gözlemlendi. Örneğin; optimum olarak kabul edilen asit liçi deney sonucu için Fe tenörünün besleme malzemesi tenörü olan %30.97'den %24.22'ye düştüğü gözlemlendi. Bu durum nedeniyle, çalışmanın sonucunda, ters flotasyon yönteminin, konsantre demirin besleme malzemesinden geri kazanılması açısından asit liç yönteminden ve manyetik ayırma yönteminden daha verimli olduğu düşünülmüştür. Öte yandan, Zn giderimi açısından asit liç yöntemi ters flotasyon yönteminden daha verimlidir. Denenen yöntemler birbirleriyle karşılaştırıldığında farklı avantaj ve dezavantajlara sahip oldukları için, çalışmanın sonunda, bu yöntemlerin üst üste uygulanmasının denenmesi önerilmiştir.

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LIST OF SYMBOLS

°	: Degree
°C	: Centigrade degree
K	: Kelvin degree
%	: Percent
µm	: Micrometer
Al	: Aluminium
As	: Arsenic
BDL	: Below the detection limits
BOS	: Basic Oxygen Steelmaking
BF	: Blast Furnace
BFS	: Blast Furnace Sludge
C	: Carbon
Ca	: Calcium
Cu	: Copper
cm	: Centimeter
Cr	: Chromium
EAF	: Electric Arc Furnace
EDTA	: Ethylenediaminetetraasetic Acid
EDXRF	: Energy Dispersive X-Ray Fluorescence
Fe	: Iron
g	: gram or grams
H	: Hematite
K	: Potassium or Kelvin
kV	: Kilovolt
L	: Liter
M	: Molar
m	: Meter

mA	: Milliampere
min	: minute or minutes
Mg	: Magnesium
mg	: Milligram
ml	: Milliliter
MIBC	: Methyl isobutyl carbinol
Mn	: Manganese
Mu	: Mullite
mV	: Millivolt
Na	: Sodium
O	: Oxygen
P	: Phosphor
pH	: Power of Hydrogen
Pb	: Lead
Q	: Quartz
rpm	: Rounds per min
S	: Sulphur
sec	: second or seconds
SEM	: Scanning Electron Microscopy
Si	: Silicium
T	: Tesla
Ti	: Titanium
V	: Vanadium
W_f	: Final weight
W_i	: Initial weight
X	: Magnetite
XRD	: X-Ray Diffraction
XRF	: X-Ray Fluorescence
Zn	: Zinc

1. INTRODUCTION

1.1. Information Iron and Steel

1.1.1. History of Iron Production in Turkey

Iron and steel industry in Turkey, has gained a rapid growth momentum particularly about investments of flat steel after 2001. Between the years of 2006 and 2012 Turkey's crude steel production capacity reached 50 million tons per year with an increase of 28.4 million tons. This increment is of importance in terms of showing that 130% of the capacity reached in 66 years has been put into operation in the last 6 years. However, absence of high quality stainless steel production in our country is an important disadvantage. Compared to the year of 2011, rising of 2 rows, Turkey completed year of 2012 as 8th of the world's top crude steel producing countries with 35.9 million tons of crude steel production. According to data from the year of 2012, Turkey has raised its crude steel production 39% than 2007 the pre-crisis level. In this respect, Turkey was one of the 5 countries which raised their production of steel above to pre-crisis level among the 10 largest steel producers of the world (Vapur and Top, 2016).

1.1.2. Comparison of Consumption of Iron and Steel According to Countries and Years

Iron is one of the major contributors to the economic and social development of societies and is one of the fundamental inputs of the industry. Between the years of 1960-1974, world steel production has grown tremendously with an average annual increase of 7%. The establishment of integrated and large iron and steel facilities in Western Europe and Japan has been the characteristic industrial investments of this period (Vapur and Top, 2016).

While at the end of 1980s iron and steel consumption across the world was 750 million ton/year, especially at 2000s it increased rapidly since the beginning of the year and reached 1344 million ton/year in 2008. While per capita world

consumption of crude steel in 2006 was average 202.2 kg, in Turkey it was 328.7 kg. This amount was 459.4 kg in EU countries called EU15. In the USA, it was 424.5 kg. China was the leader of crude steel production with 489.2 million tons in 2006. There was 26.4 million tons of steel production in Turkey in 2008 (Şen et al., 2010).

World iron and steel consumption, which was 28 million tons at the beginning of the 20th century, was 780 million tons at the end of the century. With the investments made especially in China after 2000, the world crude steel production capacity in 2014 was close to 2.2 billion tons. China, which made real 77% of the increase in this capacity, became the decisive country in iron supply (Kayır, 2016).

1.1.3. Iron Ore Reserves across the World and Turkey

The world's iron ore reserves are known as $160x10^9$ tons. Most of these reserves are located in Australia, Brazil, Canada, India, USA, South Africa, Liberia, Sweden, Peru, China and Russia (Boyrazlı, 2008).

Turkey mineable iron ore reserves are around 137 million ton. The troubled iron ore whose grades vary between 19-54% Fe is about 1 billion tons with the apparent reserve and probable reserve. However, since these ores contain some impurities that the plants do not desire, the majority of these deposits are kept idle for today. The annual amount of iron ore produced in Turkey are around 5,000,000 tons. After the investments made in 1985, there has been a significant decrease in ore production, especially in recent years, as a result of the fact that there was no significant investment in this sector and the sector mostly tended to importation. Exploitable iron ore reserves in Turkey are in Sivas, Erzincan, Kayseri, Adana, Malatya, Kırşehir and Balıkesir cities today. One of the major problems in high-grade iron ore production in Turkey is quite limited exploitable reserves. In this case, in addition to reserve development activities in high-grade iron ore deposits, facilities should be established to enrich low-grade iron ore deposits. Parallel to the

consumption ratio of operational iron ore reserves in Turkey, it is reported that it will be depleted in the next 20 years. Potential reserves and problematic ore deposits are obligatory to operate (Boyrazlı, 2008).

1.1.4. Iron and Steel Production Process

Iron and steel production holds an important place in the world industry. Iron ores which are used to produce pig iron generally are obtained from nature. Beneficiation of low grade iron ore is required because low grade iron ore cannot be fed into blast furnace (Yang et al., 2017). After the beneficiation process iron ore is fed into blast furnace. Iron ore is melted and reduced in the blast furnace which consumes huge amount of energy (Hashimoto et al., 2019). Iron and steel making plants bring about high amount waste materials. It was stated that an average iron and steel plant creates 400 kg of solid waste material per ton of produced steel (Bayat et al., 2009). The main aim of blast furnace process is to produce high amount high quality molten iron together with low fuel cost (Chen et al., 2010). In order to obtain low fuel cost, inside of the blast furnace covered with refractory bricks. Refractory materials are heatproof. In case of the usage of refractory material in combustion environments, heat escape is the least; fuel savings are achieved, and carbon dioxide generation is reduced. If refractory bricks were produced from materials which contain high percentage of Al_2O_3 components, it is thought that they would be more resistant. If refractory bricks have Al_2O_3 above 50%, they might be considered resistant materials. In addition to this, if these bricks contain low percentage of Fe_2O_3, then their showing of high level durability against corrosion and erosion is thought (Kılıç and Yarbil, 2016). In order to obtain enough energy for the process, firstly, coke is needed to be produced. Owing to this, coal is used to produce coke before the process. Then coke is fed in the blast furnace together with other necessary materials which are iron ore and slag makers (He and Wang 2017). Reducing gases melt and reduce the

iron ore (Yang et al., 2010). In the blast furnace, these reactions occur which were written below (Luz et al. 2018).

Reduction Zone (673-1073 K) (1.1)

$Fe_2O_{3\,(solid)} + CO_{(gas)} \rightarrow Fe_3O_4 + CO_{2\,(gas)}$

$Fe_3O_4 + CO_{(gas)} \rightarrow 3FeO + CO_{2\,(gas)}$

$FeO + CO_{(gas)} \rightarrow Fe_{(solid)} + CO_{2\,(gas)}$

$FeO + C_{(gas)} \rightarrow Fe_{(solid)} + CO_{(gas)}$

Slag Zone (1273 K) (1.2)

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + SiO_2 \rightarrow CaSiO_3$

Fusion Zone (1673-1773 K) (1.3)

$Fe_{(solid)} \rightarrow Fe_{(liquid)}$

Combustion Zone (1773-2100 K) (1.4)

$C+O_2 \rightarrow CO_2$

$CO_2+C \rightarrow 2CO$

After all of these reactions occur, liquid slag and melted iron consist in the lower zone and they are separated from each other because of their difference of densities. Melted iron stays under the slag. Then they drains through two different outputs. After this, gained pig iron is used to produce steel. Huge amount of products are produced in the blast furnace, and as a result of this situation, even a little bit development of the process provides huge benefits (Chen, 2001).

1.2. Ore Preparation Processes

1.2.1. Magnetic Separation Process in Ore Preparation

In the separation of valuable minerals from gangue, being different of the materials from each other can be utilized by magnetic separators (Wang et al., 2018). According to their magnetic field intensities there are two types of magnetic separators. One of them is high intensity magnetic separators and the other is low intensity magnetic separators. High intensity magnetic separators are used to prepare ores which have low magnetic susceptibility. For example; the iron mineral ore named hematite (Fe_2O_3) has low magnetic susceptibility therefore the high intensity magnetic separator is needed to be used to separate hematite from gangue minerals. In spite of this, the iron mineral ore which is named as magnetite (Fe_3O_4) has high magnetic susceptibility. Due to this, the low intensity magnetic separator is used to separate magnetite from gangue minerals. These high and low intensity magnetic separators split off two parts between each other. High intensity magnetic separators are separated into two groups. These are high intensity dry magnetic separators, and high intensity wet magnetic separators. In the high intensity dry magnetic separators there are two rotating tanburs and a powerful stationary magnet. Three types of products be gained from them and they are named primary and secondary and non-magnetic product respectively. When it comes to high intensity wet magnetic separators, there is a funnel in it between two strong magnets. Firstly, the feeding material is fed into separator when device is open to hold magnetic particles. After the non-magnetic particles flow, the separator is closed and magnetic particles be obtained. Low intensity magnetic separators be separated into two groups too. These groups are low intensity dry magnetic separators, and low intensity wet magnetic separators. In the low intensity dry magnetic separators there is a rotating tanbur, and there is a stationary magnet on it. Magnetic and non-magnetic products are gained from them. In the low intensity wet magnetic separators there is a rotating tanbur again and there is a rotating

magnet on it in an aqueous medium. Two kind of products also are obtained from them as magnetic product and non-magnetic product.

1.2.2. Flotation Process in Ore Preparation

Flotation is a process that depends on the differences of the mineral sorts which works according to the physicochemical rules (Dhubaibi et al., 2019). One of the most crucial and miscellaneous mineral-processing method is flotation (Yu et al., 2018). Since the first portrayals of flotation technique have been obtained from relics of ancient Greeks and Persian societies, flotation process can be dated to antique ages. First using of the process was about mining industry.

The first patent of flotation which is about mineral preparation was gotten in 1860 by Harnes (Bentli, 2001). The first flotation studies based on different wetting capabilities of mineral particles in a medium which consist of water or oil. Oil flotation applied to minerals which show metallic luster. This method based on being passed of gangue minerals which are more wetted by the help of wettable surfaces through oil-water interface. However, usage of oil was quite high. Although amount of oil was reduced to 10 kg/ton, it is much more than the usage of froth flotation (0.3 kg/ton).

Froment and Potter found that bubbles are ideal in flotation of oily and S minerals in 1902. Sulman, Ballot and Piccard used rising bubbles in a medium in 1906. Due to this situation, the required oil amount decreased.

With the usage of non-selective oils and acidic pulps in the froth flotation, economic gaining of a great number of S ore minerals became possible. In time, a great number of selective flotation equipment were developed. Owing to this, economic gaining S ore minerals and non-S ore minerals became possible. Keller used xanthate in flotation for the first time in 1925. Therefore, 1925 is accepted as the beginning of modern flotation.

Flotation process is a prevalent method in separation of fine grained minerals (Li et al., 2019). This method utilises floatabilities and surface properties

of mineral ores. There are two notion about this. One of them is hyrophobicity and the other one is hydrophility. Each ore mineral has different surface properties and different hidrophobicities. On account of this, two different minerals can be separated from each other by using these properties. In the flotation process, bubbles rise in an aqueous medium. These bubbles are composed by the help of air, and be attached the surface of hydrophobic mineral grains. Therefore these grains rise with bubbles. When it comes to hydrophilic grains, these are left bottom of the medium. While iron containing parts are prevented from floating owing to usage of depressants, making coal float is easily possible by the help of reagents such as diesel, pine oil, methyl isobutyl carbinol (MIBC). Vapur et al. (2010) stated that froth flotation was the most influential method to separate ash from carbonaceous part.

Reagents which are used in this study can group as collectors, frothers and depressants.

Collectors cover the ore particles which is desired to float. And render them more hydrophobic and more floatable. Air bubbles can easily adsorb to the surfaces of the minerals by the help of collectors. For the sake of example; both diesel and kerosene are good collectors in coal flotation. Collectors split off into two types. One of them anionic collectors and the other is cationic collectors.

Frothers reduce the surface tension. In this way, bubbles do not blow up when they arrive the surface of flotation cell. If being given examples as to frothers are desired, MIBC and pine oil can be easily said.

Depressants cover the surfaces of mineral particles which are not desired to float, and they render them less floatable in other words more hydrophilic. For example; both water glass and corn starch are depressants in reverse flotation of iron oxides. It was stated that corn starch is a cosmic depressant on iron ores (Araujo et al. 2005). Water glass is commonly utilized as depressant/dispersant in flotation process (Ding and Laskowski, 2006). Depressants can split into two

groups. One of them is organic depressants and the other one is inorganic depressants.

These reagent groups are a part of the important parameters in both coal and reverse iron flotation processes. Quantity of each reagent and interactivity between them are very important parameters for the processes.

1.2.3. Acid Leaching Process in Ore Preparation

The leaching process, which is generally conducted by the help of the acidic or basic solvents, is one of the most important methods in ore enrichment or ore preparation. At acid leaching method, the material is contacted with an acidic medium for a while. The medium can be also heated or stirred. Molar concentration of the acid, stirring speed, temperature of medium, time are primary parameters to optimize in the acid leaching process. By the help of arranging these parameters, the medium resolving the desired or the undesired materials is provided. After the leaching process, metal recovery process is started.

1.3. Minimum Requirements for the Concentrate Iron Ore

The properties of the iron ores are important for the industry and it is desired that iron concentrates have certain level quality. The minimum Fe grades of the iron concentrates to be used in the production of iron and steel vary by the type of iron mineral. Iron concentrates are required to contain more than 50-55% Fe for magnetite and hematite, more than 45% Fe for limonite and more than 35% Fe for siderite. The ratio of the total grade of the CaO and the MgO divided by the total grade of the SiO_2 and the Al_2O_3 must be approximately 1 or more. At the same time, the maximum bearable SiO_2 grade is 5%. If this ratio is more than 1, even the aluminium grade which is 3.5% can be tolerable (Çilingir, 1996).

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} \geq 1$$

Formula 1.1. The ratio Çilingir to which referred

S in iron ores or in coke reduces the quality of production. If S grade of the used coke more than 2%, it is desired that the S grade of the iron concentrates not be more than 0.15-0.35%. If the S grade of the coke to be used is less than 0.5%, it is desired that the S grade of the iron concentrates not be more than 0.75-1.0%. Some other important impurities are the Pb content and the Cu content in the iron ores. The Pb grade in the iron concentrates must be lower than 0.05%. The Cu in the iron ores decreases the quality of the steel by turning into pure metal. Therefore, it is desired that the Cu grade in the iron concentrates not be more than 0.06%. Approximately, 60-70% of the Mn passes into steel. If manganese steel is desired to be produced, the iron concentrates containing between 0.5-1.2% Mn (as the minimum by weight) are beneficial; however, if grey pig iron is desired to be produced, Mn must be below 0.2% (Çilingir, 1996).

One of the most harmful impurities for pig iron production is Zn. Bayat et al. (2009) stated for the iron concentrates that when the Zn grade was more than 0.03%, quality of steel substantially decreased.

1.4. The Purpose of the Study

The purpose of this study is to investigate how much possible the blast furnace flue dusts may be recycled in terms of being obtained concentrate iron minerals and to try to find the most suitable method so as to achieve this by comparing different methods with each other. In order to do that 3 different methods were implemented to the sample as reverse flotation method, magnetic separation method and acid leaching method. After that, advantages and disadvantages of these methods in being recycled of the blast furnace flue dusts were tried to find and compared with each other.

2. PREVIOUS STUDIES

Bayat et al. (2009) conducted a study named "Bioleaching of Zn and iron from steel plant waste using Acidithiobacillus ferrooxidans". They tried to remove the Zn in the Isdemir iron and steel plant solid wastes. Their feeding material was a solid waste sample which was obtained from electric arc furnace (EAF) which was found in Isdemir iron and steel making plant. Firstly, they analysed the sample by the help of a Philips X Pert SW-binary diffractometer with CuKα radiation (40 kV, 50 mA). After the X-Ray Diffraction (XRD) analysis they found that the material was mostly composed of magnetite (Fe_3O_4), calcite ($CaCO_3$), and hematite (Fe_2O_3). The feeding material also contented 54.73% Fe and 1.23% Zn. They also desired to compare chemical leaching process to bioleaching process. So as to achieve this, they conducted sulfuric acid leaching experiments in 3 different concentrations which consisted of 5%, 10%, 15% (m/v) sulfuric acid respectively. The solid rate was 10% and time was 10 hour, the rate of agitation was 120 rpm, and the volume of the flask was 250 ml. They also impeded the system from evaporation by the help of using a clock glass. After the chemical leaching process was completed, in order to investigate the effectiveness of the bioleaching in terms of the removal of the Zn content from the feeding material, they conducted bioleaching process by the help of a bacterium named "Acidithiobacillus ferrooxidans". So as to prepare bacteria to the process, in 500 ml erlenmeyer flask, 200 ml medium with 10% (v/v) inoculum was constituted. By the help of 0.5 molar acid pH was decreased to 1.5. The rate of agitation was 150 rpm and provided by means of a rotary shaker. Temperature was 30 °C. After the logarithmic phase, cells were harvested and washed by diluted sulfuric acid (1.5 PH). Then, in 250 ml flask, bioleaching experiments were conducted in ferrous-free 9K nutrient medium without the presence of bacteria and with the presence of bacteria, respectively. In order to decrease pH to 1.5, 5% sulfuric acid was added into the flask. To obtain 100 ml final slurry volume, 10 ml aliquot was inoculated. At 30 °C the flasks were agitated by means of an ordinal shaker. Leaching time was 21 days. They compensated the water loss owing to the evaporation by adding distilled water into the system, and

the volume loss because of the sampling by adding ferrous-free 9K nutrient. They conducted each experiments at least 2 times. After the experiments, they found that, for chemical leaching, Zn was dissolved more than Fe in time, as grade. In the results of the chemical leaching experiments, when Zn was dissolved 70%, Fe was dissolved 40%. In the results of the bioleaching experiments, Bayat et al. observed that while there was no bacterium in the medium, the dissolved Zn and Fe were less than 6% and 2% by weight respectively; however, while there were bacteria in the medium, the dissolved Zn and Fe ratios increased to 25% and 16% respectively. At the end of the study, they reported that 35% of the Zn and 37% of the Fe were dissolved when solid rate was 1% and pH was approximately 1.3.

Wang et al. (2019) conducted a study named "Removal of Zn from basic oxygen steelmaking filter cake by selective leaching with butyric acid". They obtain their feeding material from a basic oxygen steelmaking furnace by the help of water scrubbing and press filter as a filter cake. After that, they crushed and sieved the filter cake. As a result of X-Ray Fluorescence (XRF) analysis, it was observed that the feeding material was composed of 56.40% Fe, 6.52% Zn, 1.40% SiO_2, 0.084% Al_2O_3, 3.97% Cao, 0.67% Mn, 1.93% MgO, 0.047% TiO_2, K_2O 0.053, 0.085% Pb, 0.022% Cr, 0.008% Ni, 0.012% V, and 1.89% other elements. After the experiment in order to carry out chemical analyses "inductively coupled plasma-optical emission spectrometry" was used. The brand of the butyric acid and the standard Fe, and Zn solutions were Sigma-Aldrich. The experiments were conducted in 150 ml acid solutions which were in 250 ml erlenmeyer flasks. The stirring speed was 120 rpm and it was providing by a "horizontally oscillating shaker (RM2, Ratek, Australia)". Experiments were conducted for different L/S stoichiometric ratios (Acid/Solid ratios) which were 10%, 30%, 50%, 70%, for different molar concentrations which were 0.1, 0.2, 0.5, 1.0, 1.5, 2.0. The experimental temperatures was the room temperature. The leaching time was 10 hours. At 90% stoichiometric ratio, and in 0.5 molar medium the leaching efficiency for iron was maximum and it was 29%. They proposed 1.5 molar acid concentration, 10 hours leaching time, 120 rpm stirring speed, and 70%

stoichiometric ratio as the optimum parameters for the experiments. After the experiments the concentrate with 60.40% Fe and 3.4% Zn was obtained.

Zeydabadi et al. (1997) conducted a study named "Zn recovery from blast furnace flue dust". They tried hydrogen peroxide, and 3 type of acids which were hydrochloric acid, sulfuric acid, nitric acid. After these trials, they chose sulfuric acid from them because sulfuric acid had higher selectivity on Zn than the other tried acids. Their feeding material was blast furnace flue dusts which were obtained from Isfahan Ironmaking Complex furnaces, Iran. The feeding material was composed of 4.03% FeO, 30.00% Fe_2O_3, 9.42% SiO_2, 2.21% Al_2O_3, 17.20% CaO, 5.35% MgO, 0.19% P, 0.91% S, 0.67% MnO, 2.52% ZnO, 0.83% TiO_2, 0.28% K_2O, 0.12% Na_2O, 0.04% PbO, 0.02% Mo, 5.62% Cd, 4.51% As, 6.01% Sb, and 4.31% Co. The experiments were conducted at 1/5, 1/10, 1/15, and 1/20 g/cm^3 solid ratios. 18, 35, 50, 65 °C temperatures were also tried. Leaching times were 5, 10, 15, 30, 45, 60 min. Molar concentrations were 0.125, 0.250, 0.500, 1.000 molar for the experiments. They found that in a medium which consists of 1.0 molar sulfuric acid concentration and 1/10 solid/liquid ratio 82% of Zn, and 5% of Fe passed into the solution after 1 hour. They determined the optimum operational conditions as 1.0 molar sulfuric acid concentration, 1/10 solid ratio, and 10 min leaching time at the room temperature.

Zhang et (2017) al. conducted an investigation about blast furnace flue dusts named "Selective leaching of Zn from blast furnace dust with mono-ligand and mixed-ligand complex leaching systems". Their feeding material was flue dust and it obtain from a steel plant which is in Yunnan region of China. By the help of a "Rigaku Smartlab Automatic Powder Diffractometer" they conducted X-Ray Diffraction (XRD) analysis of their feeding material. XRD analysis demonstrated that their sample was composed of Znite (ZnO), magnetite (Fe_3O_4), hematite (Fe_2O_3), wustite (FeO), Zn silicate (Zn_2SiO_4) and quartz (SiO_2). After the XRD analysis, they also stated that because franklinite ($ZnFe_2O_4$) is isostructural with magnetite (Fe_3O_4), it is hard to prove the existence of franklinite in the sample by means of the XRD analysis. Their sample was composed of 38.49% Fe, 5.10% Zn, 20.39% O, 4.66% Si, 2.57% Al, 2.25% Ca, 0.94% Pb, 21.90% C. Zn content was

composed of 4 different kinds of Zn mineral in different grades. 49.76% of the Zn content was composed of Zn oxides; 28.12% of the Zn content was composed of Zn ferrite; 15.38% of the Zn content was composed of Zn silicate; 6.74% the Zn content was composed of Zn sulfide. They determined the surface composition and the granularity of the sample by the help of use a "Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM, JEOL, Ltd., JSM-6360LV)". They conducted the acid leaching experiments 400 rpm stirring speed. They tried 4 different organic acids as glycine, iminodiacetic acid, nitrilotriacetic acid, and citric acid. For 2 molar glycine, pH of the medium was 6.40; for 2 molar iminodiacetic acid, pH of the medium was 1.93; for 2 molar nitrilotriacetic acid, pH of the medium was 1.89; for 2 molar citric acid, pH of the medium was 1.85. Amongst the 4 different acids, iminodiacetic acid was chosen because it was observed that while it solves Zn effectively, it solves the iron less effectively. Experiments were conducted to find out the effects of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 molar acid concentrations respectively. Different temperatures which were 20, 40, 60, 80 °C; different times which were 0.5, 1, 2, 3, 4 hours; different pH values which were 2, 3, 4, 5, 6, 7, 8, and different solid ratios which were 2, 5, 8, 10, 20, 40 mg/L were implemented to the feeding material. It was observed that at 20 °C, 62.78% Zn leaching rate; at 40 °C, 64.48% Zn leaching rate; at 60 °C, 64.90% Zn leaching rate, and at 80 °C, 64.85% Zn leaching rate were attained. After these experiments they determined that the optimum results were obtained from the experiments which consisted of 0.2 molar iminodiacetic acid concentration, 20 °C temperature, 10 mg/L solid ratio, and 2 hours leaching time. In the optimum results, 62.78% of the Zn and 6.07% of the iron passed into the leaching liquid.

Omran and Fabritius (2019) conducted experiments and render them an article named "Utilization of blast furnace sludge for the removal of Zn from steelmaking dusts using microwave heating". Blast furnace sludge (BFS) was used in the study together with other 3 kinds of steelmaking dusts. The BFS sample which was used in the study was attained from SSAB Europe Oy, Raahe, Finland. The two of the other steelmaking dusts were ferrochrome converter (CRC) dusts and electric arc furnace stainless steel dusts which were obtained from Outokumpu

Tornio stainless stell plant, Finland. The other one was electric arc furnace carbon steel dust which were obtained from Ovako Imatra, Finland. The blast furnace sludge was composed of 38.95% Fe, 0.45% Zn, 24.90% C, 7.76% CaO, 7.07% SiO_2, 1.57% MgO, 2.21% Al_2O_3, 0.52% Na_2O, 0.42 K_2O. Experiments were conducted at 1100 W for 20 min. When ferrochrome converter dust and graphite mixture was heated, the content of the Zn decreased from 10.29% to 0.34%. When ferrochrome converter dust and blast furnace dust mixture heated, the content of the Zn was decreased from 10.29% to 2.97%. After the experiments which were conducted with an electric arc furnace stainless steel dust and graphite mixture, the content of the Zn was decreased from 19.84% to 1.22%. The Zn content of the mixture which was composed of electric arc furnace carbon steel dust and graphite was decreased from 35.76% to 5.29% by heating process. This situation meant that Zn removal was 85.20%. Ceteris paribus, when a mixture which was composed of electric arc furnace carbon steel dust and blast furnace sludge was heated, the Zn content of the residue was decreased from 35.76% to 5.98% with 83.27% Zn removal. After these experiments, they observed that adding blast furnace dust into the steelmaking dusts was increased the efficiency of the process. They also observed that as CaO or coke percentage in the mixture increased and iron percentage in the mixture decreased, percentage of the Zn removal increased.

Steer and Griffiths (2013) conducted a study named “Investigation of carboxylic acids and non-aqueous solvents for the selective leaching of Zn from blast furnace dust slurry” in 2013. Their sample was obtained from 5 different points of settling lagoons. By the help of this, the sample which included 1-month dusts were attained. They determined the particle size distribution by sieving the sample by the help of 20, 45, 63, 106, 850 micrometer sieves. They found that d_{50} median value of the sample was 14.60, and d_{80} median value of the sample was 45.20 micrometer. They determined the chemical composition of the feeding material by means of an “atomic emission spectroscopy”. The chemical composition of the feeding material was composed of 36.20% Fe, 18.50% C, 5.00 Ca, 4.60 Si, 1.80 Al, 1.00% Mg, 0.60 Zn, and 0.30 Mn. They conducted the acid leaching experiments in a stoppered conical flask which was 250 ml. 1/10, 1/1, and

2/1 solid ratios were tried. They tried using different types of organic carboxylic acids which were prop-2-enoic acid, ethanoic acid, propanedioic acid, and ethanedioic acid. In this way, they aimed to understand whether these acids solves high amount Zn while they solves low amount iron simultaneously. After the trials, they chose prop-2 enoic acid because they stated that while prop-2 enoic acid solved the Zn content as much as possible, it solved the iron content as less as possible. In the experiments the molar concentrations changed between 0.15 mol/L and 2.90 mol/L, and the temperatures changed between 22 and 95 °C. They found that at ambient temperature 83.10% of the Zn content successfully removed with 8.50% Fe loss by the help of the prop-2 enoic acid in 1/10 solid ratio after 24 hours.

Hu et al. (2018) conducted a study named "Difference of Zn volatility in diverse carrier minerals: The critical limit of blast furnace dust recycle". They took the coke which was used in the study from Shandong province in China. Their feeding material was blast furnace dusts and they took them from a large iron and steel company in Hebei province. The chemical composition of the feeding material was composed of 37.91% Fe_2O_3, 24.34% C, 5.01 SiO_2, 4.90% K_2O, 4.20% ZnO, 3.90% SO_3, 3.07% CaO, 2.93% Al_2O_3, 2.39% Na_2O, 1.26% PbO, 0.45% MgO, 0.23% TiO_2, 0.13% P_2O_5, 0.11% MnO, 0.08% NiO. They conducted the experiments between 300 and 1500 sec time range. Coke dosages changed between 0% and 20% were tried. Temperature changed between 1050 and 1150 °C were tried. By the help of the study they found that almost half of the Zn in carbonaceous parts and irony parts were Znite but in silicate franklinite. They found that volatilization of the franklinite was very hard compared to Znite.

3. MATERIAL AND METHOD

3.1. Material

3.1.1 Feeding Material and Its Chemical Composition

The flue dust sample which is used in this study was taken from Isdemir iron and steel plant. After the X-Ray Fluorescence analyses and crosschecking their results according to whether the grades of the elements which were desired to be measured was above 7% or not either by atomic absorption spectrometer or by volumetric analyses, chemical composition of the material was determined. The chemical composition of the material was presented below (Table 3.1).

Table 3.1. Chemical composition of the feeding material

	%
Fe	30.97
SiO_2	5.61
Al_2O_3	1.89
Zn	1.22
S	0.61
As	BDL
Na_2O	BDL
K_2O,	0.50
Cu	0.02
P	0.03
Ni	BDL
Cr	0.008
Pb	0.57
Mn	0.36
MgO	2.52
CaO	1.88
Ti	0.13
V	0.02

3.1.2 Used Chemical Reagents

In this study, “EMSURE Hydrocloric acid fuming %37” was used for the leaching experiments. In the flotation tests, “Sigma Aldrich” brand methyl isobutyl carbinol (MIBC), pine oil, and water glass and “Bağdat” brand corn starch was used. 4 numbered fuel oil which was used in the flotation tests again was obtained from Cukurova University Automotive Engineering Department. Diesel and kerosene which were used in this study were obtained from laboratories of the Cukurova University Mining Engineering Department.

3.2. Methods

3.2.1. Experimental Methods

3.2.1.1. Magnetic Separation Experiments

Magnetic separation method was also tried to regain the iron minerals. In order to conduct experiments “Eriez L4-20 WHIMS laboratory model high intensity wet magnetic separator” was used. The feeding material was stirred at 300 rpm stirring speed for 1 min and it was fed into the high intensity wet magnetic separator. For the process the solid ratio was %20. After the tailings was obtained, concentrate was obtained by the help of the lavation. Effects of magnetic field was investigated by the help of being changed the magnetic field intensities. 0.25, 0.50, 0.75, 1.00, 1.25, 1.50 Tesla (T) magnetic field intensities were tried. After the magnetic separation experiments, the concentrates and the tailings were filtered and dried at 85 °C in drying-oven.

3.2.1.2. Reverse Flotation Experiments

In the reverse flotation tests, effects of the collectors, frothers and depressants were investigated respectively. 7500 g/ton collector, 500 g/ton frother, and 500 g/ton depressant levels was accepted as constant parameters. After that, related parameter was changed. By the help of this, effects of collectors, frothers,

and depressants were tried to be understood separately. 4 numbered fuel oil, diesel, and, kerosene were tried as collectors for 2500, 5000, 7500, 10000, and 12500 g/ton usages respectively. Methyl isobutyl carbinol (MIBC) and pine oil were tried as frothers for 300, 400, 500, 600, and 700 g/ton usages. Water glass and corn starch were tried as depressants for 300, 400, 500, 600, and 700 g/ton usages. Experiments were performed using a laboratory-type Denver flotation device. After the reagents which were composed of a collector, a frother, and a depressant were added into the tap water solution, the feeding material at 15% solid ratio, which approximately accounts for 176.47 g solid feeding, was put into the flotation cell, and then the device was turned on for 3 min at 1350 rpm stirring speed. At the end of 3 min, the air tap of the flotation device was opened and the froths was started to be taken. The froths were taken for 1 min and then the test was completed. Concentrates and wastes were filtered by the help of utilizing from the pressure filter and dried by the help of using the drying oven at 85 °C until they comes to a constant weight. After the drying process, the chemical analyses were implemented onto the concentrate and tailings of the reverse flotation experiments. After the chemical analyses completed, the experimental results which were obtained from different experiments with different type or different amount reagents were compared with each other to find out that which chemical how and how much affect the reverse flotation process of the blast furnace flue dusts.

After all of experiments finished and most effective reagent types determined by the help of the reverse flotation process, using Design Expert software, Box-Behnken experiment design was implemented to find out blended effects of reagent quantities. Concentrate from 0 to 30 sec, by-product from 30 to 60 sec and tailing are obtained in the each Box-Behnken experiment. After then, obtained by-products were distributed. After the Box-Behnken experiments reuse of the water of the process was implemented in the reverse flotation process. By the help of this, it was thought that more optimum and economic result could be obtained from the reverse flotation process.

3.2.1.3. Acid Leaching Experiments

Leaching method was implemented on 10 g feeding material in 100 ml medium which were composed of water and hydrochloric acid. 6 molar molar concentration, 300 rpm stirring speed, 90 min time interval, and 24 ±5 °C temperature were accepted as constant parameters. After that, only related parameter was changed. In this way, the experiments were performed. In order to prevent evaporation, watch glass was used. 4, 5, 6, 7, 8 molar concentrations; 100, 200, 300, 400, 500 rpm stirring speeds; 30, 60, 90, 120, 150 min time intervals were tried on the feeding material. The temperatures were also tried for 24 ±5, 34 ±5, 44 ±5, 54 ±5, 64 ±5 °C.

3.2.2. Chemical Analysis Methods

One of the most important parts of the study was the part of the chemical analyses was implemented. Because doing chemical analyses, in true way, is important in terms of obtaining more precise and true results. Due to this situation, the sample should be prepared to chemical analyses correctly and then chemical analyses should be conducted carefully. In order to conduct these processes, there are some different quantitative and qualitative chemical analysis methods. XRF analyses, atomic absorption spectrometer analyses, and volumetric chemical analyses can be demonstrated as examples for quantitative chemical analyses methods. X-Ray Diffraction analyses can be demonstrated as an example for qualitative analyse methods. There are also some other laboratory devices which are available to help the chemical analyses which to be implemented.

3.2.2.1. Chemical Grade Analyses

Determination of the chemical compositions of the materials is also a quite important parameter to be successful of the results of the experiments. In this study, in order to conduct chemical grade analyses X-Ray Fluorescence (XRF) device was used. In order to crosscheck the obtained values, atomic absorption

spectrometer analyses were used for low graded elements, and volumetric analyses were used for high graded elements.

3.2.2.1.(1). Grade Analyses by X-Ray Fluorescence (XRF) Device

In order to conduct chemical analysis of materials XRF device is one of the useful devices and it was used to determine of chemical compositions of the materials.

XRF is a chemical analysis method which is practical and it can be used easily and fast. XRF analysis is both useful and partially reliable.

In this study, in order to conduct chemical composition analyses of the samples, "PANalytical's Minipal 4 - a benchtop energy dispersive X-Ray Fluorescence (EDXRF) spectrometer" was used in its standard measurement range (Voltage= 13 kV Current= 0.030 mA). For the elements which were needed to be measured for the study and were not in the measurement scale as standard, estimations were repeated after the options which were regarding the elements were opened.

Samples cannot be used in XRF device in dust form. Owing to this situation, samples need to be tabletted. To use XRF device, initially pellets need to be prepared. Pellets are put into XRF device to analyse chemical contents. X-Ray beams need to find thick surfaces to rebound enough. Pellets need to have a certain thickness for realising a precise chemical analysis. On account of this situation, hydraulic press device is also needed. By the help of mechanical parts and hydraulic press, pellets can be easily prepared and XRF analyses are conducted.

3.2.2.1.(2). Crosschecking by Atomic Absorption Spectrometer Analyses

In this study, in order to crosscheck the XRF results of the samples, "PinAAcle 900 H atomic absorption spectrometer" was used.

In order to prepare concentrate for atomic absorption spectrometer analysis, a certain amount of the concentrate which is obtained from flotation or

magnetic separation tests is taken into solution. If it has a high percentage, it is sufficiently diluted. After that, device is used and a value is read as ppm (1000000 g/ml or mg/L). The amount of metal in the solution is found by considering how much the solution has been diluted before. The percentage of metal can be easily found by dividing the amount of metal in the solution to the amount of concentrate initially used. It should also not be forgotten that the higher the dilution ratio, the greater the margin of error. If the element concentration which is desired to be analysed is above 7% the results which are obtained from atomic absorption spectrometer are not reliable enough.

3.2.2.1.(3). Crosschecking by Volumetric (Titrimetric) Chemical Analyses

In this study, Fe element grades were also crosschecked by volumetric analysis method. Volumetric analysis method was implemented by the help of using the Ethylenediaminetetraasetic acid (EDTA) solution and a suitable indicator. Before launching the titrimetric analysis, the value of the real normality of the EDTA is needed to be determined sensitively. Because the normality value of the EDTA changes as the time passes. After that, indicator is added to the metal solution and then EDTA is dripped into it. When colour changing is completed, the percentage of the metal can be easily found by the help of the exhausted amount of the EDTA.

3.2.2.1.(4). Volumetric Fe Analysis

In order to prepare the sample for the volumetric analysis, firstly, the sample is dissolved by a strong acid except for hydrofluoric acid because hydrofluoric acid solves the SiO_2. The undissolved silicium is separated from the liquid part by filtering. After that, by the help of ammonium pH is decreased at least until 8.2. Below pH 8.3 the iron and the aluminium minerals precipitate as solid. The solid and the liquid are separated. This liquid part which contains the calcium and the magnesium minerals part is named as A solution. After that, the

solid part are dissolved by the help of a strong acid, and it becomes liquid. This second liquid which contains the iron and the aluminium minerals is named as B solution.

In order to conduct volumetric analysis, firstly, 50 ml B solution is put into the 250 ml beaker. It is heated until its boiling point on the heating plate. After that, it is taken from the heating plate, and its pH is adjusted as 1.5 by the help of the ammonia. The sample on which 5ml 1N HCI and 1 ml 20% salicylic acid added, and which turned black colour is titrated with 0.05N EDTA until its colour turns to the colour which it was in B the solution.

$$\mathrm{Fe}(\%) = \frac{S \times N \times Meg \times 250 \times 100 \times 0.6994}{m \times m_1}$$

Formula 3.1. Calculation of the Fe grade for volumetric Fe analysis

0.6994= Fe_2O_3 to Fe conversion coefficient
S= 0.05 N EDTA consumption
N= Actual normality of the 0.05 N EDTA
Meg= Milliequivalency weight of the Fe_2O_3
250= The volume of the B solution
100= The constant number for the percentage of the Fe_2O_3
m= The weight which was the beginning in the analysis
m_1= The amount which was taken from the B solution for the iron

3.2.2.2. Sulphur Determination

Two measurement were implemented to determine S grade of feeding material. The total Sulphur content was determined by “Eltra Cs 580 Carbon S Determinator” device as 0.61%. Because iron and steel industry wants the

concentrates with the low amount of Sulphur, the percentage of the Sulphur is an important parameter for concentrates which obtained from the experiments.

3.2.2.3. Ash and Volatile Component Analyses by Ash Furnace

Ash furnace branded "PROTHERM" was used so as to carry out ash and volatile component analyses, in the American standards (ASTM D3174-11, and ASTM D3175-11).

During the ash analyses firstly, by the help of the precision scales, a crucible and sample were weighed respectively. Then sample was put into the crucible and was baked in 825 °C in the ash furnace for 4 hours. When sample came to a fixed weight it was taken out from the ash furnace with the crucible. Ash proportion could be found by dividing the final weight (W_f) to initial weight (W_i). Then ash percentage could be effortlessly found by the help of multiplying the ratio of ash to 100.

In the light of this information, the ash grade of feeding material was experimentally determined as 63.72%.

The feeding material was also baked in the ash furnace at 950 °C for 7 min with the aim of determining percentage of volatile components. Then the final weight (W_f) was divided to initial weight (W_i). After that, conclusion was subtracted from 1. Thus, ratio of volatile component was found. After that, percentage of volatile component was found by multiplying the ratio and 100. In this way, volatile component of the feeding material was found as 8.7%.

$$\text{Ash grade}(\%) = \frac{W_i - W_f}{W_i} \times 100$$

Formula 3.2. Ash grade (%) calculation formula after 4 hours baking at 825 °C

$$\text{Volatile components (\%)} = \frac{W_i - W_f}{W_i} \times 100$$

Formula 3.3. Volatile components (%) calculation formula after 7 min baking at 950 °C in terms of weight

3.2.2.4. Density Determination by Pycnometer Experiment

In pycnometer experiment firstly weight of a dried pycnometer is weighed. Then a certain amount of the sample is put into the dried pycnometer and weighted with the pycnometer together. By the help of water distilling apparatus, distilled water is added until the pycnometer become full. Then the sample, the water, and the pycnometer is weighed together. After the weight of the water found, the water and the sample which are in the pycnometer are poured. The water whose weight was found can be named as 1 numbered water. After the water and the sample being poured, the pycnometer is filled with distilled water and weighed again. This time water can be named as 2 numbered water. Because the density of the water was known in advance as 1 g/ml, by using the weights of the 1 numbered water, the 2 numbered water, the sample, and the pycnometer the density of material can be easily found. By using this method, the density of the feeding material was experimentally determined as 2.67 g/cm^3 by doing this calculations.

3.2.2.5. Grain Size Determination by the help of the Sieves

The feeding material which was blast furnace flue dusts was sieved by the help of the knitting wire sieves with different hole diameters. The sieving process was implemented by the means of using a wet sieving device. After the sieving process, based on the figure below d_{50} and d_{80} values were determined to be

approximately 75 µm (micrometer) and 150 µm for the feeding material (Figure 3.1).

Figure 3.1. Particle size distribution of the feeding material

3.2.2.6. Qualitative Mineral Composition Analysis by Using X-Ray Diffraction (XRD) Device

In order to conduct the qualitative analysis of the blast furnace flue dusts, "Rigaku Miniflex II X-Ray Diffractometer" which was equipped with Cu K radiation was used in its standard adjustments (Step size= 0.02, 2θ range= 5-85°, Voltage= 40 kV, Current= 15 mA). XRD results were interpreted by PDXL XRD analysis software with the current mineral database. The analysis demonstrated that the feeding material which were blast furnace flue dusts mainly consisted of hematite mineral in terms of iron minerals. Besides the hematite, magnetite also existed in the iron minerals of the feeding material. There was a hump between 17 and 29 degrees. This hump in the figure below means that there is amorphous (non-crystalline) mineral, it is thought that most of time it might be carbonaceous or glassy. This amorphous mineral might be a kind of coal. This material also contained impurities such as mullite and silica (Figure 3.2).

Figure 3.2. X-Ray Diffraction (XRD) analysis of the feeding material

4. RESULTS AND DISCUSSIONS

In this section of the study, the results of 3 different experimental methods which were magnetic separation method, reverse flotation method, and acid leaching method were respectively presented by the help of graphs, tables, and explanations. By the help of the obtained data, advantages and disadvantages of these methods on each other tried to be understood.

4.1. Results of the Magnetic Separation Experiments and Discussions

For the flue dust samples d_{80} value of which is 150 µm, the results of the experiments which were conducted with respect to different magnetic field intensities were given below.

As magnetic field intensity (Tesla) was increased, the Fe grades of the concentrates were decreased. This situation signified that as magnetic field intensity was increased, magnetic particles which were except for Fe, and less magnetic particles were pulled together with the Fe. It was thought that, the sources of this situation might be flocculation or that being insufficient of the liberalization size and that the separation process might become more complicated due to the disseminated iron particles on the coal particles. When the Fe recoveries of the concentrates were looked at, it was observed that as the magnetic field intensity increased the Fe recoveries of the concentrates increased. The minimum Fe recovery for the concentrates was obtained from the experiment which was conducted by 0.25 T magnetic field intensity as 63.03%. When the magnetic field intensity arranged as 0.50 T, the Fe recovery of the concentrate was 83.30%. For more intense magnetic fields the increment ratio as regards to Fe recoveries increased. When magnetic field intensity was 0.75 T, the Fe recovery was 85.69%. For 1 T, Fe recovery was 87.42%. For 1.25 T magnetic field intensity, this value was 87.59%. The maximum Fe recovery of concentrate was 88.25% in the experiments at 1.5 T. As the magnetic field intensity increased, the ash grades of the concentrates increased. With the increments of magnetic field intensities, the

continuous increments of ash percentages in the concentrates showed that being pulled of the magnetic particles were increased by the help of the increments of the magnetic field intensity. But it was thought that the possibility of the flocculation and absence of the sufficient liberalization size might overshadowed the positive aspects of this. For 0.25 Tesla magnetic field intensity, ash grade of the concentrate was 68.72%. For 0.50 Tesla magnetic field intensity, this value increased and its value was 71.26%. The largest increment ratio of the ash grades of the concentrates were between the 0.25 Tesla and 0.50 Tesla. For 0.75 Tesla magnetic field intensity, ash grade of the concentrate was 71.29%. This value reached 71.56% when the magnetic field intensity reached 1.00 Tesla. When magnetic field intensity was 1.25 Tesla, the ash grade of the concentrate was 72.24%. Finally, for 1.50 Tesla magnetic field intensity, the ash grade of the concentrate reached 73.45% (Figure 4.1).

After the magnetic separation tests, although, low enough Zn could not be reached, it was thought that the observed decrements could ease possible additional processes to enrich the flue dusts. In the first experiments the magnetic field intensity was 0.25 Tesla. The Zn grade of the concentrate was 1.10%. This value decreased to 1.07% when the magnetic field intensity was 0.50 Tesla. For 0.75 Tesla magnetic field intensity, this value was 1.06%. For 1.00 Tesla magnetic field intensity, the Zn grade of the concentrate was 1.02%. 0.98% value was obtained as a result of the experiments which were conducted with 1.25 Tesla magnetic field intensity. Finally, for 1.5 Tesla magnetic field intensity, the Zn grade of the concentrate was 0.94%. (Figure 4.1).

Figure 4.1. Fe grades (%), Fe recoveries (%), ash grades (%), and Zn grades (%) of magnetic separation concentrates by different magnetic field intensities

For 0.25 T magnetic field intensity, the combustible grade of the tailings was 51.31%. When the magnetic field intensity arranged as 0.50 T, the combustible grade of the tailings was found as 55.52%. For 0.75 T, this value was 60.10%. After the magnetic field intensity at the 0.75 Tesla, combustible grades of the tailings continued to increase. The maximum combustible value was obtained as 61.39% for 1.5 T.

With the increments of the magnetic field intensity, combustible recoveries of the tailings decreased (Figure 4.2).

Figure 4.2. Combustible grades (%) and combustible recoveries (%) of magnetic separation tailings by different magnetic field intensities

For the magnetic separation experiments, the experiment which were conducted with 0.25 Tesla magnetic field intensity was chosen as the optimum. Of the magnetic separation experiments, in the results of the experiment which were accepted as optimum the Fe grade of the concentrate was maximum and 41.29%. 41.29% value was below the 50% minimum limit. In the magnetic separation experiments, on the other hand, the impurities could not be removed effectively. Zn grade of the concentrate was 1.10%. The magnetic separation experiments did not give satisfactory results in terms of both increasing the grades of the desired material (Fe) and decreasing the grades of the undesired materials.

4.2. Results of the Reverse Floatation Experiments and Discussions

4.2.1. Effects of Collectors

To investigate effect of different types and different amounts of the collectors, three types of collectors were tried and used in the reverse flotation process in different amounts respectively. One of them was four numbered fuel oil, other one was diesel, and the other was kerosene. In the experiments which were conducted to determine effects of the collectors, 2500 g/ton, 5000 g/ton, 7500 g/ton, 10000 g/ton, 12500 g/ton collectors were used respectively in a medium which consisted of 1000 g water. Together with the collectors 500 g/ton MIBC were used as frother and 500 g/ton corn starch were used as depressant.

Experiments were performed using a laboratory-type Denver flotation device. After the reagents were added into the medium, the feeding material at 15% solid ratio, which approximately accounts for 176.47 g solid feeding, was put into the flotation cell and the device was run for 3 min at 1350 rpm. At the end of 3 min, the air tap was opened and the froths was started to be taken. The froths were taken for 1 min and then the test was completed. Concentrates and wastes were filtered by the help of pressure filter and dried by the help of drying oven at 85 °C until they have come to a constant weight. After drying, the analyses were implemented to the concentrates and the results were investigated in detail.

4.2.1.1. Effect of fuel oil as a Collector.

The Fe grades were investigated between 2500 g/ton and 12500 g/ton usages of fuel oil as collector. By the help of the results, it was understood that as the amount of the fuel oil were increased towards 12500 g/ton level, the Fe grades of the concentrates constantly increased. For 2500 g/ton fuel oil level, the Fe grade of the concentrate was 41.79%. For 5000 g/ton fuel oil level, the Fe grade of the concentrate was 47.71%. For 7500 g/ton fuel oil level, the Fe grade of the concentrate was 49.10%. 49.71% value was obtained as the Fe grade for 10000

g/ton collector usage. When the amount of the fuel oil level was 12500 g/ton level, it was observed that the Fe grade of the concentrate was 50.01% (Figure 4.3).

Fe recoveries of the concentrates were investigated between 2500 g/ton and 12500 g/ton fuel oil usages. For 2500 g/ton fuel oil level, the Fe recovery of the concentrate was 62.96%. This value was found as 59.24% for 5000 g/ton fuel oil level, 58.71% for 7500 g/ton fuel oil level, 57.97% for 10000 g/ton fuel oil level, and 54.84% for 12500 g/ton fuel oil level. Due to this situation, it was observed that as long as the amount of the fuel oil increased, the recovery values (%) of the concentrates decreased. It was thought that this situation originated from the decrements of the amounts of the concentrates as the amount of used collector were increased. As the amount of the fuel oil increased the Fe recoveries of the concentrates decreased to the 54.84% level (Figure 4.3).

Figure 4.3. Fe grades (%) and Fe recoveries (%) of the reverse flotation concentrates by different fuel oil dosages

The SiO_2 grades of the concentrates were investigated. Their values were changing between 6.38% and 4.69%. After The experiments, it was observed that as long as the usage amount of the fuel oil as a collector increased, the SiO_2 grades

of the concentrates decreased. For 2500 g/ton fuel oil level, the SiO_2 grade of the concentrate was 6.38%. This value was found as 6.25% for 5000 g/ton fuel oil level, 5.51% for 7500 g/ton fuel oil level, 5.10% for 10000 g/ton fuel oil level; and it found as 4.69% for 12500 g/ton fuel oil level. It was understood that the SiO_2 grade of the concentrate, could be decreased below 5%, only in the experiments in which 12500 g/ton fuel oil was used (Figure 4.4).

Figure 4.4. SiO_2 grades (%) of the reverse flotation concentrates by different fuel oil dosages

The Zn grades were investigated between 2500 g/ton and 12500 g/ton usage of fuel oil in detail. It was observed that the Zn grade of the concentrate was decreased to 0.85% by the help of arrangement the fuel oil quantity. For 2500 g/ton fuel oil level, the Zn grade of the concentrate was 0.91%. This value was found as 0.90% for 5000 g/ton fuel oil level, 0.89% for 7500 g/ton fuel oil level, 0.86% for 10000 g/ton fuel oil level, and 0.85% for 12500 g/ton fuel oil level. As the amount of fuel oil increased, the Zn grades of the concentrates decreased (Figure 4.5).

It was observed as to Cu and S grades that for 2500 g/ton fuel oil level, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.16%; for 5000 g/ton fuel oil level, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.16%; for 7500 g/ton fuel oil level, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.11%; for 10000 g/ton fuel oil level, the Cu grade of the concentrate was 0.03% and the S grade of the concentrate was 0.11%; for 12500 g/ton fuel oil level, the Cu grade of the concentrate was 0.03% and the S grade of the concentrate was 0.11% (Figure 4.5).

When the Pb grades of the concentrates were looked at, it was observed that they took values which were 0.33% or 0.32%. For 2500 g/ton fuel oil level, the Pb grade of the concentrate was 0.33%; for 5000 g/ton fuel oil level, the Pb grade of the concentrate was 0.33%; for 7500 g/ton fuel oil level, the Pb grade of the concentrate was 0.33%; for 10000 g/ton fuel oil level, the Pb grade of the concentrate was 0.33%; for 12500 g/ton fuel oil level, the Pb grade of the concentrate was 0.32% (Figure 4.5).

When Mn grades of the concentrates were looked at, it was observed that they took different values which changed between 0.53% and 0.68%. It was observed that these values are too high for production of the grey pig iron. On the other hand, if a steel which contains more manganese is desired to be produced, these values of Mn are suitable for the production then (Figure 4.5).

Figure 4.5. Zn, Mn, Pb, S, Cu grades (%) of the reverse flotation concentrates by different fuel oil dosages

4.2.1.2. Effect of Diesel as a Collector

After the experiments which were conducted with diesel, it was observed that as the amount of the diesel were increased, the Fe grades of the concentrates increased. When the diesel was at the 10000 g/ton level, the Fe grade of the concentrate was 50.20%, and when it reached to 12500 g/ton, the Fe grade of the concentrate was 51.02%. The Fe which was above 50% and was reached in the experiments in which 12500 g/ton fuel oil was used could be also obtained in the experiments in which 10000 g/ton diesel was used (Figure 4.6).

For 2500 g/ton diesel, the Fe recovery of the concentrate was 56.70%. This value was found as 56.02% for 5000 g/ton diesel, 55.67% for 7500 g/ton diesel, 55.49% for 10000 g/ton diesel level, and 54.20% for 12500 g/ton diesel. It was observed that as the amount of the diesel increased, the recovery values (%) of the concentrates decreased. It was thought that this situation originated from decrement of the amount of the concentrates as the amount of used collector were increased. (Figure 4.6).

Figure 4.6. Fe grades (%) and Fe recoveries (%) of the reverse flotation concentrates by different diesel dosages

For 2500 g/ton diesel level, the SiO_2 grade of the concentrate was 6.09%. This value was found as 5.92% for 5000 g/ton diesel, 5.21% for 7500 g/ton diesel, 4.69% for 10000 g/ton diesel, and it found as 4.44% for 12500 g/ton diesel. It was understood that SiO_2 grade of the concentrate could be decreased below 5%, only in the experiments in which 10000 and 12500 g/ton diesel was used. The results which were obtained from the experiments which were conducted with 10000 and 12000 g/ton diesel were only possible the experiments which were conducted with 12500 g/ton fuel oil. Because of this situation, it is understood that the effect of the diesel was more powerful than the effect of the fuel oil, according to used quantities, in terms of the removal of the SiO_2 (Figure 4.7).

Figure 4.7. SiO_2 grades (%) of the reverse flotation concentrates by different diesel dosages

The Zn grade of the concentrate was decreased to 0.85% by the help of some arranging the diesel level. For 2500 g/ton diesel, the Zn grade of the concentrate was 1.01%. This value was found as 0.93% for 5000 g/ton diesel, 0.90% for 7500 g/ton diesel, 0.87% for 10000 g/ton diesel, and 0.85% for 12500 g/ton diesel. (Figure 4.8).

For 2500 g/ton diesel level, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.16%; for 5000 g/ton diesel level, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.16%; for 7500 g/ton diesel level, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.11%; for 10000 g/ton diesel level, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.11%; for 12500 g/ton diesel level, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.11%. For 2500 g/ton diesel level, the Pb grade of the concentrate was 0.36%; for 5000 g/ton diesel level, the Pb grade of the concentrate was 0.34%; for 7500 g/ton diesel level, the Pb grade of the concentrate was 0.34%; for 10000 g/ton diesel level, the Pb grade of the concentrate was 0.33%; for 12500 g/ton

diesel level, the Pb grade of the concentrate was 0.32%. When Mn percentages was observed, they took values which was between 0.59% and 0.68%. These values are too high for production of the grey pig iron and suitable for the production of the manganese steel (Figure 4.8).

Figure 4.8. Zn, Mn, Pb, S, Cu grades (%) of the reverse flotation concentrates by different diesel dosages

4.2.1.3. Effect of Kerosene as a Collector

After the experiments, it was observed that as the amount of the kerosene were increased towards 12500 g/ton level, the Fe grades of the concentrates increased. For 2500 g/ton kerosene, the Fe grade of the concentrate was 47.18%. For 5000 g/ton kerosene, the Fe grade of the concentrate was 47.94%. When the kerosene amount was 7500 g/ton, the Fe grade of the concentrate was 50.09%; when it was 10000 g/ton, the Fe grade of the concentrate was 50.35%, and when it was 12500 g/ton level, it was observed that the Fe grade of the concentrate was 51.17% (Figure 4.9).

For 2500 g/ton kerosene, the Fe recovery of the concentrate was 56.18%. This value was found as 55.77% for 5000 g/ton kerosene, 53.58% for 7500 g/ton kerosene, 50.19% for 10000 g/ton kerosene, and 49.69% for 12500 g/ton kerosene.

It was observed that as the amount of the kerosene increased, recovery values (%) of the concentrates decreased. (Figure 4.9).

Figure 4.9. Fe grades (%) and Fe recoveries (%) of the reverse flotation concentrates by different kerosene dosages

The SiO_2 grade of the concentrate was decreased to 4.35% by arranging kerosene dosage. For 2500 g/ton kerosene level, the SiO_2 grade of the concentrate was 6.05%. This value was found as 5.85% for 5000 g/ton kerosene level, 5.49% for 7500 g/ton kerosene level, 4.55% for 10000 g/ton kerosene level, and it found as 4.35% for 12500 g/ton kerosene level. It was understood that the SiO_2 grades of the concentrates could be decreased below 5%, only in the experiments in which 10000 and 12500 g/ton kerosene was used (Figure 4.10).

Figure 4.10. SiO_2 grades (%) of the reverse flotation concentrates by different kerosene dosages

For 2500 g/ton kerosene, the Zn grade of the concentrate was 1.01%. This value was found as 0.92% for 5000 g/ton kerosene, 0.90% for 7500 g/ton kerosene, 0.87% for 10000 g/ton kerosene, and 0.84% for 12500 g/ton kerosene. For 2500 g/ton kerosene, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.17%; for 5000 g/ton kerosene, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.17%; for 7500 g/ton kerosene, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.11%; for 10000 g/ton kerosene, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.11%; for 12500 g/ton kerosene, the Cu grade of the concentrate was 0.04% and the S grade of the concentrate was 0.11%. For 2500 g/ton kerosene, the Pb grade of the concentrate was 0.36%; for 5000 g/ton kerosene, the Pb grade of the concentrate was 0.34%; for 7500 g/ton kerosene, the Pb grade of the concentrate was 0.34%; for 10000 g/ton kerosene, the Pb grade of the concentrate was 0.33%; for 12500 g/ton kerosene, the Pb grade of the concentrate was 0.32%. Mn grades took values which were between 0.59% and 0.68%. These values are too high for production of the grey pig iron. On the other

hand, if a steel which contains more manganese is desired to be produced, these values of Mn are suitable for the production then (Figure 4.11).

Figure 4.11. Zn, Mn, Pb, S, and Cu grades (%) of the reverse flotation concentrates by different kerosene dosages

4.2.2. Effects of the Frothers

Frothers which were Methyl isobutyl carbinol (MIBC) and pine oil were tried for 300 g/ton, 400 g/ton, 500 g/ton, 600 g/ton and 700 g/ton usages respectively. Frothers were fed into the process together with 7500 g/ton kerosene which is a collector and 500 g/ton corn starch which is a depressant. Experiments were performed using a laboratory-type Denver flotation device. After the reagents were added into the medium, the feeding material at 15% solid ratio, which approximately accounts for 176.47 g solid feeding, was put into the flotation cell and the device was run for 3 min at 1350 rpm. At the end of 3 min, the air tap was opened and the froths was started to be taken. The froths were taken for 1 min and then the test was completed. Concentrates and wastes were filtered by the help of pressure filter and dried by the help of drying oven at 85 °C until they have come to a constant weight. After drying, the analyses were implemented.

4.2.2.1. Effect of the MIBC as Frother

At the tests which were conducted with 300 g/ton Methyl isobutyl carbinol (MIBC) the Fe grade of the concentrate was 49.57%. When this usage was 400 g/ ton, the Fe grade of the concentrate was 49.58%. For 500 g/ton MIBC, this value was 50.09%. When the usage of the MIBC was 600 g/ton, the Fe grade of the concentrate was 50.79%. Whereas at the 700 g/ton MIBC usage, the Fe grade of the concentrate slightly decreased to 49.85% (Figure 4.12).

In the experiments, it was observed that the more usage of MIBC meant the less Fe recovery until the 700 g/ton level. When this usage reached 700 g/ton level an increment was observed in the Fe recovery of the concentrate. At 300 g/ton usage of the MIBC the Fe recovery was observed as 56.01%. This value decreased to 55.51%, 53.58%, and 50.29% for each stage of increment of the MIBC usage except for the last increment in which the usage of the MIBC reached 700 g/ton level (Figure 4.12).

Between 300 g/ton and 600 g/ton MIBC, as the MIBC quantity increased, the SiO_2 grades of the concentrates increased. For 300, 400, 500, and 700 g/ton MIBC, the SiO_2 of the concentrate was 6.49%, 5.77%, 5.59%, 5.37% respectively. This value decreased below 5% as 4.79% only in the experiments which were conducted with 600 g/ton MIBC (Figure 4.13).

Figure 4.12. Fe grades (%) and Fe recoveries (%) of the reverse flotation concentrates by different MIBC dosages

Figure 4.13. SiO_2 grades (%) of the reverse flotation concentrates by different MIBC dosages

For 300 g/ton MIBC, the Zn grade of the concentrate was 0.98%. The value of the Zn grade as 0.90% was obtained after the experiments which were conducted with 600 g/ton MIBC. When the MIBC was 700 g/ton, it was observed that the Zn grades of the concentrates slightly increased. Between 500 g/ton and

600 g/ton MIBC uses, significant change in Zn grades of the concentrates was not observed. On the other hand, the lowest Zn grades were observed in the experiments which were conducted with both 500 and 600 g/ton MIBC usages. The Cu grades of the concentrates were between 0.04% for 300, 400, 500, and 600 g/ton MIBC and 0.03% for 700 g/ton MIBC. The Pb percentages were between 0.35% and 0.32%. These values were also below 0.5% which is the maximum limit. S grades of the concentrates were between 0.11% and 0.19%. These values were below 0.35%. When Mn grades was look at, it was understood that they took values which changed between 0.65% and 0.68%. These values are too high for production of the grey pig iron. On the other hand, if a steel which contains more manganese is desired to be produced, these values of Mn are suitable for the production then (Figure 4.14).

Figure 4.14. Zn, Mn, Pb, S, and Cu grades (%) of the reverse flotation concentrates by different MIBC dosages

4.2.2.2. Effect of the Pine Oil as Frother

As the pine oil quantity increased, the values of the Fe grades of the concentrates increased. In the experiments which were conducted with 300 g/ton

pine oil, the Fe grade of the concentrate was 49.10%. When pine oil was 400 g/ton, the Fe grade of the concentrate was 49.32%. For 500 g/ton pine oil, this value was 49.67%. When the pine oil was 600 g/ton, the Fe grade of the concentrate was 50.52%. Whereas at the 700 g/ton pine oil, the Fe grade of the concentrate slightly decreased to 49.43% (Figure 4.15).

As the pine oil quantity increased, the Fe recoveries of the concentrates decreased. For 300 g/ton pine oil, the Fe recovery of the concentrate was 59.15%. This result was 56.22% for the experiments conducted with 400 g/ton pine oil. In the experiments which were conducted with 500 g/ton pine oil the Fe recovery of the concentrate was 55.75%. The minimum value of Fe recovery was attained as a result of the experiments which were conducted with 600 g/ton as 55.59%. When the usage of the pine oil reached 700 g/ton level, the Fe recovery of the concentrate slightly increased to 56.74% (Figure 4.15).

Figure 4.15. Fe grades (%) and Fe recoveries (%) of the concentrates by different pine oil dosages

Between 300 g/ton and 700 g/ton usages of pine oil, as the pine oil quantity increased, the values of the SiO_2 grades of the concentrates decreased. This situation could be particularly observed when the usages increased above 500 g/ton

level. Between 300 g/ton and 700 g/ton usages of the pine oil, the SiO_2 grades of the concentrates changed between 5.63% and 4.84 %. Of all different usage amounts of the pine oil, only in the experiments which were done 700 g/ton pine oil the value below 5% was obtained as 4.84 % (Figure 4.16).

Figure 4.16. SiO_2 grades (%) of the reverse flotation concentrates by different pine oil dosages

The Zn grades of the concentrates were between 0.91% and 0.98%. In the experiments which were conducted with 400 g/ton pine oil, the Zn grade of the concentrate was 0.98%. This value was found as the maximum value for the Zn. In the experiments which were conducted with 300 g/ton pine oil, the Zn grade of the concentrate was 0.96%. The minimum value of Zn was obtained in the experiments which were conducted with 600 g/ton pine oil as 0.91%. When the usage of the pine oil decreased to 700 g/ton level, the Zn of the concentrate increased to 0.95% (Figure 4.17).

The Cu grades of the concentrates changed between 0.04% and 0.03%. These values were below the 0.06% value to which Çilingir referred. The Pb grades of the concentrates were between 0.37% and 0.31%. These values were also below 0.5% which is the maximum limit. The S grades of the concentrates were

between 0.15% and 0.20%. These values were below 0.35%. When Mn grades was look at, it was understood that they took values which changed between 0.53% and 0.68%. These values are too high for production of the grey pig iron. On the other hand, if a steel which contains more manganese is desired to be produced, these values of Mn are suitable for the production then (Figure 4.17).

Figure 4.17. Zn, Mn, Pb, S, and Cu grades (%) of the reverse flotation concentrates by different pine oil dosages

4.2.3. Effects of the Depressants

Two different types of depressants were tried at 300 g/ton, 400 g/ton, 500 g/ton, 600 g/ton and 700 g/ton amounts respectively in the reverse flotation process. Depressants were fed into the reverse flotation process together with 7500 g/ton kerosene which is a collector and 500 g/ton MIBC which is a frother. Experiments were performed using a laboratory-type Denver flotation device. After the reagents were added into the medium, the feeding material at 15% solid ratio, which approximately accounts for 176.47 g solid feeding, was put into the flotation cell and the device was run for 3 min at 1350 rpm. At the end of 3 min, the air tap was opened and the froths was started to be taken. The froths were taken for 1 min

and then the test was completed. Concentrates and wastes were filtered by the help of pressure filter and dried by the help of drying oven at 85 °C until they have come to a constant weight. After drying, the analyses were implemented. After the process, the effects of the depressants on the reverse flotation process were investigated in detail.

One of the two type depressants which were tried in the reverse flotation process is water glass. The other one was corn starch. In 2019 Peçanha et al. conducted a sequence of experiments and saw that starch powerfully adsorbs onto hematite (Peçanha et al., 2019). Shrimali and their colleagues stated in 2017 that the most used depressant in reverse flotation of iron ores is corn starch (Shrimali et al., 2017). Due to this situation, these experiments were also repeated using corn starch as depressant instead of water glass in natural pH and it was found that the results of the experiments with the water glass a little bit more effective than the results of the experiments with the corn starch. This situation was valid in the natural pH in terms of Fe quantities of the concentrates in the reverse flotation process.

When it comes to the water glass it can be stated that the water glass has some advantages and some disadvantages. The water glass has a dispersive effect as well as its depressant effect these are advantages of the water glass. Disadvantage of the water glass is that water glass particles cannot fall apart homogeneous in its water and some particles precipitate; namely, weighing of the corn starch is more reliable than weighing of the water glass. The corn starch is also much more economical than the water glass and it can be found much easier compared to water glass.

4.2.3.1. Effect of the Corn Starch as Depressant

For the experiments which were conducted with 300 g/ton corn starch, the Fe grade of the concentrate was 48.92%. For the experiment which were conducted with 400 g/ton, 500 g/ton, and 600 g/ton corn starch this values were 50.03%,

50.09%, and 50.27% respectively. When 700 g/ton corn starch was used, the Fe grade of the concentrate was 50.99%. For the experiments which were conducted with 300 g/ton, 400 g/ton, 500 g/ton, and 600 g/ ton corn starch, the Fe recoveries of the concentrates were 55.67%, 53.99%, 53.58%, and 52.71% respectively. When the use of the corn starch was 700 g/ton, this value was 51.74% (Figure 4.18).

Figure 4.18. Fe grades (%) and Fe recoveries (%) of the reverse flotation concentrates by different corn starch dosages

As the amount of the corn starch increased, the SiO_2 grades of the concentrates decreased. For 300 g/ton corn starch use, the SiO_2 grade of the concentrate was 6.42%. For 400 g/ton corn starch usage this value was found as 6.01%. For 500 g/ton corn starch dosage, the SiO_2 grade of the concentrate was 5.59%. In the experiment of which corn starch amount was 600 g/ton, the SiO_2 grade of the concentrate was found as 4.68. While corn starch use 700 g/ton, this value was found as 3.75%. It was observed that, when the use of the corn starch reached 600 and 700 g/ton level, the values which are below 5% were obtained by arranging the corn starch quantities (Figure 4.19).

Figure 4.19. SiO_2 grades (%) of the reverse flotation concentrates by different corn starch dosages

When the corn starch was 300 g/ton, the Zn grade of the concentrate was 1.07%. This value fell to 0.93% for 400 g/ton corn starch. When the corn starch reached to 500 g/ton, the Zn grade of the concentrate was 0.90%. Between 500 g/ton and 700 g/ton corn starch uses, a significant change was not observed in terms of Zn grades (Figure 4.20).

Reverse flotation experiments were conducted to observe the effects of the corn starch as a depressant on the Cu, the Pb, the Mn, and the S percentages of the concentrates in detail. After the experiments, it was observed that the maximum Cu of the concentrates was found as 0.04%, the maximum Pb of the concentrates was found as 0.37% and the maximum S of the concentrates was found as 0.11%. The Mn grades of the concentrates were between 0.60% and 0.65%. These Mn values are too high for production of the grey pig iron. On the other hand, if a steel which contains more manganese is desired to be produced, these values of the Mn are suitable for the production then (Figure 4.20).

Figure 4.20. Zn, Mn, Pb, S, and Cu grades (%) of the reverse flotation concentrates by different corn starch dosages

4.2.3.2. Effect of the Water Glass as Depressant

As the water glass quantity increased, the values of the Fe grades of the concentrates increased. At the tests which were conducted with 300 g/ton water glass, the Fe grade of the concentrate was 49.77%. When this usage was 400 g/ ton, the Fe grade of the concentrate was 50.03%. For 500 g/ton water glass, this value was 50.22%. When the usage of the water glass was 600 g/ton, the Fe grade of the concentrate was 50.35%. When 700 g/ton water glass was used, the Fe grade of the concentrate increased to 51.16% (Figure 4.21).

Between 300 g/ton and 700 g/ton water glass usages, as the water glass quantity increased, the Fe recoveries of the concentrates decreased. The Fe recoveries of the concentrates changed between 55.49% and 54.81%. For 300 g/ton usage of the water glass, the value of the Fe recovery was 55.49%. This value decreased to 55.34% when the usage of water glass was 400 g/ton. When the use of the water glass was 500 g/ton, this value was 55.13%. At the use of 600 g/ton water

glass, this value was 55.12%. The value of 54.8% was obtained as the Fe recovery at the usage of 700 g/ton water glass (Figure 4.21).

Figure 4.21. Fe grades (%) and Fe recoveries (%) of the reverse flotation concentrates by different water glass dosages

After the experiments which were conducted by means of being changed the amount of the water glass, it could be observed that as the quantity of the water glass increased between the 300 g/ton and 700 g/ton levels, the SiO_2 grades of the concentrates decreased from 6.51% level to 3.78% level. In the experiments which were conducted with 300 g/ton, 400 g/ton, and 500 g/ton water glass, the values of the SiO_2 grades of the concentrates were found as 6.51%, 5.65%, and 5.61% respectively. On the other hand, when the usage of the water glass was reached 600 g/ton, the SiO_2 of the concentrates fell below 5% as 4.70%. Owing to this situation, it was thought that 600 g/ton level is an important level for the process. For 700 g/ton use of the water glass, the SiO_2 of the concentrate was minimum and 3.78% (Figure 4.22).

Figure 4.22. SiO_2 grades (%) of the reverse flotation concentrates by different water glass dosages

When the level of the water glass was increased from 300 g/ton level to 700 g/ton level, it was understood that the values of the Zn grades of the concentrates were prone to decrease. When the amount of the usage of the water glass and the values of the Zn grades of the concentrates were compared, it was observed that; for 300 g/ton and 400 g/ton water glass usages, the values of the Zn grades of the concentrates were 1.05% and 0.98% respectively. For 500 g/ton level, 600 g/ton level, and 700 g/ton level water glass usages, the values of the Zn grades of the concentrates were almost the same as each other and the value of them was 0.90% (Figure 4.23).

The Cu grades of the concentrates were 0.04% for all experiments and below the 0.06% limit. The Pb grades of the concentrates were between 0.41% and 0.38% and below 0.5% limit. The S grades of the concentrates were between 0.11% and 0.26% and below 0.35% limit. When Mn grades was look at, it was observed that they took values which changed between 0.62% and 0.65%. These

values are too high for production of the grey pig iron. On the other hand, if a steel which contains more manganese is desired to be produced, these values of Mn are suitable for the production then (Figure 4.23).

Figure 4.23. Cu, Pb, Mn, S grades (%) of the reverse flotation concentrates by different water glass dosages

4.2.4. Results of the Box-Behnken Design Experiments

In order to obtain graphs with two variables, by means of the "Design Expert" computer program, "Box-Behnken" experimental design was formed. After that, the experiments were conducted by the help of the use of the given different amounts of the diesel, the pine oil, and the water glass reagents. In the "Box-Behnken" experiments 100 g feeding material was used in a 1000 g medium of water; namely, solid ratio was 10%. After each one of the "Box-Behnken" experiments was conducted, by the help of the sweeping the froths, the tailings were obtained between 0 and 30 sec, the by-product were obtain between 30 and 60 sec. After that, remained parts were obtained as concentrate. Obtained by-products were distributed to the concentrates and tailings. (Table 4.1).

Table 4.1. Box-Behnken experimental design reagent quantities.

Experiment Number	Diesel Quantity (g/ton)	Pine Oil Quantity (g/ton)	Water Glass Quantity (g/ton)
1	15000	400	600
2	15000	50	100
3	25000	400	350
4	5000	50	350
5	15000	50	600
6	25000	50	350
7	15000	225	350
8	5000	225	600
9	5000	400	350
10	15000	225	350
11	15000	400	100
12	25000	225	600
13	25000	225	100
14	15000	225	350
15	5000	225	100

By Figure 4.24, the Figure 4.25, and the Figure 4.26, it could be observed that the Fe percentages of the concentrates generally tended to increase as the water glass amount, the pine oil amount, or the diesel amount of the reverse flotation process increased. By the help of the evident declinations in the 4.24 numbered and the 4.25 numbered 3 dimensional figures, it was observed that diesel collector was the most effective reagent amongst the three reagents in terms of the Fe grades (%) of the concentrates. On the other hand, by the help of the Figure 4.25, it could be observed that an adverse effect occurred when both of the water glass and the diesel were increased to high amounts simultaneously. It was thought that when they reached in high amounts, because of that the pine oil quantity remained too low compared to them, they might have deadened the effectiveness of the pine oil for the reverse flotation process of the blast furnace flue dusts. If it was looked at the graphs in the Figure 4.24 and Figure 4.25, when the amounts of the two variable reagents were maximum, a kind of collapsing effect could be obviously observed (Figure 4.24, 4.25, 4.26).

Figure 4.24. Fe grades (%) of the reverse flotation concentrates by different pine oil and diesel dosages while water glass 350 g/ton

Figure 4.25. Fe grades (%) of the reverse flotation concentrates by different water glass and diesel dosages while pine oil 225 g/ton

Figure 4.26. Fe grades (%) of the reverse flotation concentrates by different water glass and pine oil dosages while diesel 15000 g/ton

Table 4.2. Analysis of variance for the Fe grades of the concentrates

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	241,21	9	26,80	9,04	0,0130	significant
A-Diesel	124,29	1	124,29	41,92	0,0013	
B-Pine oil	19,19	1	19,19	6,47	0,0516	
C-Water glass	15,89	1	15,89	5,36	0,0684	
AB	0,0159	1	0,0159	0,0054	0,9444	
AC	5,67	1	5,67	1,91	0,2251	
BC	4,80	1	4,80	1,62	0,2591	
A^2	53,94	1	53,94	18,19	0,0080	
B^2	6,59	1	6,59	2,22	0,1962	
C^2	9,44	1	9,44	3,18	0,1345	
Residual	14,82	5	2,96			
Lack of Fit	6,22	3	2,07	0,4820	0,7282	not significant
Pure Error	8,60	2	4,30			
Cor Total	256,03	14				

Table 4.3. Fit statistics for the Fe grades of the concentrates

Std. Dev.	1,72	R^2	0,9421
Mean	45,27	Adjusted R^2	0,8379
C.V. %	3,80	Predicted R^2	0,5357
		Adeq Precision	10,6012

Figure 4.27, Figure 4.28 and Figure 4.29 showed that Fe recovery percentages of the concentrates generally tended to increase as the water glass or the pine oil amount increased. The exact opposite of this was valid for the diesel amount. It could be stated that between these reagent usage ranges, some change of the amount of the water glass was more effective than some change of the amount of the other reagents. But it was observed that excessive amount of the water glass usage might have a little degree adverse effect on the Fe recoveries of the concentrates if it was looked at Figure 4.28 and Figure 4.29. When Figure 4.27 was investigated in terms of the pine oil and the diesel amounts, it could be observed that Fe recovery percentages of the concentrates generally tended to decrease as long as the amount of any one of them increased. It might be thought that this expected situation originated from properties of the types of the reagents and the interactions of them with the process of reverse flotation. (Figure 4.27, 4.28, 4.29).

Figure 4.27. Fe recoveries (%) of the reverse flotation concentrates by different pine oil and diesel dosages while water glass 350 g/ton

Figure 4.28. Fe recoveries (%) of the reverse flotation concentrates by different water glass and diesel dosages while pine oil 225 g/ton

Figure 4.29. Fe recoveries (%) of the reverse flotation concentrates by different pine oil and water glass dosages while diesel 15000 g/ton

Table 4.4. Analysis of variance for the Fe recoveries of the concentrates

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	965,78	9	107,31	4,81	0,0493	significant
A-Diesel	313,32	1	313,32	14,04	0,0133	
B-Pine oil	108,95	1	108,95	4,88	0,0782	
C-Water glass	57,45	1	57,45	2,57	0,1696	
AB	4,35	1	4,35	0,1951	0,6772	
AC	40,17	1	40,17	1,80	0,2375	
BC	71,35	1	71,35	3,20	0,1338	
A^2	182,89	1	182,89	8,19	0,0353	
B^2	16,87	1	16,87	0,7556	0,4245	
C^2	144,07	1	144,07	6,45	0,0519	
Residual	111,62	5	22,32			
Lack of Fit	90,44	3	30,15	2,85	0,2707	not significant
Pure Error	21,18	2	10,59			
Cor Total	1077,40	14				

Table 4.5. Fit statistics for the Fe recoveries of the concentrates

Std. Dev.	4,72	R^2	0,8964
Mean	68,97	Adjusted R^2	0,7099
C.V. %	6,85	Predicted R^2	-0,3873
		Adeq Precision	8,1609

After the reverse flotation experiments which were conducted according to "Box-Behnken" experimental design, by the help of the Figure 4.30, Figure 4.31 and Figure 4.32 which were formed by means of the "Design Expert" computer program, it was observed that the Zn grades of concentrates tended to decrease as the water glass amount increased. By the help of the Figure 4.30 below, it could be observed that as the one of the pine oil or diesel quantity increased, the Zn grades of the concentrates increased. It could be also observed that excessive amount of pine oil usage could create an adverse effect. This kind of adverse effect might be beneficial in terms of reducing the Zn grades of the concentrates but it should not be forgotten that it was harmful for the process when it was looked at by a holistic approach. By the help of the 3 dimensional figures below, it was also observed that the effect of the water glass on the Zn grades of the concentrates were lesser than the effects of the other reagents when they were compared with each other. (Figure 4.30, 4.31, 4.32).

Figure 4.30. Zn grades (%) of the reverse flotation concentrates by different pine oil and diesel dosages while water glass 350 g/ton

Figure 4.31. Zn grades (%) of the reverse flotation concentrates by different diesel and water glass dosages while pine oil 225 g/ton

Figure 4.32. Zn grades (%) of the reverse flotation concentrates by different water glass and pine oil dosages while diesel 15000 g/ton

Table 4.6. Analysis of variance for the Zn grades of the concentrates

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0,1474	6	0,0246	3,84	0,0417	significant
A-Diesel	0,0384	1	0,0384	6,01	0,0398	
B-Pine oil	0,0012	1	0,0012	0,1818	0,6811	
C-Water glass	0,0244	1	0,0244	3,82	0,0864	
AB	0,0620	1	0,0620	9,70	0,0143	
AC	0,0027	1	0,0027	0,4266	0,5320	
BC	0,0187	1	0,0187	2,92	0,1260	
Residual	0,0511	8	0,0064			
Lack of Fit	0,0468	6	0,0078	3,63	0,2318	not significant
Pure Error	0,0043	2	0,0022			
Cor Total	0,1985	14				

Table 4.7. Fit statistics for the Zn Grades of the concentrates

Std. Dev.	0,0799	R^2	0,7424
Mean	1,20	Adjusted R^2	0,5492
C.V. %	6,68	Predicted R^2	-0,2093
		Adeq Precision	7,0976

Figure 4.33, Figure 4.34 and Figure 4.35 showed that when the diesel was stable, the combustible grades of the tailings increased as the water glass amount was increased. This circumstance was also valid for the pine oil adding. In the experiments, in which the water glass amount was stable, the combustible materials of the tailings increased while the pine oil amount was increased. According to Figure 4.34, it could be thought that if there wasn't sufficient amount of depressant in the medium, the combustible grades of the tailings would tend to decrease as the diesel amount increased; but if there was sufficient amount of depressant in the medium, combustible grades of the tailings would tend to increase. It was thought that this situation originated from that the ash content became more floatable by the help of increasing diesel quantities, and that the effect of the depressant suppressed this property of the diesel (Figure 4.33, 4.34, 4.35).

Figure 4.33. Combustible grade (%) of the reverse flotation tailings by different pine oil and diesel dosages while water glass 350 g/ton

Figure 4.34. Combustible grade (%) of the reverse flotation tailings by different water glass and diesel dosages while pine oil 225 g/ton

Figure 4.35. Combustible grade (%) of the reverse flotation tailings by different water glass and pine oil dosages while diesel 15000 g/ton

Table 4.8. Analysis of variance for the combustible grades of the tailings

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2854,82	9	317,20	3,91	0,0737	not significant
A-Diesel	76,69	1	76,69	0,9451	0,3756	
B-Pine oil	92,28	1	92,28	1,14	0,3350	
C-Water glass	867,78	1	867,78	10,69	0,0222	
AB	1,09	1	1,09	0,0135	0,9122	
AC	177,69	1	177,69	2,19	0,1990	
BC	949,26	1	949,26	11,70	0,0188	
A^2	1,06	1	1,06	0,0131	0,9134	
B^2	1,78	1	1,78	0,0219	0,8881	
C^2	678,29	1	678,29	8,36	0,0341	
Residual	405,73	5	81,15			
Lack of Fit	371,30	3	123,77	7,19	0,1245	not significant
Pure Error	34,42	2	17,21			
Cor Total	3260,55	14				

Table 4.9. Fit statistics for the combustible grades of the tailings

Std. Dev.	9,01	R^2	0,8756
Mean	50,76	Adjusted R^2	0,6516
C.V. %	17,75	Predicted R^2	-0,8458
		Adeq Precision	7,0210

Figure 4.36, Figure 4.37 and Figure 4.38 showed that combustible recovery percentages of the tailings generally tended to increase as the water glass and the pine oil amounts increased. When it comes to the combustible recovery percentages of tailings, it was observed that, water glass and pine oil perfectly worked together by the help of the decrements or the increments of their quantities. It was also observed that when the water glass and the pine oil quantities increased, the combustible recovery percentages of the tailings also increased. On the other hand, this recovery percentage values generally tended to increase as the diesel quantity increased. But it lasted until a certain point because high amounts of diesel affected in a negative way to the combustible recovery of tailings. The biggest gaining of recovery percentages of the tailings is observed between 20000 and 25000 g/ton diesel amounts according to figures below (Figure 4.36, 4.37, 4.38).

Figure 4.36. Combustible recovery (%) of the reverse flotation tailings by different pine oil and diesel dosages while water glass 350 g/ton

Figure 4.37. Combustible recovery (%) of the reverse flotation tailings by different water glass and diesel dosages while pine oil 225 g/ton

Figure 4.38. Combustible recovery (%) of the reverse flotation tailings by different water glass and pine oil dosages while diesel 15000 g/ton

Table 4.10. Analysis of variance for the combustible recoveries of the tailings

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4365,44	9	485,05	5,48	0,0378	significant
A-Diesel	935,97	1	935,97	10,57	0,0227	
B-Pine oil	927,84	1	927,84	10,48	0,0230	
C-Water glass	700,90	1	700,90	7,92	0,0374	
AB	15,99	1	15,99	0,1806	0,6885	
AC	1,74	1	1,74	0,0197	0,8939	
BC	111,44	1	111,44	1,26	0,3129	
A^2	1489,10	1	1489,10	16,82	0,0093	
B^2	48,14	1	48,14	0,5437	0,4940	
C^2	129,08	1	129,08	1,46	0,2813	
Residual	442,71	5	88,54			
Lack of Fit	373,39	3	124,46	3,59	0,2254	not significant
Pure Error	69,32	2	34,66			
Cor Total	4808,15	14				

Table 4.11. Fit statistics for the combustible recoveries of the tailings

Std. Dev.	9,41	R^2	0,9079
Mean	66,04	Adjusted R^2	0,7422
C.V. %	14,25	Predicted R^2	-0,2750
		Adeq Precision	7,7289

When the Figure 4.39, the Figure 4.40 and the Figure 4.41 was looked at, it could be observed that the ash grades of the tailings generally tended to decrease as the water glass and the pine oil amounts increased. In Figure 4.40 the effect of the change of the water glass quantities could be observed when the pine oil quantity was stable. On the other hand, due to the adverse effect which occurred when both of the water glass and the pine oil were increased to high amounts simultaneously, it was thought that in high amounts, one of them might have partially prevented the effects of the other one. In 2017, Koca and their colleagues obtained a figure which had similar fluctuation and is similar to Figure 4.41 (Koca et al. 2017). The ash percentages of the tailings generally tended to decrease as the diesel amount decreased. It was understood from the declination of the graph which was in the figure with diesel quantities, the effect of the diesel amounts on the ash percentage results was quite lesser compared to the effect of the water glass amounts or the pine oil amounts. (Figure 4.39, 4.40, 4.41).

Figure 4.39. Ash grade (%) of the reverse flotation tailings by different pine oil and diesel dosages while water glass 350 g/ton

Figure 4.40. Ash grade (%) of the reverse flotation tailings by different water glass and diesel dosages while pine oil 225 g/ton

Figure 4.41. Ash grade (%) of the reverse flotation tailings by different pine oil and water glass dosages while diesel 15000 g/ton

Table 4.12. Analysis of variance for the ash grades of the tailings

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2854,82	9	317,20	3,91	0,0737	not significant
A-Diesel	76,69	1	76,69	0,9451	0,3756	
B-Pine oil	92,28	1	92,28	1,14	0,3350	
C-Water glass	867,78	1	867,78	10,69	0,0222	
AB	1,09	1	1,09	0,0135	0,9122	
AC	177,69	1	177,69	2,19	0,1990	
BC	949,26	1	949,26	11,70	0,0188	
A^2	1,06	1	1,06	0,0131	0,9134	
B^2	1,78	1	1,78	0,0219	0,8881	
C^2	678,29	1	678,29	8,36	0,0341	
Residual	405,73	5	81,15			
Lack of Fit	371,30	3	123,77	7,19	0,1245	not significant
Pure Error	34,42	2	17,21			
Cor Total	3260,55	14				

Table 4.13. Fit statistics for the ash grades of the tailings

Std. Dev.	9,01	R^2	0,8756
Mean	49,24	Adjusted R^2	0,6516
C.V. %	18,29	Predicted R^2	-0,8458
		Adeq Precision	7,0210

4.2.5. The Optimum Flotation Result and Reuse of Water

By regaining and reusing the process water, the maximum marginal benefits of chemicals were wanted to be utilized and used amount of chemicals were radically decreased. The half amounts of the chemicals were added into the regained water at each stage. First 4 stages were done in 1000 g water medium at 15% solid ratio. At the 5th stage the concentrates which were obtained from the first 4 stages and were totally 241 g were gathered and transferred into cleaning flotation process. On account of this, the solid ratio, only in the 5th stage, was approximately 20%. In the first stage of the experiments, 2500 g/ton kerosene, 600 g/ton MIBC, and 600 g/ton water glass were used as chemicals, and the half amount of them were added into the regained water at each stage. By the help of reusing water again, the Fe grade for the optimum reverse flotation experiment result was 52.61%. Ash grade of the concentrate was quite high and 96.31%. Weight of the concentrate was equal to 22.10% of the total raw feeding material. (Figure 4.42).

Figure 4.42. Weight (%), ash grades (%) and Fe grades (%)

When the process was looked at as a whole, if obtaining process of the concentrate was taken into account as one stage amongst all of the stages of the last experiment series in which the process water reused and each one of the tailings is taken into account separately, Fe recovery of the concentrate would be 37.99%, and ash recovery of the concentrate would be 32.96%. The nearest values to the values which were obtained from concentrate were obtained from the results of the 5 numbered tailings approximately as a half of the values which were obtained from the results of the concentrate in terms of the Recovery values (%) and ash recoveries (Figure 4.43).

Figure 4.43. Fe recoveries (%) and ash recoveries (%) for 5 stages

When only the final stage was taken into account, the Fe recovery of the concentrate was 68.41% and the ash recovery of the concentrate was 67.58%. The Fe recovery and the ash recovery of the final tailings was approximately half of the Fe recovery and the ash recovery of the concentrate and they had values of 31.59% and 32.42% respectively. These data are important because by the help of these data, both Fe percentage of the concentrate and Fe recovery of the concentrate

could be evaluated together to understand the situation of how much being successful of the experiments (Figure 4.44).

Figure 4.44. Fe recoveries (%) and ash recoveries (%) at the last stage of the experiments

After the reverse flotation experiments which were conducted by the help of regaining and reusing the process water, the SiO_2 and the Al_2O_3 grades of the concentrates were found as 4.82% and 1.93% respectively. The ratio referred by Çilingir before was found as 0.44 (Table 4.14).

Table 4.14. SiO_2, Al_2O_3, CaO+MgO and K_2O+Na_2O grades (%) of the leach solids

	SiO_2(%)	Al_2O_3(%)	CaO+MgO(%)	K_2O+Na_2O(%)
Final concentrate	4.82	1.93	3.02	0.10
Final tailings	4.45	1.71	3.85	0.23
Tailings-4	4.28	2.04	3.57	0.44
Tailings-3	4.31	1.94	3.57	0.41
Tailings-2	4.34	1.93	3.38	0.44
Tailings-1	4.69	2.06	3.23	0.42

For the reverse flotation experiments, the Zn grade of the concentrate was 0.81% and it was above the limit referred by Bayat et al. (2009). The Pb grade of the concentrate was 0.37% and it was above the maximum tolerable limit which is 0.05%. The S grade of the concentrate was 0.08%. This value was between 0.15% and 0.35% limits. It meant that this material could be fed into blast furnace with coke which contains more than 2% S only when the S percentage of the material taking into account. For 5 numbered tailings, 4 numbered tailings, 3 numbered tailings, and 2 numbered tailings this situation was the same. But the S of the 1 numbered tailings was found as 0.37%. This situation meant that it could be only used with the coke which contains less than 2% S only when the S percentages taking into account. The Mn grade of the concentrate was 0.64%. This value was not suitable for the production of grey pig iron but it was between 0.5% and 1.2% and it was suitable for production of the Manganese steel only given the percentage of the Mn of the material. There was also titanium but it was below the detection limits (Table 4.2).

Cu, P, Cr, and V grades of the concentrate were investigated. Percentages of these materials were below the detection limits. Ni or As could not be detected. It was thought that they would not create a risk for the process (Table 4.15).

Table 4.15. Zn, Pb, S, Mn, Ti, Cu, P, Cr, and V grades (%) of the concentrates

	Zn	Pb	S	Mn	Ti	Cu	P	Cr	V
Final concentrate	0.81	0.37	0.08	0.64	0.12	0.04	0.04	0.01	0.02
Final tailings	0.89	0.35	0.17	0.48	0.12	0.03	0.04	0.01	0.01
Tailings-4	0.94	0.33	0.49	0.35	0.11	0.03	0.04	0.01	0.01
Tailings-3	0.97	0.33	0.52	0.31	0.11	0.02	0.04	0.01	0.01
Tailings-2	1.04	0.32	0.52	0.28	0.10	0.02	0.02	0.01	0.01
Tailings-1	1.07	0.32	0.54	0.27	0.10	0.02	0.02	BDL	0.01

Table 4.16. Obtained results and the requirements for optimum flotation concentrate

	Results	The Requirements
Fe grade	52.61%	The minimum limit: 50%.
SiO_2 grade	4.82%	The maximum limit: 5%.
Al_2O_3 grade	1.93%	The maximum limit: 3.5%.
The ratio in formula 1.1	0.44	The minimum required: 1.
S grade	0.08%	The maximum limit: 0.35% or 1%.
Cu grade	0.04%	The maximum limit: 0.06%.
Pb grade	0.37%	The maximum limit: 0.05%.
Mn grade	0.64%	The maximum limit to produce grey pig iron: 0.2%.
Zn grade	0.81%	The maximum limit: 0.03%.

4.3. Results of Acid Leaching Experiments and Discussions

Leaching efficiencies of different types of acids were compared through years by a great number of researchers. In leaching of Zn, it is found that hydrochloric acid and sulfuric acid were more effective than other types of acids (Ajiboye et al., 2019). In the light of such information, one of these acids was chosen and the leaching experiments were implemented to the feeding material. At first, with the 6 molar 100 milliliter hydrochloric acid solution, 10 g feeding material was leached at the 300 rpm stirring speed for 90 min. Conditions of this experiment were chosen as mean point of the conditions for the experiments. Then, the paramaters such as molarity, time and stirring speed were changed, respectively. While liquid part accepted as waste material, solid part accepted as concentrate.

4.3.1. Effect of Time

To understand effect of time on the leaching process experiments were conducted. Ceteris paribus, time was changed as 30, 60, 90, 120 and 150 min, respectively. After that, chemical analyses were implemented to the concentrates.

The leach efficiencies of the experiments changed between 7.54% and 49.88% for pure Zn elements. For 30 min time period, the value of the acid leaching efficiency as regards to the Zn elements was 7.54%. When this time interval extended to 60 min, this value changed to 28.72%. For 90 min leaching duration, the acid leaching efficiency was 40.75%. When the time interval of the reverse flotation experiments was arranged as 120 min, acid leaching efficiency was 46.42%. Finally, the value of 49.88% was obtained by means of 150 min of acid leaching of the raw feeding material which was blast furnace flue dusts in terms of the Zn elements. This data demonstrated that as time interval expanded, the acid leaching efficiency in terms of the Zn elements in the feeding material increased (Figure 4.45).

Figure 4.45. Leach efficiency (%) for Zn by different time durations

At the results of the leaching experiments, it could be observed that together with the extending time intervals, the losses of the Fe elements increased. On the grounds of this situation, the remained Fe quantities in the concentrates decreased in time. For 30 min the remained Fe grade of the concentrate was 71.18%. When the time was 60 min, the remained Fe grade of the concentrate was 60.03%. When the time was extended as 90 min, the remained Fe in the concentrates was 56.12%. For 120 min, this value was 51.87%. When the time interval was 150 min, the remained Fe grade of the concentrate was found as 47.90%. It was observed by the help of these data that the remained Fe grades of the concentrates changed between 71.18% and 47.90% as regards to time intervals which were between 30 and 150 min time intervals (Figure 4.46).

For 30 min, the weight of the concentrate was 70%, the ash grade of the concentrate was 54.52%, and the Fe grade of the concentrate was 30.47%. For 60 min, the weight of the concentrate was 63%, the ash grade of the concentrate 52.20%, and the Fe grade of the concentrate was 28.56%. When it was looked at concentrates that were obtained after 90 min, 120 min, and 150 min of time intervals, it is observed that these values were continuing to decrease increasingly.

For 90 min, the weight of the concentrate was 60%, the ash grade of the concentrate was 51.63%, and the Fe grade of the concentrate was 28.03%. For 120 min, the weight of the concentrate was 58%, the ash grade of the concentrate was 48.30%, and the Fe grade of the concentrate was 26.80%. For 150 min, the weight of the concentrate was 55%, the ash grade of the concentrate was 47.65%, and the Fe grade of the concentrate was 26.10% (Figure 4.47).

After the experiments, the SiO_2 grades were below the 5% limit. When it comes to Al_2O_3, it was observed that the Al_2O_3 grades of the concentrates changed between 1.64% and 1.43%. These values were 1.45% and 1.43% for 120 and 150 min acid leaching processes respectively. When it was calculated at the ratio of (Cao+MgO)(%)/(SiO_2+Al_2O_3)(%), the result obtained as 0.26 for the experiments which were conducted by being changed of the time (Table 4.17).

Figure 4.46. Remained Fe amounts (%) in terms of weight in the leach solids, compared to the beginning of the tests by different time durations

Figure 4.47. Weight (%), ash grades (%) and Fe grades (%) of the leach solids by different time durations

Table 4.17. SiO_2, Al_2O_3, CaO+MgO and K_2O+Na_2O grades (%) of the leach solids by different time durations

	SiO_2(%)	Al_2O_3(%)	(CaO+MgO)(%)	(K_2O+Na_2O)(%)
30 min	4.31	1.64	1.57	0.32
60 min	4.12	1.57	1.50	0.30
90 min	4.08	1.55	1.49	0.30
120 min	3.82	1.45	1.39	0.28
150 min	3.76	1.43	1.37	0.28

After 30 min, the Zn grade of the concentrate was 0.08%. When the time was 60 min, this value was 0.07%. In the results of the experiments which were continued until 90 min this value was 0.06% and this value was above the 0.03% level to which Bayat et al. (2009) referred previously. For 120 and 150 min this value hardly changed. The Pb grades of the concentrates changed between 0.32%

and 0.27% and they were above the 0.05% maximum limit. The S grades of the concentrates varied between 0.60% and 0.53%. These values were above the 0.15-0.35% limits and they were below the 0.75-1.00% limits. It could be concluded that the concentrates could be used with the coke which contains between 0.5-2% S. When it was looked at the Mn grades of the concentrates, it could be observed that the value of them changed between 0.11% and 0.12%. These values were below the 0.2 percentage limit and the concentrates were suitable for the production of the grey pig iron in terms of the Mn percentages. Ti was below the detection limits (Table 4.18).

Cu, P, Cr, Ni, As, and V grades of the concentrates were investigated. Percentages of these materials were below the detection limits. Ni could not detected. It was thought that they would not create a risk for the process (Table 4.19).

Table 4.18. Zn, Pb, S, Mn and Ti grades (%) of the leach solids by different time durations

	Zn(%)	Mn(%)	Ti(%)	Pb(%)	S(%)
30 min	0.08	0.12	0.13	0.32	0.60
60 min	0.07	0.12	0.13	0.31	0.58
90 min	0.06	0.11	0.13	0.28	0.55
120 min	0.06	0.11	0.12	0.28	0.55
150 min	0.06	0.11	0.12	0.27	0.53

Table 4.19. Cu, P, Cr, As, and V grades (%) of the leach solids by different time durations

	Cu(%)	P(%)	Cr(%)	As(%)	V(%)
30 min	0.03	0.02	0.01	0.01	0.02
60 min	0.03	0.02	0.01	0.01	0.01
90 min	0.03	0.02	0.01	0.01	0.01
120 min	0.03	0.02	0.01	0.01	0.01
150 min	0.03	0.02	0.01	0.01	0.01

4.3.2. Effect of Molarity

To understand effect of molarity on the leaching process, experiments were conducted. Ceteris paribus, molarity was changed as 4, 5, 6, 7 and 8 molars, respectively. After that, chemical analyses were implemented to the concentrates.

In this section of the study, the leaching process efficiencies according to the amount of the solved Zn were investigated in detail. It could be observed that the Zn efficiencies of the acid leaching processes increased, as the molar concentrations increased. For 4 molar concentration, the leaching efficiency for Zn was 11.48%. For 5 molar concentration, this value was 18.18%. 40.75% value was obtained at the end of the experiments which was conducted in a 6 molar medium. This value increased 48.76% for 7 molar concentration. When the experiments conducted in 8 molar medium, 61.69% was obtained as the value of the Zn leaching efficiency (Figure 4.48).

Figure 4.48. Leach efficiency (%) for Zn by different molar concentrations

The remained Fe grades in the concentrates were investigated in detail according to the time. It was observed that remained Fe from the feeding material to the concentrates changed between 86.59% and 37.70%. It was also observed that as the molar concentrations increased, the remained Fe percentages to the concentrates radically decreased. As passing from 4 molar concentration to 5 molar concentration, it was seen that the remained Fe in the concentrates decreased from 86.59% to 70.68%. This decrement continued at the result of the experiments which were conducted with 6 molar concentration and the value was found as 56.12%. For medium which formed with 7 molar concentration, the obtained value was 51.84 %. When the experiments which were in 8 molar medium was conducted, the value was 37.70% (Figure 4.49).

When it was looked at the results of the experiments, it was observed that by being changed of molar concentration, the obtained weights changed between 73% and 47%. At the same time, the obtained ash values changed between 55.94% and 45.66%, and the obtained Fe values changed 31.27% and 24.04%. For 4 molar, Fe of the concentrate was 31.27%. For 5 molar concentration, his value was 30.26%. When molar concentration was 6, the Fe grades of the concentrates

28.03%. For 7 molar medium, this value was found as 26.79%. After the experiment which conducted in 8 molar medium, the Fe percentage of the concentrate was detected as 24.04% (Figure 4.50).

When the SiO_2, the Al_2O_3, the CaO, the MgO grades of the concentrates were looked at, it was observed that the SiO_2 grades of the concentrates were below the 5% maximum limit, and changed between 4.42% and 3.61% for the range of 4 and 8 molar concentrations. For 4 molar, 5 molar and 6 molar experiments, the Al_2O_3 grades were below the 3.5% limit which is the maximum tolerable limit as long as the $(CaO+MgO)/(SiO_2+Al_2O_3)$ ratio is more than 1. When the ratio that referred before by Çilingir (1996) was looked at, it was observed that the value of the ratio was 0.26 for all of the experiments which were conducted by being changed of their molar concentrations, and it was understood that this value was not also above 1 (Table 4.20).

Figure 4.49. Remained Fe amounts (%) in terms of weight in the leach solids, compared to the beginning of the tests by different molarities

Figure 4.50. Weight (%), ash grades (%) and Fe grades (%) of the leach solids by different molar concentrations

Table 4.20. SiO_2, Al_2O_3, CaO+MgO and K_2O+Na_2O grades (%) of the leach solids by different molar concentrations

	SiO_2(%)	Al_2O_3(%)	(CaO+MgO)(%)	(K_2O+Na_2O)(%)
4M	4.42	1.68	1.61	0.32
5M	4.26	1.62	1.55	0.31
6M	4.08	1.55	1.49	0.30
7M	3.91	1.48	1.43	0.29
8M	3.61	1.37	1.32	0.26

The Zn grade of the concentrate was 0.08% for 4 molar, and 0.07% for 5 molar concentrations. For 6 molar medium, this value was 0.06%. For 7 and 8 molar mediums, changes in terms of the Zn grades of the concentrates were scarcely seen compared to the 6 molar medium. Zn was 0.05% for 8 molar concentration. The grades of the concentrates in Pb were above the 0.05% value and as the molar concentration was increased, they changed between 0.36% and

0.23%. As the concentration increased from 4 molar to 8 molar, the S grade of the concentrate was found 0.60% as the maximum and it was found 0.51% as the minimum respectively. These values were above the 0.15-0.35% limits and they were below the 0.75-1.00% limits. It could be concluded that the concentrates could be used with the coke which contains between 0.5-2% S. The Mn grades were below the 0.2% limit for all of the tried molar concentrations and were suitable for the production of the grey pig iron in terms of Mn grades. Ti was below the detection limits (Table 4.21).

Cu, P, Cr, Ni, As, and V grades of the concentrates were investigated. Percentages of these materials were below the detection limits. Ni could not detected. It was thought that they would not create a risk for the process (Table 4.22).

Table 4.21. Zn, Pb, S, Mn and Ti grades (%) of the leach solids by different molar concentrations

	Zn(%)	Pb(%)	S(%)	Mn(%)	Ti(%)
4M	0.08	0.36	0.60	0.12	0.14
5M	0.07	0.34	0.57	0.12	0.13
6M	0.06	0.28	0.55	0.11	0.13
7M	0.06	0.24	0.52	0.11	0.12
8M	0.05	0.23	0.51	0.10	0.11

Table 4.22. Cu, P, Cr, As and V grades (%) of the leach solids by different molar concentrations

	Cu(%)	P(%)	Cr(%)	As(%)	V(%)
4M	0.03	0.02	0.01	0.01	0.01
5M	0.03	0.02	0.01	0.01	0.01
6M	0.03	0.02	0.01	0.01	0.01
7M	0.03	0.02	0.01	0.01	0.01
8M	0.02	0.02	0.01	0.01	0.01

4.3.3. Effect of Stirring Speed

To understand effect of stirring speed on the leaching process experiments were conducted. Ceteris paribus, stirring speed was changed as 100, 200, 300, 400 and 500 rpm (rounds per min), respectively. After that, chemical analyses were implemented to the concentrates.

When acid leaching efficiencies was looked at, it was observed that by means of the increments of the stirring speed from 100 rpm to 500 rpm, the acid leaching efficiency increased from 9.29% to 57.20%. While for the experiments which were conducted with 100 rpm stirring speed the acid leaching efficiency as regards to Zn was 9.29%, for the experiments which were conducted with 200 rpm stirring speed this value was 27.72%. For 300 rpm stirring speed, the acid leaching efficiency in terms of Zn was 40.75%. The leaching efficiency value which was 48.68% was obtained for the experiments which were conducted with 400 rpm stirring speed. When the stirring speed was 500 rpm, the acid leaching efficiency in terms of Zn was 57.20% (Figure 4.51).

Figure 4.51. Leach efficiency (%) for Zn by different stirring speeds

Remained Fe percentages after the acid leaching processes decreased as stirring speed increased. When the stirring speed 100 rpm the remained Fe was maximum as 73.71%. The value which was 65.56% was obtained after the experiments which were conducted with 200 rpm stirring speed. For 300 rpm stirring speed, the remained Fe was 56.12%. When the stirring speed reached 400 rpm, this value became 52.61%. For 500 rpm stirring speed, the remained Fe in the concentrate was 42.09% (Figure 4.52).

For 100 rpm stirring speed, it was observed that the weight of the concentrate was 72%, ash grade of the concentrate was 54.89%, and the Fe grade of the concentrate was 30.68%. For 200 rpm stirring speed, these values were 66%, 53.68%, and 29.77% respectively. For 300 rpm stirring speed, the weight of the concentrate was 60%, the ash grade of the concentrate was 51.63%, and the Fe grade of the concentrate was 28.03%. When the stirring speed reached 400 rpm, the weight of the concentrate was 57%, the ash grade of the concentrate was 50.44 %, the Fe grade of the concentrate was 27.66%. These values were obtained for the 500 rpm stirring speed as 48%, 49.95%, and 26.28% respectively (Figure 4.53).

Figure 4.52. Remained Fe amounts (%) in terms of weight in the leach solids, compared to the beginning of the tests by different stirring speeds

Figure 4.53. Weight (%), ash grades (%) and Fe grades (%) of the leach solids by different stirring speeds

For 100 rpm stirring speed, the SiO_2 grade of the concentrate was 4.89%. This value was the highest level which was obtained from the experiments in terms of the stirring speed and it was below the maximum level which is 5%. At the

results of the other experiments which were conducted with 200, 300, 400, and 500 rpm these values decreased more. Al_2O_3 grades of the concentrates changed between 1.65% and 1.50% depending on the stirring speed. These value range was below the 3.5% which is the maximum tolerable limit as long as the ratio which were referred before is above 1 (Çilingir, 1996). This ratio was found as 0.25 for the experiments which were conducted with 100 rpm stirring speed and it was found as 0.26 for the experiments which were conducted with different stirring speeds except for 100 rpm (Table 4.23).

When Zn grades was looked at, it was observed that for 100 rpm, the Zn grade of the concentrate was found as 0.08%. When the stirring speed was 200 rpm, this value was obtained as 0.07%. For 300, 400, and 500 rpm, the value of the Zn grades of the concentrates hardly changed, they were approximately 0.06%, and they were above the 0.03% value to which referred before (Bayat et al. 2009). The Pb grades of the concentrates changed between 0.28% and 0.33%. These values were above 0.05% the maximum limit. The S grades of the concentrates were found between 0.54% and 0.60%. These values were above the 0.15-0.35% limits and they were below the 0.75-1.00% limits. It could be concluded in terms of this that the concentrates could be used with the coke which contains between 0.5% and 2% S. The Mn grades were below the 0.2% limit for all of the tried stirring speeds and they were convenient for the production of the grey pig iron in terms of Mn grades. Ti was below the detection limits (Table 4.24).

When it was looked at the Cu, P, Cr, As, and the V percentages of the concentrates it was observed that these materials were below the detection limits. Ni could not detected. It was thought that they would not create a risk for the process (Table 4.25).

Table 4.23. SiO_2, Al_2O_3, CaO+MgO and K_2O+Na_2O grades (%) of the leach solids by different stirring speeds

	SiO_2(%)	Al_2O_3(%)	(CaO+MgO)(%)	(K_2O+Na_2O)(%)
100 rpm	4.89	1.65	1.58	0.32
200 rpm	4.24	1.61	1.55	0.31
300 rpm	4.08	1.55	1.49	0.30
400 rpm	3.98	1.51	1.45	0.29
500 rpm	3.95	1.50	1.44	0.29

Table 4.24. Zn, Pb, S, Mn and Ti grades (%) of the leach solids by different stirring speeds

	Zn(%)	Pb(%)	S(%)	Mn(%)	Ti(%)
100 rpm	0.08	0.33	0.60	0.12	0.13
200 rpm	0.07	0.31	0.59	0.12	0.13
300 rpm	0.06	0.28	0.55	0.11	0.13
400 rpm	0.06	0.28	0.54	0.11	0.12
500 rpm	0.06	0.28	0.54	0.11	0.12

Table 4.25. Cu, P, Cr, As and V grades (%) of the leach solids by different stirring speeds

	Cu(%)	P(%)	Cr(%)	As(%)	V(%)
100 rpm	0.03	0.02	0.01	0.01	0.01
200 rpm	0.03	0.02	0.01	0.01	0.01
300 rpm	0.03	0.02	0.01	0.01	0.01
400 rpm	0.03	0.02	0.01	0.01	0.01
500 rpm	0.03	0.02	0.01	0.01	0.01

4.3.4. Effect of Temperature

Acid leaching processes were conducted under different temperatures to investigate how the temperature affects to the percentages of the materials in the concentrates. For the experiments, the temperature values which were 24 ±5, 34 ±5, 44 ±5, 54 ±5, and 64 ±5 °C were chosen. After that, the acid leaching experiments were conducted.

The leaching efficiencies in terms of the Zn were investigated for 5 different temperature values. After the experiments, it was found that as the temperature of the process increased, the leaching efficiencies in terms of Zn increased. In the room temperature which was 24 °C, the acid leaching efficiency as regards to Zn was 40.75%. When the temperature was 34 °C, the leaching efficiency for Zn was 47.49%. For 44 °C, the value of the acid leaching efficiency was obtained as 53.61%. 58.05% acid leaching efficiency value was found for 54 °C temperature. When the temperature of the acid leaching process was 64 °C temperature, it was observed that the leaching efficiency as regards to Zn was 64.76% (Figure 4.54).

Figure 4.54. Leach efficiency (%) for Zn by different temperatures

The formed graphic for the remained Fe percentages according to different temperatures was more parabolic when it was compared to the graphics of the other leaching experiments which were conducted with the other different variable parameters which were stirring speed, molar concentration, and time. This situation demonstrated that the effect of the temperature was quite huge on the remained Fe percentages of the concentrates. For 24 °C, the remained Fe grade of the concentrate was 56.12%. When the temperature was 34 °C, this value decreased to 41.77%. 32.09% value was obtained for 44 °C. When the temperature was 54 °C, the remained Fe grade of the concentrate was 26.24%. Finally, 24.22% value was obtained as the remained Fe grade of the concentrate at 64 °C (Figure 4.55).

For the room temperature, the weight of the concentrate was 60%. For 34, 44, 54, and 64 °C temperatures the weight of the concentrates were 58%, 55%, 52%, and 50% respectively. As the temperature increased, the ash percentages of the material changed from 51.63% to 36.85%. Fe grades of the concentrates decreased from 28.03% to 14.52% as the temperature increased (Figure 4.56).

Figure 4.55. Remained Fe amounts (%) in terms of weight in the leach solids, compared to the beginning of the tests by different temperatures

Figure 4.56. Weight (%), ash grades (%) and Fe grades (%) of the leach solids by different temperatures

As the temperature increased, the SiO_2 grades of the concentrates increased from 4.08% to 4.79%. For 24 °C, the SiO_2 grade of the concentrate was 4.08%. For 34 °C, the SiO_2 grade of the concentrate was 4.22%. For 44 °C, the SiO_2 grade of the concentrate was 4.28%. For 54 °C, the SiO_2 grade of the concentrate was 4.47%. When temperature was 64 °C, the SiO_2 grade of the concentrate was 4.79%. All of these values was below the 5% limit. As the temperature increased, the Al_2O_3 grades of the concentrates increased from 1.55% to 2.76%. On condition that the ratio which was mentioned by Çilingir (1996) before is above 1, all of these Al_2O_3 values were below the maximum tolerable 3.5% limit. The ratio changed between 0.13 and 0.26. This value was below 1 again. (Table 4.26).

After the implementation of the changes of the temperature to the acid leaching process it was found that the obtained minimum value for the Zn grades of the concentrates were 0.04% and it was above the 0.03% limit which was mentioned by Bayat et al. (2009) before. For 24 °C and 34 °C, the Zn grades of the concentrates were 0.06%. For 44 °C and 54 °C, Zn grades of the concentrates were 0.05%. When temperature was 64 °C, the Zn grade of the concentrate decreased to 0.04%. When the Pb grades of the concentrates were looked at, it was observed that the Pb grades of the concentrates decreased from 0.28% to 0.14% as the temperature increased. These values were above 0.05% limit. The S grades of the concentrates increased from 0.55% to 0.78% as the temperature increased. These values were above the 0.15-0.35%, and below the 0.75-1.00% limits. It could be concluded that the concentrates could be used with the coke which contains between 0.5-2% S. For 54 °C and 64 °C, the S grades of the concentrates were between 0.75-1.00%. This situation meant that they could be used only with coke which contains less than 0.5% S. The Mn grades of the concentrates were below the 0.2% limit for all of the tried temperatures and they were convenient for the production of the grey pig iron in terms of Mn percentages (Table 4.27).

Cu, P, Cr, Ni, As, Ti, and V grades of the concentrates were investigated. Percentages of these materials in the concentrates were below the detection limits. It was thought that they would not create a risk for the process (Table 4.28).

Table 4.26. SiO_2, Al_2O_3, CaO+MgO and K_2O+Na_2O grades (%) of the leach solids by different temperatures

	SiO_2(%)	Al_2O_3(%)	(CaO+MgO)(%)	(K_2O+Na_2O)(%)
24 °C	4.08	1.55	1.49	0.30
34 °C	4.22	1.78	1.28	0.26
44 °C	4.28	1.95	1.05	0.23
54 °C	4.47	2.42	1.01	0.22
64 °C	4.79	2.76	1.00	0.21

Table 4.27. Zn, Pb, S, Mn and Ti grades (%) of the leach solids by different temperatures

	Zn(%)	Pb(%)	S(%)	Mn(%)	Ti(%)
24 °C	0.06	0.28	0.55	0.11	0.13
34 °C	0.06	0.25	0.60	0.08	0.11
44 °C	0.05	0.18	0.65	0.05	0.10
54 °C	0.05	0.16	0.74	0.04	0.09
64 °C	0.04	0.14	0.78	0.03	0.09

Table 4.28. Cu, P, Cr, As, and V grades (%) of the leach solids by different temperatures

	Cu(%)	P(%)	Cr(%)	As(%)	V(%)
24 °C	0.03	0.02	0.01	0.01	0.01
34 °C	0.02	0.02	0.01	0.01	0.01
44 °C	0.02	0.01	0.01	0.01	0.01
54 °C	0.02	0.01	0.01	0.01	0.01
64 °C	0.02	0.01	0.01	0.01	0.01

The acid leaching experiment which were conducted with 6 molar concentration, 300 rpm stirring speed, 24 ±5 °C temperature, and 90 min time duration was accepted as optimum for the leaching process. The obtained results and the minimum requirements which were needed to be obtained were given below (Table 4.29).

Table 4.29. Obtained results and the requirements for the optimum leaching experiment

	Results	The Requirements
Fe grade	28.03%	The minimum limit: 50%.
SiO_2 grade	4.08%	The maximum limit: 5%.
Al_2O_3 grade	1.55%	The maximum limit: 3.5%.
The ratio in formula 1.1	0.26	The minimum limit: 1.
S grade	0.55%	The maximum limit: 0.35% or 1%.
Cu grade	0.03%	The maximum limit: 0.06%.
Pb grade	0.28%	The maximum limit: 0.05%.
Mn grade	0.11%	The maximum limit to produce grey pig iron: 0.2%.
Zn grade	0.06%	The maximum limit: 0.03%.

4.4. Comparison of the Results

After the experiments, it was observed that the magnetic separation experiments did not gave satisfactory results. The reverse flotation experiments gave favourable results in terms of increasing the Fe grades. For the reverse flotation experiments, the concentrate which was acknowledged as optimum was obtained from the experiments which were conducted by the help of reuse of the process water. The acid leaching experiments gave favourable results in terms of decreasing the grades of the undesired materials. For the acid leaching experiments, the concentrate which was acknowledged as optimum was obtained from the experiment which were conducted with 90 minute time duration, 6 molar medium, 300 rpm stirring speed, 24 ±5 °C temperature. In order to compare optimum flotation and acid leaching results, related table was given below (Table 4.30).

Table 4.30. Comparison of the reverse flotation and acid leaching according to the requirements

	Optimum results for the reverse flotation	Optimum results for the acid leaching	The Requirements
Fe grade	52.61%	28.03%	The minimum limit: 50%.
SiO_2 grade	4.82%	4.08%	The maximum limit: 5%.
Al_2O_3 grade	1.93%	1.55%	The maximum limit: 3.5%.
The ratio in formula 1.1	0.44	0.26	The minimum limit: 1.
S grade	0.08%	0.55%	The maximum Limit: 0.35% or 1%.
Cu grade	0.04%	0.03%	The maximum limit: 0.06%.
Pb grade	0.37%	0.28%	The maximum limit: 0.05%.
Mn grade	0.64%	0.11%	The maximum limit to produce grey pig iron: 0.2%.
Zn grade	0.81%	0.06%	The maximum limit: 0.03%.

5. CONCLUSIONS AND PROPOSALS

In order to understand better the recyclability properties of the iron minerals in the blast furnace flue dusts; while three different methods were implemented which were the magnetic separation method, the reverse flotation method, and the acid leaching method, a great number of different experiments were conducted. Then the values of the results of the experiments were calculated and they rendered graphs. By the help of the graphs, whether the obtain results suitable for the desired standard values or not tried to be understood. After that process, some conclusions obtained. In this part of the study, these conclusions were stated and in the light of these conclusions some proposals were advised.

After the magnetic separation experiments, it was seen that Fe percentages of the concentrate decreased, as the magnetic field intensity increased. For 0.25 Tesla magnetic field intensity, the Fe grade of the concentrate was 41.29%. At this level, the Fe recovery of the concentrate was 63.03% and the ash grade of the concentrate was 68.72%. It was observed that when the magnetic field intensity increased to 0.5 Tesla, the Fe of the concentrate decreased to 40.39% and it continued to decrease until 36.50% value as the magnetic field intensity increased towards 1.5 Tesla. At the same time, the Fe recoveries of the concentrates increased from 63.03% to 88.25%. Ash values also increased from 68.72% to 73.45%. The Zn grades of the concentrates decreased from 1.22% to 1.04% when magnetic field intensity increased from 0.25 Tesla towards 1.5 Tesla. The magnetic separation experiment which were conducted with 0.25 Tesla was chosen as optimum for the magnetic separation experiments. After the magnetic separation experiments, satisfactory results could not be obtained in terms of both increasing the grades of the desired materials and decreasing the grades of the undesired materials.

After the reverse flotation experiments, kerosene as the collector, MIBC as the foaming agent, and water glass as depressant were chosen as the most effective

chemical agents for the reverse flotation process. By the help of the reuse of water with the most effective reagents as kerosene, MIBC, and water glass, the Fe grades of the concentrates could be increased to 52.61%. At the same time, ash grade was 96.31%. The Fe recovery (%) of the concentrate was 68.41%. The Zn grade of the concentrate was decreased to 0.81%. Due to this situation, the experiment which were conducted by reusing the process water was chosen as optimum for the flotation results. Flotation results were found partially successful in terms of increasing the desired materials.

The experiment which were conducted with 6 molar medium, 300 rpm stirring speed, 24 ±5 °C temperature, and 90 min time duration was chosen as optimum for the acid leaching experiments. When it comes to the acid leaching process, the acidic leaching agent solving the impurities also solved significant amount of the desired material such as iron. As dissolution of the undesired materials decreased their grades, dissolution of the desired materials increased automatically the grades of the undesired materials. Although this situation caused an adverse effect for the process, it was observed that the grades of the undesired materials tended to decrease. Owing to this situation, the acid leaching process was found partially successful in terms of decreasing undesired materials except for S.

When the processes was looked at collectively, it could be observed that the reverse flotation method was more effective than both of the magnetic separation and the leaching methods in terms of increment of the desired materials. The acid leaching method was more effective than both of the magnetic separation method and the reverse flotation method in terms of the removal of the undesired materials. In terms of both increment of the grades of the desired materials and decrement of the grades of the undesired materials, the magnetic separation method was between both of the acid leaching method and the reverse flotation method.

By the help of the data which were obtained from this study, it was observed that reverse flotation and acid leaching methods have different advantages and disadvantages when they were compared with each other. On the

purpose of being tried of utilizing different advantages of each one of them, being used of these methods in a row can be proposed.

Implementing of the magnetic separation method with lower magnetic field intensities, regaining of the elements from the acid leaching solution, and grinding the feeding material before the process may be also secondarily proposed.

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