Techniques for Iron Recovery from Chalcopyrite (CuFeS$_2$): A Review

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Abstract

To date there are limitations on commercial practices that aims directly at extracting Iron from chalcopyrite. This is because for years chalcopyrite has mostly been mined for copper and Iron discarded with slag. A technique called beneficiation that involves hydrometallurgical and pyro-metallurgical processes is applied on chalcopyrite to recover both Iron, copper and even Sulphur. During the process of beneficiation copper is separated from iron and tapped off as copper matte while iron exit the furnace in the form of Fayalite (Iron [II] silicate). Some new approaches have focused specifically at reducing Iron (II) silicate to element Iron for economic utilization. Such operations are done at temperatures of 1000+ °C. The recovered iron can be used as an alternative feed material to replace scrap steel in the steelmaking processes. This continued invention that aims at utilization of iron from chalcopyrite will be of economic value and at the same time addressing environmental associated with steelmaking using scrap. A Detailed review of techniques for processing chalcopyrite and methods for iron recovery from chalcopyrite were discussed. Methods that are found suitable in Iron recovery from chalcopyrite are the Direct reduction and Magnetic separation. A combination of the two methods is effective.

Keywords
Chalcopyrite, Fayalite, direct reduction, beneficiation, Magnetic separation

1. Introduction

Chalcopyrite is the name given to the copper iron sulphide mineral. Chalcopyrite is derived from the 2 Greek words “chalkos” and “pyrites” meaning copper and strike fire respectively (Baba et al, 2012). Appearing to be a brassy to gold mineral in color it also has distinct chemical, physical and structural properties. These properties includes; variation of valence states, non-magnetic and semi-conductor properties (Caircoss, 2004 & Vaughan et al, 2017). Although it contains Sulphur and reasonable to high amount of iron, mostly it has been mined for the world copper. Chalcopyrite ore is usually melted and the iron is discarded with the slag as Fayalite (2FeO.SiO$_2$) and or in the form of magnetite (Fe$_3$O$_4$) whereas the Sulphur can be removed as dilute sulfuric acid. It mixes with water solution and discarded as gypsum waste. Even though Sulphur is removed as waste, in hydrometallurgy it plays an indirect role during heap leaching technique as it helps in extraction of copper. In most chalcopyrite mining the main reason why Iron is not considered to be a metal of interest is because it’s available in large quantities from its ore(s) ‘giant deposit’ such as the banded iron formation and Kiruna-type ore deposits. Chalcopyrite ore is processed by a beneficiation technique to extract copper as copper matte and Iron removed as iron (II) silicate and processed further by reduction mechanisms. In beneficiation of chalcopyrite two known metallurgical processes can be applied namely pyrometallurgy and hydrometallurgy. In quest to achieve the highest possible concentrates of copper some researchers have concluded that hydrometallurgical processes are preferred over Pyrometallurgy because of low cost, high metal concentrate recovery and less environmental effects associated with it (Amstutz, 1961).
Pyrometallurgy of copper is a flash and shaft technology which involves roasting the mineral cake at high temperature under oxygen exposure whereas in hydrometallurgy chloride or sulfide leaching is incorporated to the mineral cake and metal are extracted from leach solutions. During beneficiation of chalcopyrite, first copper is separated from the mineral through smelting and the resulting iron tapped off the furnace in the form of iron (II) silicate and can be recovered reduction processes. In this paper the objective is to review methods/techniques that are used to recover iron from chalcopyrite. Such methods are the direct reduction and magnetic separation processes. This processes follows after recovery of copper through smelting or leaching techniques. In direct reduction the Iron(II) silicate that is tapped off the first beneficiation furnace flows into a separate furnace (reduction furnace). In the reduction furnace the iron (II) silicate is reduced to element iron by reacting with coke. CaO can be added to alter the operating temperature of the furnace and other additives such as Na$_2$CO$_3$ can also be introduced which acts as a catalyst to the reduction process of iron (II) silicate to iron (Cao et al, 2016).

2. Methodology

The study of iron ore and separation of Iron from fayalite and ores such as magnetite is a field that has been studied and discussed by many researchers and engineers (David 2017). Fayalite and magnetite forms can be a by product of chalcopyrite. According to AzoMining the first magnetic separator was invented by John Prince and used to separate iron from wolframite. Dworzanskowski et al has conducted research using a magnetic separator on Iron oxide copper-gold (IOCG) to recover element iron. The reduction or utilization of iron (II) silicate to element iron helps minimize economic losses and also reduce environmental pollution. (Li et al, 2013) investigated the recovery of iron from iron fayalite using a combination of deep reduction magnetic beneficiation using a coke powder containing carbon of 86 (wt%) as a reductant hence recovering iron of up to 96.21%. In attempts to directly recover iron from fayalite, Cheng at al pioneered a method for such recovery but there were no results reported on any iron recovery. Chen’s failure is supported by many literatures that suggest that Fayalite is considered hard to recover using conventional beneficiation technique (Cao et al, 2016). Reference is also made to Cao et al (2016) wherein a combination of 2 methods (Direct reduction and magnetic separation) was used to solve problems associated with the conventional routes hence optimizing recovery rates. Limitations of the two methods are covered in depth in the next chapters.

2.1 Pyrometallurgical processes

The separation of minerals of interest (valuables) can be separated from gangue materials through hydrometallurgical processes. The smelting of cakes of chalcopyrite to remove copper and separating gangue materials is a practice that has been going on for decades. The removal of copper as a first step in roasting process is known to be an important factor in environmental protection and also has economic benefits as supported by Ghosh et al (2012) study. Previous practices involved the use of a roster where chalcopyrite is heated with Silicon dioxide at elevated temperatures in oxygen atmospheres in a series of furnaces producing Copper (II) sulfate, Iron (II) Silicate and sulfur dioxide. Copper (II) sulfate is further reduced for extraction of copper. A contact process can be used to convert Sulphur dioxide to sulphuric acid while Iron (II) Silicate ((FeO SiO$_2$ or FeSO$_3$) melt is tapped off the furnace and further treated for extraction of iron.

Equation below shows the separation mechanisms of chalcopyrite to produce Cu$_2$S, FeO-SiO$_2$ and Sulphur dioxide during smelting process

$$2CuFeS_2(s) + 2SiO_2(s) + 4O_2(g) \rightarrow Cu_2S(s) + 2FeSiO_3(s) + 3SO_2(g)$$

Modern smelting practices are not much different from the roasting practices. In this practice chalcopyrite is subjected to high temperatures and oxygen pressure in a blast furnace (Baba et al, 2012). This process involves multiple steps. First the iron ore is separated from the copper ore (EQ 2) followed by addition of SiO$_2$ to convert the Iron Oxide produced during the First stage to Iron (II) Silicate (EQ 3) which is of lower density than other products hence floats on top the copper matte. Another reaction that can occur in parallel is the reaction of the produced troilite (FeS) with the added Silicon dioxide to produce additional iron (II) silicate under oxygen pressure conditions.
of the furnace (EQ 4). Calcine, limestone and silica are also added to increase the rate of reactions and also help the matte and iron (II) silicate to melt and flow at the bottom to be tapped out. The FeSiO₃ is further processed for extraction of iron. The above method is fuel consuming and to rectify such the new processes are calibrated be self-induced and other reactions from the 2nd step of the process can be carried out in a separate furnace to reduce the emissions of Sulphur dioxide (Yücel et al, 1997).

\[
2\text{CuFeS}_2(s) + 4\text{O}_2(g) \rightarrow \text{Cu}_2\text{S} + 2\text{FeO} + 2\text{SO}_2(g) \quad \text{EQ 2}
\]

\[
\text{FeO (l)} + \text{SiO}_2(s) \rightarrow \text{FeO-SiO}_2 \quad \text{EQ 3}
\]

\[
2\text{FeS} + 3\text{O}_2 + 2\text{SiO}_2 \rightarrow 2\text{FeO-SiO}_2 + 2\text{SO}_2(g) \quad \text{EQ 4}
\]

Figure 1 shows a typical compound resulting from a smelting process in separation of copper and iron to produce iron (II) silicate and additional compound CaMg.SiS₂ characterized by Hwang et al, (2018). The figure below proves that Iron (II) silicate can be tapped of with other gangue material that needs to be removed in the next reduction furnace.

Figure 1 XRD pattern of the fayalite (Hwang et al, 2018)

Hwang et al analysis on the sample was conducted using XRD and observed peculiar to amorphous phase of glass peaks. In most cases fayalite forms an oxide phase therefore Hwang et al found it necessary to also perform XRF analysis of the oxide hence analyzing most of the stable oxide phase composition ratios. The XRD pattern above shows that the compound resulting from smelting had more contents of fayalite and contents of diopside where observed. The findings did not rule out occurrences of other elements (gangue materials) as show by chemical analysis in table 1.0. The resulting compound from smelting as a copper-iron separation technique had Significant levels of Fe₂O₃ (38.51wt %). Li at el also conducted XRD and sample analysis of fayalite and found levels of Fe₂O₄ and FeO to be 13.17 wt % and 41.07 wt% respectively. Basically the constituents and weight % depends on the type and reactants used to separate chalcopyrite valuable elements from gangue materials. Another author (Fernández-Caliani et al, 2012) XRD analysis on products obtained during the Pyrometallurgical processing of chalcopyrite concentrates at the Huelva smelter (Spain) and found contents of feathery elongated crystals of Iron (II) Silicate (50-56 vol %) and delicate dendritic magnetite (27-34 vol %) occurring to have rims of ferrosilite (FeSiO₃).
Table 1. Chemical analysis of the fayalite [1]

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>38.51</td>
</tr>
<tr>
<td>SiO₂</td>
<td>21.17</td>
</tr>
<tr>
<td>CaO</td>
<td>16.25</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.75</td>
</tr>
<tr>
<td>ZnO</td>
<td>6.27</td>
</tr>
<tr>
<td>MgO</td>
<td>2.61</td>
</tr>
<tr>
<td>CuO</td>
<td>2.09</td>
</tr>
<tr>
<td>MnO</td>
<td>1.34</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.11</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.02</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.72</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.58</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Smelting of chalcopyrite in order to separate copper and iron can results in production of large quantities of Sulphur dioxide which can pollute the environment. This S0₄ need to be converted to sulphuric acid and extracted in liquid form. The smelters in this method can be costly to construct (Fuestenau et al, 2005).

2.2 Hydrometallurgy

In this technique copper-iron separation is done by means of aqueous processing using leaching agents. The technique is conducted at modest temperature and pressure. The copper is extracted as copper (II) sulphate while iron is collected as Iron (II) sulphate and can be further reduced to element iron by further reduction techniques. Hydrometallurgy has attracted a mass of commercial productions due to low operating costs. The practice involves crushing of mineral crystals to desired particle size and incorporation of leach solutions. Metals concentrates can then be extracted from leach solutions and processed further leaving the discard or gangue which can be processed further. The type of products in this technique usually depends on leaching agents. Leach agents used can be ferric and cupric chloride, ferric sulphate etc. Some authors have outline the problems associated with the storage and corrosiveness of chlorine hence its use as a leaching agent was restricted for a while (Ghosh et al, 2012). However, with development and new inventions that aims at manufacturing of corrosion resistant metals and alloy they seem to be a potential in use of chlorine as a leaching agent (Ekinci et al, 1998).

Equation 5 shows chalcopyrite subjected under leaching conditions to form Copper sulphate, Iron (II) sulphate etc. The experimentation was conducted by Jones et al (1999) when studying dissolution kinetics of chalcopyrite leaching under oxidizing acidic media. FeSO₄ can then be exposed to oxidizing conditions to ferric sulfate (equation 6) followed by further reactions for Iron extraction. This type of experimentation has been adopted since the 1960s and since then a lot of work had been (Baba et al,) pioneered the bioleaching of chalcopyrite in a stirred reactor tank.

\[
\begin{align*}
\text{CuFeS}_2 + \frac{4}{3} \text{NaNO}_3 + \frac{8}{3} \text{H}_2\text{SO}_4 & \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + \frac{2}{3} \text{H}_2\text{SO}_4 + 2\text{SO} + \frac{4}{3} \text{NO} + \frac{8}{3} \text{H}_2\text{O} \quad \text{EQ 5} \\
\text{FeSO}_4 + \frac{1}{3} \text{H}_2\text{SO}_4 + \frac{1}{4} \text{O}_2 & \rightarrow \frac{1}{2} \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \quad \text{EQ 6}
\end{align*}
\]

Sodium nitrate in equation 5 helps increase the rate constant of the system.

3. Methods for iron extraction from chalcopyrite

To this end it is understood that after beneficiation of chalcopyrite the fayalite (FeSiO₃) is mostly Iron rich (25-45wt %) as compared to other gangue materials (Lil et al, 2013). Few proposed techniques do not only recover the iron
and copper from chalcopyrite but also other valuable elements from gangue materials e.g. Hwang et al’s study was aimed at re-melting the (Fe (II) Silicate or fayalite in a high frequency induction melting furnace to recover iron and a few contents were recovered from gangue materials such as CuO. The iron recovery from the fayalite methods includes but are not limited to direct/smelting reduction (e.g. RHF-DR), Oxidative modification of iron oxide to recover iron element and magnetic separation. However, Cao et al’s studies has outlined the low Iron recovery rates associated with the direct beneficiation and oxidative modification processes while smelting reduction method was energy consuming (Hwang et al, 2018 and Cao et al, 2016). A combination of 2 or more methods can yield a high recovery rates. Yang et al, (2011) used direct reduction method followed by magnetic separation to obtain an Iron recovery rate of 81.01 % from 92.05% recovered iron powder while Wang et al, (2014) recovered 92.96% from 93.49% iron powder. Yang and Wang's recovery rates were only done on the bench test in the laboratory and where never applied on a large scale due lack of industrial equipment.

3.1 Direct Reduction (DR)

In practice, this method can use different set ups of rotary kilns, tunnel kilns and rotary hearth furnaces (RHF-DR) etc. Although the RHF is conducted at high temperatures hence energy consuming, it is applied to large scale iron recoveries while the tunnel kilns are of low capacity, energy consuming and also associated with negative environmental effects. Therefore, a large-scale method which requires less energy consumption is in great demand for the recovery of iron not only iron (II) silicate from chalcopyrite but most copper ores gangue materials.

In this method reducing agents and additives plays a crucial role in reducing the fayalite. Viscosity and the melting point are important factors in iron (II) silicate processing. Understanding the viscosity and the melting point of the fayalite is fundamental in acquiring knowledge on the behavior of iron (II) silicate in the presence of additives and reducing agents. 1\textsuperscript{st} the FeO·SiO\textsubscript{2} (from Eq. 3 and/ or 4) is made into carbon bearing pellets of about 15 mm average, dried and fired into the RHF-DR furnace. These pellets goes through 4 different temperature zones of the RHF namely preheating zone, mid-temperature zone, high zone and the cooling zone where most of the iron oxide in the pellets would have reduced to a metallic Iron as shown by reduction mechanisms of FeO·SiO\textsubscript{2} in equation 7. The reaction is endothermic.

\[ \text{FeO} \cdot \text{SiO}_2 (s) + \text{C} (s) \rightarrow \text{Fe} (s) + \text{SiO}_2 (s) + \text{CO} (g) \]

Normally for the above reduction reaction is slow but in order to increase the reaction rate the roasting temperature is increased. Alternatively, CaO oxide as an additive can be added (EQ 8) in the DR to avoid increasing the reaction temperature and this lower energy usage (Cao, 2016). Another author outline that CaO is needed to in formation of a solid-phase reaction of dicalcium silicate (Wollastonite) which contributes to removal of iron from iron (II) silicate plus other gangue materials through a natural pulverization process, Lin et al, (2015). Another way to increase the activity of FeO reduction rate is addition of Sodium carbonate. Na\textsubscript{2}CO\textsubscript{3} that react with SiO\textsubscript{2} in the iron (II) silicate to form a silicate that destroys the olivine structure of the iron hence increase the reduction process. Reaction of sodium carbonate with silicone dioxide is shown in Eq 9 (Cao et al, 2016).

\[ \text{Fe}_2\text{SiO}_4(s) + 2\text{CaO(s)} + 2\text{C(s)} \rightarrow \text{Ca}_2\text{SiO}_4(s) + 2\text{Fe(s)} + 2\text{CO}(g) \]

\[ \text{Na}_2\text{CO}_3(s) + \text{SiO}_2(s) \rightarrow \text{Na}_2\text{SiO}_3(s) + \text{CO}_2(g) \]

3.2 Magnetic separation (M-S)

This technique has been adopted in ore processing for purification even the process of physical separation of minerals. It involves the use of magnets to separate magnetite crystals (Iron in this case) from gangue materials (David, 2017). A typical and commonly adopted techniques of magnetic separators uses the principles similar to the ball norton and porter magnetic separator. Iron (II) silicate material is fed into a separator with a conveyer belt that pass through two pairs of magnets. other two sets of belts ran at 90 degrees to the feed belt. iron (II) silicate is paramagnetic and when it goes through the separator the ferromagnetic element (iron) form aggregates as they attach
on the magnetic component of the separator. Non and magnetic material are collected at separate exits as shown on figure 2. In magnetic separation if a strong magnetic field of at least 2000 gauss is used, flocculation time is lowered. Magnetic flocculation is formation of aggregates of a ferromagnetic component due to their magnetization in the presence of an external magnetic field. If flocculation time is lower than the residence time, formation of agglomerates is favoured. Also aggregates that are formed must have a sufficient magnetic strength to avoid rupture by hydrodynamic forces of the separator (Dworzanowski, 2012).

![Figure 2. showing the operating principle of a magnetic separator (jkmagnetics.com)](image)

There are other few methods of magnetic separation that are currently used e.g. the multistage magnetic separation, High-intensity separation and dry high-intensity separation etc. M-S is usually carried out on the reduced pellets after direct reduction roasting and the process is effective with optimum reaction parameters e.g. the ratio of 6: 100 additives (sodium carbonate) to Iron (II) silicate plus other gangue materials respectively, and a ratio of carbon powder to iron (II) silicate combined with other gangue materials of 18: 100 and melting temperature of 1300°C done at 6600 seconds. The pellets are ground up to 90% in a magnetic field intensity of 0.08 Tesla and the overall recovered iron will be of values more than 95%. This process alone is not an effective method for Iron recovery. When combined with DR usually a recovery rate of up to 90% can be achieved (Zhu et al, 2012).

4. Industrial application and market potential of Iron

Iron is considered as an important and useful metal on the earth. It is ranked fourth as a common element (Feick, 2018 and Woodford, 2018). From the start of civilization iron has been widely used in making of structures and tools. Iron applications has advanced with technology and discovery on new methods of making alloys made it possible to in-cooperate it with a number of metal materials to make alloys with even improved properties (Swanston, C, 1950). Iron concentrates recovered from chalcopyrite can be sold to steelmaking plants to be used as feed material to replace scrap steel. Potential markets would be the likes of pula steel, Tata steel etc. It can also be in-cooperated in making of alloys such as Anthracite iron, gray iron (also known as cast iron), ferroboron and ferronickel etc (Walker, 2017). Iron has high strength and toughness making it an attractive metal in manufacturing of wide range of products such as industrial machinery, transportation industry, instruments, and sports equipment etc. To date the largest consumer of iron element is the steel industry which uses it as a feed material in making of steel. Iron can also be mixed with different chemicals to enhance its properties. Iron is usually cast by pouring it on a mold with shape of product, extracted and cooled down. In manufacturing of iron products different casting techniques such as sand, centrifugal and shell molding etc. can be used. The products of casted Iron includes; engine blocks, pump housing and electrical boxes and many more (Bell and Walker 2018).

5. Discussion and conclusions

4.1 Experimental recommendations
In practice during beneficiation of chalcopyrite as reactions come to completions the layer of fayalite (Iron (II) silicate) plus other gangue materials containing iron is tapped or drained through a hole of the furnace just above the copper matte layer while matte flows into ladles and carried by cranes to converters. In previous practices iron (II) silicate was tapped out together with other gangue materials, solidified and re-melted later for extraction for other elements that might be useful. To avoid re-melting these tapped out products later for iron recovery purpose, at this point when it’s tapped off beneficiation furnaces it can be carried by cranes directly to a direct reduction furnace (RHF-DR) and the process of iron recovery can start. RHF-DR plants can be connected in series as a tap off exit for Iron (II) silicate thus saving future costs for re-melting.

Recovery of copper from chalcopyrite followed by iron extraction from iron (II) silicate seems like a costly technique involving a multiple of furnaces and refinery equipment. However, new developments have been conducted on simultaneous recovery of iron and copper in oxygen and chlorine gas media with recovery rates of up to 77.4% and 44.6% respectively (Gosh et al, 2012 and Haver et al, 1971). The recovery rates in this method were found to be greatly dependent on solubility of oxygen during leaching.

4.2 Conclusions

Beneficiation of chalcopyrite is a growing technology (Hyvarinen et al, 1999). Recent investigation has focused on beneficiation chalcopyrite mainly to recover copper. Although iron occurred in the mineral in high content for many years it has been disposed as waste during the beneficiation of chalcopyrite. For the past years its supply was from its major iron ores such as Kiruna-type ore deposits. Research on recovery of iron from chalcopyrite is aimed directly at providing an alternative feed material for steel electrical arc furnaces.

During beneficiation, copper remains as copper matter while iron is tapped off as FeO.SiO2 the furnace and can be carried out to RHF reduction furnaces for iron recover. Reaction mechanisms in the reduction smelter show that the fayalite is reduced to Fe upon reaction with carbon or graphite in the direct reduction process. The reaction requires high temperatures of more than 1200°C and hence high energy usage at a roasting temperature of 3 hours. CaO as additive has effect on smelting temperature. There is a decrease in smelting temperature with increase in CaO. Literature suggests that the smelting reduction method has good iron recovery rates up to 90%wt Iron powder but combining the reduction method and magnetic reduction the recovery rate is improved and recovered iron powder can have up to 96.21% iron grade (Li et al, 2013). Iron can also be recovered simultaneously from chalcopyrite through chloride leaching.

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Biography

Nenguba Poloko obtained his Masters in Advanced Metallurgy (MMet) and BEng in Materials and Science Engineering at The University of Sheffield (UK). Prior to his studies at Sheffield he studied BSc at The University of Botswana. He is currently pursuing a PhD in Chemical, Materials and Metallurgy (CMME) at Botswana International University of Science and Technology where he also works as a Teaching and Research assistant in his department. He has a background in curriculum development for metals and manufacturing modules with Entrepreneurial Agricultural Techniques. He also worked as a chemist for The Hugg Group. His research interest center around metallurgical processing techniques, materials replacement and properties improvement. His current research focuses on beneficiation of chalcopyrite, an iron rich mineral. His research aims at providing iron as an alternative feed material for steel blast furnaces other than scrap steel. His previous societies include math and science clubs, MATSoc and IOM3.

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