Surface Characterization of Activated Chalcopyrite Particles

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Surface Characterization of Activated Chalcopyrite Particles

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Dissertation submitted for the degree of Philosophiae Doctor (PhD)

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**Thesis summary**

The world’s most abundant copper mineral, chalcopyrite (CuFeS$_2$), experiences slow kinetics in atmospheric leaching using traditional acidic ferric sulfate lixiviants because of its unique physicochemical properties and the passivating product layer formed during leaching. To overcome this, FLSmidth® has devised a novel process, which alters the properties of semiconducting minerals and increases chemical reactivity and dissolution kinetics. In the FLSmidth® Rapid Oxidative Leach (ROL) process, a combination of chemical and mechanical processes is responsible for enhancing the leach kinetics. The former comes about from a surface pretreatment that “activates” the mineral with 0.1 to 5 mol% of copper (II), and latter is assisted by using a Stirred Media Reactor to cleave fresh surfaces during leaching. As a result, surface passivation problems are diminished, and the process can achieve copper recoveries >95% in under 6 h. Since lattice restructuring can play a major role in semiconductor reactivity, it is critical to understand the associated physico-chemical phenomena and their influence in the ROL process. With respect to this, it is important to investigate the relationship between the activation steps and its impact on the chalcopyrite crystal lattice.

In this study, it was found that the key markers of activation could be identified as changes in the physical structure and electrochemical properties of the mineral. Diffraction with transmission electron microscopy (TEM) was critical in uncovering the expansion of the crystal lattice after activation, which would facilitate the extraction of ions since the expanded structure would allow atoms to move more freely. Parts of the mineral, particularly the surface, had significant modification of the structure, which indicated a phase transformation to structural resembling the mineral covellite, CuS. Chemical analysis with x-ray photoelectron spectroscopy (XPS) was capable of proving that significant oxidation occurs in the copper and sulfur, corresponding to a change of phase on the surface and supporting the hypothesis of the formation of covellitic phase. Finally, calculations using density functional theory (DFT) gave fundamental foundations for the importance of electrochemical changes, whereby it was found that copper activation contributes to increased conductivity of the mineral. Increased conductivity has positive impacts on the flow of ions, which provides further proof for the influence on leaching kinetics. The combination of these three studies provides a better understanding on the role of activation than a single approach would.
Dansk sammendrag
Verdens mest almindelige kobbermineral, chalcopyrit (CuFeS₂) udviser langsom kinetik ved atmosfærisk udvaskning med anvendelse af traditionelle, sure ferrisulfat-lixivianter. Dette tilskrives mineralets unikke fysisk-kemiske egenskaber og et passiverende produktlag dannet under udvaskning. For at overvinde dette har FLSmidth® opfundet en ny proces, som ændrer egenskaberne for halvledende mineraler og øger den kemiske reaktivitet og oplosningskinetik. I FLSmidth® Rapid Oxidative Leach (ROL) -processen er en kombination af kemiske og mekaniske processer ansvarlig for at forbedre udvaskningskinetikken. Den førstnævnte, kemiske proces er en overflade-forbehandling, der "aktiverer" mineralet med 0,1 til 5 mol% kobber (II), og sidstnævnte, mekaniske proces er understøttet ved anvendelse af en "omrørt-medie reaktor" (Stirred Media Reactor) til spaltning af friske overlader under udvaskning. Som følge heraf reduceres overfladepassiverings-problemer, og processen kan opnå kobberudvindinger >95% på under 6 timer. Da ændringer i krystalgitter-strukturen kan spille en vigtig rolle for halvleder-reaktiviteten, er det afgørende at forstå de associerede fysisk-kemiske fænomener og deres indflydelse i ROL-processen. Med hensyn hertil er det vigtigt at undersøge forholdet mellem aktiveringstrinnet og dets indvirkning på chalcopyrit-krystalgitteret.

List of publications and presentations

Publications during this study


Conferences and workshops
• Materials Science & Technology 2016, Salt Lake City, UT, U.S.A. (oral)
• CHEC Annual Day 2016, Kgs. Lyngby, Denmark (poster)
• Hands-on Workshop Density-Functional Theory and Beyond: Accuracy, Efficiency and Reproducibility in Computational Materials Science, 2017, Berlin, Germany (poster)
• KT Research Day 2017, Kgs. Lyngby, Denmark (poster)
• Materials Science & Technology 2017, Pittsburgh, PA, U.S.A. (oral)
• CHEC Annual Day 2017, Kgs. Lyngby, Denmark (poster)
• Solid Liquid Interfaces – Challenging Molecular Aspects for Industrial Applications (SLIMAIA 2018), Rueil-Malmaison, France (poster)
• FHI-aims Users and Developers Meeting 2018, Munich, Germany (poster)
• Extraction Meeting 2018, Ottawa, ON, Canada (oral)
• International Workshop on Computational Design and Discovery of Novel Materials (COMDI 2018), Lausanne, Switzerland (poster)
• European Materials Research Society (e-MRS) Fall Meeting 2018, Warsaw, Poland (oral)
• Materials Science & Technology 2018, Columbus, OH, U.S.A. (poster)
• CHEC Annual Day 2018, Kgs. Lyngby, Denmark (oral)
• Venture Cup Denmark: Idea Competition 2019, Odense, Denmark (oral)
• COSMOtherm workshop, 2019, Leverkusen, Germany
• FTIR and Raman Microscopy Seminar, 2019, Gothenburg, Sweden
Chapter 1. Introduction

1.1 Motivation

The atmospheric leaching of the world’s most abundant copper mineral, chalcopyrite (CuFeS₂), has proven to be difficult arising from its semiconducting properties. These properties cause it to be refractory, as compared to the traditional acidic ferric sulfate lixivants in copper leaching processes. Further contribution to this has been the formation of surface-bound polysulfides, elemental sulfur product layers, and a host of passivating intermediate layers with compositions that can be described as Cu₁₋ₓFe₁₋ₓS₂₋₂ₓ.¹⁻⁵ Because of these challenges to the hydrometallurgical processing of chalcopyrite, there has been a high amount of research performed over the past decades in order to understand the thermodynamics and electrochemistry of the reactions involved in leaching.

Because of the depleting supply of primary sulfides, there has been an increase in the near-term transitioning of many mining sites from copper oxide heap leaching to primary copper sulfide processing. As a result, there is much interest in finding a cost-effective leach process, which is compatible with current process plant infrastructures. Many approaches to improve the leach kinetics through activation of the CuFeS₂ particles have been attempted but, unfortunately, at the expense of high CAPEX and/or OPEX.

The focus of this thesis is the investigation of a novel method to overcome this, developed by FLSmidth®, which utilizes a surface pretreatment to “activate” the mineral particles followed by a mechano-chemical Rapid Oxidative Leach (ROL) that mildly attacks the particle surfaces. Consequently, there is a reduction of the surface passivation problems, and this process achieves copper recoveries >97% in under 6 hours.⁶ The important contribution of the activation step is of special interest, and it constitutes the incorporation of a few mol% or less of copper (II) ions to dope the mineral and thereby activate chalcopyrite.

Although FLSmidth has reported reduced leaching times for chalcopyrite concentrates that had been activated in reductive conditions,⁶ the role of activation and the mechanisms involved that contribute to rapid leaching rates remain unknown. FLSmidth has also proposed theories,⁶ such as the activation-modified surface causing the particle to exist in a high-energy state due to lattice stress imparted by the formation of a covellitic structure (CuₓSᵧ, where x ≈ y). For this reason, advanced nano-scale characterization techniques were utilized during this study to draw conclusions upon this matter. High-resolution electron microscopy (in Chapter 2) and surface spectroscopy (in Chapter 3) were used during the PhD project to identify key structural and chemical details.

Advanced characterization methods were able to give insights into the reasons for increased activity during leaching; however, the scope would be limited without support from relevant fundamental models. By tying together the experimental evidence with theory, a better understanding of key phenomena was established (see Chapter 4), through the aid of density functional theory (DFT). By drawing upon DFT, it became possible to correlate the structural and electrochemical properties observed with experimentation with quantum mechanical concepts in a way that could lead to improvement of activation (discussed in Chapter 5).
1.2 Background

1.2.1 Extraction of copper

The copper extraction process can be summarized using Figure 1.1, which provides an overview of the main routes for copper recovery. Extraction begins after receiving the run-of-mine (ROM) ores, which are ores in their natural and unprocessed form that have been crushed and ground. The ores, typically containing less than 1% copper, need to be concentrated, which involves a different process depending which of two main categories they belong to. As shown in the figure, copper oxide minerals are primarily processed through simple and cost-effective hydrometallurgical processing, such as heap leaching. Copper and iron sulfides, on the other hand, are more refractive to such leaching methods. Hence, in metallurgical applications the sulfide minerals are typically subjected to pyrometallurgical treatment after concentration by a flotation process.

![Figure 1.1. Overview of the main routes for copper recovery from oxide and sulfide ores.](image)

Atmospheric sulfide leaching is an example of an emerging, cost-effective leach process that is compatible with existing copper processing processes (adapted from Chaiko, et al.\(^7\)). ROM: Run-of-mine. SX: Solvent extraction. EW: Electro winning.

1.2.2 Overview of the Rapid Oxidative Leaching process

The main objective of this project (which is part of the platform project MiCeTech – Minerals and Cement Process Technology, funded by Innovation Fund Denmark, FLSmidth, Hempel, and DTU)
is to support FLSmidth in their efforts to take their new leach technology – the Rapid Oxidative Leach (ROL) process – to market. Methods to control the surface properties of minerals on an industrial scale are under development at FLSmidth, however a better understanding of the mechanism(s) and limitations are needed. FLSmidth has reported on different aspects of the new, two-stage approach for enhanced, atmospheric leaching of chalcopyrite (CuFeS$_2$). The approach involves reductive activation of the chalcopyrite surface to grow a binary copper sulfide intermediary layer, followed by oxidative leaching of copper in acid ferric sulfate with the aid of a Stirred Media Reactor (SMRt).

Most copper sulfide minerals require the application of both an acidic environment and an oxidizing agent to leach copper as cupric (Cu$^{2+}$). These conditions are achieved using oxidizing agents – the most common being ferric (Fe$^{3+}$) ion as a sulfate or chloride. However, atmospheric leaching of chalcopyrite concentrates using acidic ferric sulfate lixiviants is well known to suffer from slow leach kinetics and poor copper recoveries, due to the formation of a passivation layer on the surface of the chalcopyrite particles. Furthermore, the nature of this passivation layer is not well understood (partly responsible due to the variety of species which form around the chalcopyrite particles), and there are competing theories regarding the rate of dissolution. 1,8–13

To overcome the slow kinetics, FLSmidth has proposed the ROL process as a novel approach that is compatible with existing solvent extraction/electrowinning (SX/EW) processes and claimed to be cost-effective. SX/EW is a two-step hydrometallurgical process that involves the extraction of copper from leaching solvents using strong acids, followed by deposition of the copper onto cathodes using electrolysis (i.e., electrowinning). As mentioned before, this process achieves copper recoveries >97% in under 6 hours.6

The ROL approach is a two-stage process (shown schematically in Figure 1.2) which consists of the following:

1. **Reductive activation of the chalcopyrite surface by intermediary layer** for enhanced reactivity (with or without the use of a SMRt for mechanochemical treatment) under mildly reducing conditions at elevated temperatures (60 – 100 °C).

2. **Oxidative leaching of copper in a batch leach circuit comprised of a continuous stirred tank reactor (CSTR), optionally assisted by SMRt**, at elevated temperatures (60 – 100 °C) in atmospheric pressure conditions. The CSTR provides the oxidative ferric sulfate leaching conditions, and the SMRt mitigates the passivation of the particles by damaging the passivating layer.

Although greatly improved kinetics are observed, it is not clearly understood what the mechanisms involved in the surface reactions of activated and leached chalcopyrite particles are. In particular, the structural details, such as lattice parameters and crystal structure, and electrochemical property identification/determination of the activated and leached chalcopyrite particles are formidable topics to investigate; thus, the application of advanced characterization was utilized in this work. The project was directed at using surface and bulk materials characterization techniques to explore – and to better
elucidate – the structural details of activated and leached chalcopyrite particles. Design and conduction of relevant activation/leaching experiments and mathematical modeling (primarily with density functional theory, DFT) of the ROL process were important contents of this project.

**Figure 1.2**. The ROL process showing the reductive activation step (left) and continuous oxidative leaching step (right). Bench-scale reactors has volumes of 200 mL or higher. Pilot-scale CSTR’s could be 40 L with up to 50% loading of mineral slurry. The CSTR:SMRt volume ratio could be found in the range of 10 – 50:1.

### 1.2.2.1 The Stirred Media Reactor

A sketch of the (bench-scale) stirred media reactor (SMRt), developed by FLSmidth, is provided in Figure 1.3. The SMRt reactor is essentially a chemically-resistant steel-walled reactor, heated by circulating thermostated water and stirred by an overhead mixer equipped with a steel-rod impeller. While the SMRt reactor is fitted with a lid to prevent significant water evaporation, it is not gas-tight to avoid pressurization. An example of its usage can be found on a report of pilot plant testing.¹⁴
During the ROL experiments, the SMRt reactor is loaded with grinding media (e.g., ceramic beads) to impart high mechanical energy through a combination of stirring, agitation, tumbling, and/or vibration. Hence, the SMRt reactor effectively acts as a mechano-chemical reactor, which is elaborated below.

A mechano-chemical reaction is defined by the International Union of Pure and Applied Chemistry (IUPAC) as “a chemical reaction that is induced by mechanical energy.” However, this definition must be understood in a broader sense, and at present, a wider accepted definition of Heinicke is: “mechanochemistry is a branch of chemistry which is concerned with chemical and physico-chemical transformations of substances in all states of aggregation produced by the effect of mechanical energy.”

Mechano-chemistry has a wide range of applications. It is generally performed in high-energy ball mills using powder reactant mixtures. During milling, the intimate mixing of reactants and the continuous creation of fresh surfaces, defects, and active sites enables the gradual progression of solid-state reactions at room temperature by small diffusion pathways at the interfaces of the reactants due to the ball impacts. In water-based extractive metallurgy (hydrometallurgy), mechano-chemical processing (e.g., ACTIVOXTM) has been applied to the recovery of non-ferrous and precious metals, as an alternative to pretreatments of sulfidic concentrates by roasting and bacterial oxidation. ACTIVOXTM is a hydrometallurgical process combining ultra-fine milling with low-temperature, low-pressure oxidative leaching to liberate metals from a sulfide matrix.

While all past mechano-chemical processes used high-energy mills to affect chemical reactivity, the FLSmidth ROL approach, on the other hand, is claimed to require very low energy because the efficiency of the SMRt reactor is optimized through properly sizing the unit, the type and amount of
grinding media, residence times within both the SMRt reactors and the overall leach circuit, and the volume ratio of the overall leach circuit to the total volume contained within the SMRt reactors.\textsuperscript{7,18} These features are further described and discussed under the following description of the ROL process.

\subsection*{1.2.2.2 Acid Ferric Sulfate Leaching of chalcopyrite}

Chalcopyrite (CuFeS\textsubscript{2}), a primary copper sulfide (crystal unit cell in Figure 1.4), is the most abundant copper mineral in nature, accounting for about 70\% of the copper reserves in the world.\textsuperscript{11} While high-grade, secondary sulfide ores may be leached under atmospheric pressure with reasonable economics,\textsuperscript{19} chalcopyrite is a highly refractive mineral under hydrometallurgical conditions, suffering from slow leach kinetics and poor copper recoveries, which is due to the formation of a passivation layer on the surface of the chalcopyrite particles.\textsuperscript{11,20–22} Therefore, in metallurgical applications it is mainly subjected to pyrometallurgical treatment after up-concentration by a flotation process. Pyrometallurgical treatment, however, is expensive, and, as such, it is currently only economically viable for treating high-grade copper concentrates.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Crystal unit cell of chalcopyrite. Atoms are labeled: sulfur (yellow), copper (brown), and iron (red). Image generating using Jmol.\textsuperscript{23}}
\end{figure}

Hydrometallurgy, on the other hand, presents important advantages, such as the possibility of treating mid-grade and low-grade ores and easier control of waste, as an alternative to pyrometallurgy.\textsuperscript{7,11,19,21,22,18,6} Different hydrometallurgical processes are being investigated on both laboratory and pilot scales in attempts to implement these technologies at industrial level,\textsuperscript{7,11,19,18,6,24,25}
and, as a result, *acidic ferric sulfate leaching* is one of the most important processes for copper recovery from primary sulfides, e.g., chalcopyrite (CuFeS₂). It is a preferred process for copper recovery because of the simplicity of the leaching chemistry, low CAPEX and OPEX, and the ease with which the copper is subsequently recovered by solvent extraction (SX) and electrowinning (EW). The approach is illustrated in Figure 1.2, above.

Acidic ferric sulfate leaching involves dissolving Cu ions from copper-containing minerals into a sulfuric acid solution of ferric sulfate (known as the lixiviant) to produce what is known as a pregnant leach solution. In addition to dissolved copper and iron, the solution will also contain other impurity species, such as Al, Co, Mn, Zn, Mg, Ca, etc. These impurities are removed during the SX step, stripped with a low concentration sulfuric acid solution, and should have >99.99% copper content after EW.

### 1.2.2.3 Applied leach conditions (Eh / pH)

Most copper sulfide minerals require the application of both an acidic environment and an oxidizing agent to leach copper as Cu²⁺. The Pourbaix diagram for the Cu-Fe-S-O-H₂O system (Figure 1.5) shows that the dissolution of chalcopyrite in acid medium takes place through a solid transformation in different intermediate sulfides (Cu₅FeS₄, CuS, Cu₂S), increasingly richer in copper. Further, Figure 1.5 implies that a pH lower than 4 and a redox potential higher than +0.4 V is required to dissolve copper from chalcopyrite.

![Pourbaix diagram](image)  
*Figure 1.5:* Pourbaix diagram for the Cu-Fe-S-O-H₂O system at 25°C. [Cu] = 0.01 M, [Fe] = [S] = 0.1 M.
These conditions are achieved using oxidizing agents, the most common being ferric (Fe\(^{3+}\)) ion as a sulfate or chloride.\(^{11}\)

The oxidation of chalcopyrite in ferric sulfate can be represented by the overall reaction (Equation 1.1):\(^{24}\)

\[
\text{CuFeS}_2(s) + 2\text{Fe}_2(\text{SO}_4)_3(aq) \rightarrow \text{CuSO}_4(aq) + 5\text{FeSO}_4(aq) + 25^0
\]  
(Equation 1.1)

The resulting Fe\(^{2+}\) from Equation 1.1 is re-oxidized to Fe\(^{3+}\) by O\(_2\):

\[
4\text{FeSO}_4(aq) + O_2(aq) + 2\text{H}_2\text{SO}_4(aq) \rightarrow 2\text{Fe}(\text{SO}_4)_{3}(aq) + 2\text{H}_2\text{O}(l)
\]  
(Equation 1.2)

The Fe\(^{2+}/Fe^{3+}\) redox couple acts in a catalytic manner in these reactions. In order not to exceed a certain solution potential in a ferric leaching reactor, one must ensure that the supply of ferric iron does not exceed the demand. This means that the overall leaching reaction of Equation 1.1 must be intrinsically faster than the ferrous oxidation reaction with dissolved oxygen gas of Equation 1.2.\(^{24}\)

While both iron and copper are dissolved – to Fe\(^{2+}\)(aq) and Cu\(^{2+}\)(aq), respectively – in Equation 1.1, it is observed that the main reaction product for sulfur (oxidation of sulfide, S\(^{-2}\)), is solid, elemental sulfur (S\(^0\)). If excess O\(_2\) is available during chalcopyrite oxidation (Equation 1.1), sulfur is further oxidized to sulfate, according to Equation 1.3:\(^{22}\)

\[
\text{CuFeS}_2(s) + 2\text{Fe}_2(\text{SO}_4)_3(aq) + 3O_2(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{CuSO}_4(aq) + 5\text{FeSO}_4(aq) + 2\text{H}_2\text{SO}_4(aq)
\]  
(Equation 1.3)

1.2.3 Passivation of chalcopyrite during leaching with ferric ion

The atmospheric leaching of chalcopyrite concentrates using acidic ferric sulfate lixiviants is well known to suffer from slow leach kinetics and poor copper recoveries, due to the formation of a passivation layer on the surface of the chalcopyrite particles. However, while there is consensus in the literature with respect to the formation of a passivation layer on the surface of the chalcopyrite particles, which slows down the oxidation reaction, the nature of this film is still very much a matter of debate. It has been postulated that it must have a low porosity and/or be a bad electric conductor.\(^{11}\)

Previous studies have suggested that these layers could be sulfur, precipitated-iron compounds, a solid electrolyte interphase that slows the rate of electron transfer, a metal-deficient sulfide, or polysulfidic in nature.\(^3\)

The principal theories have suggested that the rate of the dissolution process is controlled either by the formation or evolution of a compact diffusion layer of low solubility copper polysulfide, less reactive than the original chalcopyrite and with less iron, and/or by the transport of electrons through
an insulating outer film of elemental sulfur.\textsuperscript{11} Two typical models of chalcopyrite oxidation by Fe\textsuperscript{3+}, as suggested in the literature, are provided in Figure 1.6.

![Figure 1.6: Two common models of chalcopyrite oxidation by Fe\textsuperscript{3+}.\textsuperscript{11} Left: model with formation of an inner layer of polysulfide (C\textsubscript{p}) and outer layer of porous sulfur (S\textsubscript{0}) with no controlling effect. Right: model with formation of a low-porous (insulating) layer of elemental sulfur.]

\textbf{1.3 Alternative activation schemes}

A number of approaches have been proposed for improving both leach kinetics and recoveries of copper in the acid ferric sulfate system, but many of these, while effective, suffer from high CAPEX and/or OPEX.

Some recent inventions/patent applications\textsuperscript{21,27} claim to be cost-effective as well as compatible with existing SX/EW processes, by taking advantage of the \textit{galvanic interactions} between pyrite and chalcopyrite particles to facilitate enhanced copper recovery and chalcopyrite dissolution rates in specific, acid ferric sulfate leaching processes. These inventions suggest different reaction systems, involving pyrite, silver, or other species, as catalysts.

\textbf{1.3.1 Mechanical activation of copper sulfides}

One of the more unique approaches to improving the leach kinetics involved the mechanochemical activation of chalcopyrite (CuFeS\textsubscript{2}) particles, called the Sherritt-Cominco Process.\textsuperscript{28} Their method focused on the grinding down of particles to achieve 80\% below 15 microns in diameter for shortening the diffusion pathway through the particle. Their main reaction followed the form of

\begin{equation}
CuFeS\textsubscript{2} + CuSO\textsubscript{4} \rightarrow 2CuS + FeSO\textsubscript{4},
\end{equation}

(Equation 1.4a)

also written with oxidation states

\begin{equation}
Cu^{1+}Fe^{3+}(S^{2-})_2 + Cu^{2+} \rightarrow 2Cu^{2+}S^{2-} + Fe^{2+},
\end{equation}

(Equation 1.4b)
which is performed at temperatures >150°C. Another main reaction occurs with bornite present in the concentrate, which is more desirable since it is a high-copper mineral:

\[ \text{Cu}_5\text{FeS}_4 + \text{CuSO}_4 \rightarrow 2\text{Cu}_2\text{S} + 2\text{CuS} + \text{FeSO}_4. \]  
(Equation 1.5)

However, their process also suffers from an undesirable reaction, which increases the amount of copper sulfate needed for the recycle by 20-30%:

\[ 5\text{CuS} + 3\text{CuSO}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{Cu}_2\text{S} + 4\text{H}_2\text{SO}_4. \]  
(Equation 1.6)

Furthermore, at the elevated temperatures they experience more copper sulfate consumption with the covellite (CuS) product through Equation 1.6 above and 1.7 below:

\[ 6\text{CuS} + 3\text{CuSO}_4 + \text{H}_2\text{O} \rightarrow \text{Cu}_9\text{S}_6 + 4\text{H}_2\text{SO}_4. \]  
(Equation 1.7)

To prevent this from happening, Swinkels and Berezowsky introduce dissolved oxygen in acidic solution to convert the sulfide sulfurs into elemental sulfur through the following reactions:

\[ \text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 + \text{O}_2 \rightarrow 2\text{CuSO}_4 + \text{S}^0 + 2\text{H}_2\text{O} \]  
(Equation 1.8)

and

\[ \text{CuS} + \text{H}_2\text{SO}_4 + \text{O}_2 \rightarrow \text{CuSO}_4 + \text{S}^0 + \text{H}_2\text{O}. \]  
(Equation 1.9)

As can be seen, this process is very energy intensive since it requires very high temperatures (above the boiling point of water) and a large supply of oxygen to keep it well controlled. Alternatives approaches around this time focused on temperatures below boiling.

### 1.3.2 Galvanic coupling with metals

Around the time that mechanical activation was being introduced, another method was attempted among a few groups with the idea of including metallic powders to form a galvanic couple with chalcopyrite (CuFeS$_2$) particles. The aim of creating the couple was that the metal powders would have dissimilar electric potential than chalcopyrite while in the presence of electrolytes to produce a chemical reaction (corrosion) through electrochemical action. The first of these was done by Shirts, et al. They used copper (1.5 – 2 to 1 molar ratio to chalcopyrite), iron (2 – 4 to 1 ratio), and lead (2
−4 to 1 ratio) powders as reductants for chalcopyrite. The hypothesized reaction could be summarized as:

\[ Cu^0 + CuFeS_2 + 2H^+ \rightarrow Cu_2S + Fe^{2+} + H_2S \]  
(Equation 1.10)

with respective half-cell reactions represented as, firstly cathodic:

\[ 2CuFeS_2 + 2e + 6H^+ \rightarrow Cu_2S + 2Fe^{2+} + 3H_2S, \]  
(Equation 1.11)

and, secondly, the anodic reaction half-cell:

\[ 2Cu^0 + H_2S \rightarrow Cu_2S + 2H^+ + 2e, \]  
(Equation 1.12)

which can also function as:

\[ 2Cu^0 \rightarrow 2Cu^{+} + 2e. \]  
(Equation 1.13)

Based on the experiments performed, they found that copper metallic powders did perform as reductants when there was a 2:1 molar ratio of copper to chalcopyrite. In addition, temperature had a major effect, yielded highest conversion that occurred in the range of 65 to 90 °C (Figure 1.7). Furthermore, agitation proved to have an adverse effect on the conversion (Figure 1.8), which was due to disruption of the galvanic contact between copper and chalcopyrite. Similar results were found with the iron and lead metallic powders, which had a 2 – 4:1 molar ratio for iron (varying with temperature) and 1:1 for lead (95 °C).

**Figure 1.7.** Effect of temperature on Fe extraction, Cu° reductant.29
Figure 1.8. Effect of agitation on Fe extraction, Cu° reductant.\textsuperscript{29}

Results were found to be similar in a separately verified set of experiments by Hiskey and Wadsworth\textsuperscript{30} wherein they describe the galvanic contact schematically as in Figure 1.9.

Figure 1.9. Schematic representation of the galvanic conversion model for chalcopyrite and copper and acid system.\textsuperscript{30}

They found a similar effect due to temperature and agitation. Furthermore, they observed that smaller copper particles result in faster conversion (Figure 1.10). Table 1.1 shows the corresponding particle sizes related to the mesh size as well as calculated rates, based upon the following surface reaction-limited model:\textsuperscript{31}

\[
\left[1 - \left(1 - \frac{a}{\varphi}\right)^{1/3}\right] = \frac{k_l}{r_0}t, \quad \text{(Equation 1.14)}
\]
where $\alpha$ is the fraction of CuFeS$_2$ reacted at time $t$, $r_0$ is the initial radius of the particle, $k_l$ is the linear rate constant (containing factors like the surface reaction rate constant, surface roughness, volume and cross-sectional area of the molecular reactants, and concentration) in cm/min, and $\varphi$ is the molar ratio of Cu:CuFeS$_2$.

![Figure 1.10. Curves showing the conversion of 325 x 400 mesh chalcopyrite with different copper shot sizes at 90 °C.]

**Table 1.1.** Normalized Linear Rate Constant Calculated According to Equation 10 at 90 °C ($\alpha = 1.5$), adapted from Hiskey. $^{30}$

<table>
<thead>
<tr>
<th>Copper Radius, $r_0$ (cm)</th>
<th>Mesh Size</th>
<th>Initial Slope</th>
<th>$k_l = k_{03}$, cm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0020</td>
<td>325 X 400</td>
<td>0.0191</td>
<td>$3.82 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.0032</td>
<td>200 X 270</td>
<td>0.0144</td>
<td>$4.61 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.0063</td>
<td>100 X 150</td>
<td>0.0098</td>
<td>$6.17 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.0115</td>
<td>60 X 65</td>
<td>0.0047</td>
<td>$5.41 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.0179</td>
<td>35 X 48</td>
<td>0.0030</td>
<td>$5.37 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Other factors that were found to slow the kinetics of CuFeS$_2$ conversion were low concentrations of the lixiviant, sulfuric acid (large drop below 0.5 M concentration), and any added amounts of initial cupric ions.

X-ray diffraction and microscopic characterization showed that no covellite (CuS) or digenite (Cu$_9$S$_5$) exist in the products of these reactions, only chalcocite (Cu$_2$S) and small amounts of djurleite (Cu$_5$FeS$_4$). Based on this observation, it can be said that another galvanic reaction occurs, based on Equation 1.15:

$$5CuFeS_2 + 4e^- + 12H^+ \rightarrow Cu_5FeS_4 + 4Fe^{2+} + 6H_2S.$$  

(Equation 1.15)
Because of the growing layer of chalcocite around the particles, as shown in Figure 1.9 above, they expect that cathodic half-cell potential will be more negative and the anodic half-cell will be more positive, thereby enhancing the conversion of chalcopyrite to chalcocite. This is advantageous since chalcocite has quicker leaching kinetics, due to being a secondary sulfide mineral with high copper content.

### 1.3.3 Galvanic coupling with pyrite

In recent studies, a catalytic effect involving pyrite (FeS$_2$), which is a very common (via gangue mineralization) phase in copper ores, has been evoked, and the question of a galvanic corrosion mechanism has been raised.$^{21,25,27}$ For example, it has been demonstrated that, as separate non-contacting phases, pyrite dissolves more rapidly than chalcopyrite, but, when the phases are in galvanic contact, the chalcopyrite dissolves more rapidly, protecting the pyrite. Further, it has been found that one of the most effective methods to increase the reaction rate of chalcopyrite leaching is the addition of pyrite to facilitate the galvanic interactions between pyrite and chalcopyrite.$^{25}$

The oxidation of chalcopyrite in ferric sulfate can be represented by the overall mineral dissolution reaction (Equation 1.1), which, according to Nazari and Asselin,$^{25}$ can also be expressed by the half-cell anodic and cathodic reactions as follows:

**Anodic:**

\[
\text{CuFeS}_2 + \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 25^0 + 4e^- \quad E = 0.47 \text{V S.H.E.} \quad (\text{Equation 1.16a})
\]

**Cathodic:**

\[
4\text{Fe}^{3+} + 4e^- \rightarrow 4\text{Fe}^{2+} \quad E = 0.77 \text{V S.H.E.} \quad (\text{Equation 1.16b})
\]

In this process, a soluble oxidant is reduced at one location on the CuFeS$_2$ surface and another surface of the CuFeS$_2$ acts as an anode. Thus, a potential acts across the particle.

Furthermore, Nazari and Asselin studied the morphology of chalcopyrite leaching in acidic ferric sulfate media (with and without pyrite in the leach environment), and they proposed that pyrite provides an alternative (catalytic) surface for ferric reduction in the leach solution. This enables the system to moderate the amount of ferric ions in solution and exhibit a potential within the active anodic region of the mineral. It was further proposed that sulfur atoms migrate in this active condition to form stable $S_8$ rings (Figure 1.11). Otherwise, in the absence of pyrite, iron is selectively leached over copper, leading to the formation of an iron-deficient, copper polysulfide-passivating layer (Figure 1.12).
To summarize the literature findings,\textsuperscript{11,21,22,24,25} it seems most likely that the leaching and passivation of chalcopyrite in sulfate medium is to be explained by a mixture of chemical reaction and diffusion control mechanisms, which, in turn, depend on the specific leach conditions, such as temperature, pH, ferric iron concentration, O\textsubscript{2} availability, etc. In other words, the nature of the passivation layer varies with the specific experimental conditions, and that is the reason for the lack of consensus in the literature.

\textbf{1.4 Methods and methodology}

In the remainder of this chapter, the experimental method for the activation process is explained in a more generalized approach, and it is presented within the major steps of the Rapid Oxidative Leaching (ROL) process. Some preliminary results from characterization of the activation process initiated by FLSmidth are included after. These serve as the stepping-stones, which lead to the start of the present study.
The chapters that follow will consist of the important methods that were essential in a full understanding of the activation process. Detailed experimental procedures are included where necessary in these chapters. Chapter 2 is the continuation of the characterization work done by FLSmidth. The focus of that chapter lies on electron microscopy, since the technique is most suitable to uncovering the fine detail of structural changes that occur.

Since chemical changes should be present due to activation, especially on the surface of particles, x-ray photoelectron spectroscopy (XPS) is the method of interest in Chapter 3. XPS was chosen over infrared and Raman spectroscopies, not only for its fine details, but because chalcopyrite does not produce distinctive spectra that would be necessary to discern small changes in chemistry. Mössbauer spectroscopy was also considered; however, the changes in iron are not anticipated to be major, since the oxidation of copper is more relevant as the formal charge should move from the natural +1 of chalcopyrite to +2 of the copper ions from activation.

Chapter 4 does not deal with a characterization technique, but rather computation calculations with density functional theory (DFT). The purpose of DFT was to provide theoretical foundations for the observations from characterization. It was used because it can give these insights from first principles, since is based on quantum mechanical modeling methods. It was used to corroborate or predict structural changes and electronic properties.

Finally, Chapter 5 pulls the outcomes from these last three chapters to outline conclusions that were ascertained. Suggestions for future endeavors are presented with some preliminary results.

1.4.1 Experimental procedure
Prior to oxidative leaching, the chalcopyrite concentrates are reductively activated to effect a partial conversion – not full metathesis – of chalcopyrite to a binary copper sulfide, thereby activating the chalcopyrite for rapid oxidative leaching. Thus, the experimental procedure is as follows, and the steps described below give an overview of the ROL process.

1.4.1.1 Acidulation (Step 0)
Before the reductive activation step, feed concentrate (damp filter cake) is acidulated with concentrated sulfuric acid. The acidulation reaction, which is exothermic and dissolves carbonates, may be violent (and produce froth/foam).

1.4.1.2 Reductive activation (Step 1)
In the bench-scale activation experiments that are conducted by FLSmidth in their leach lab in Salt Lake City, UT, U.S.A., and repeated at the Technical University of Denmark (DTU), the reductive stage activation is initiated by preparing a ferrous sulfate (FeSO₄) solution. Next, enough soluble copper (Cu²⁺) is provided to affect the desired degree of chalcopyrite conversion (typically a few
mol%). Cu$^{2+}$ is dissolved by using copper sulfate (CuSO$_4$), and this is then followed by adding it into the acidulated slurry in a CSTR. If possible, mixing the solution (with grinding media) in the SMRt reactor is advantageous. Although the activation reaction is aided by the SMRt reactor in the bench-scale experiments that are conducted by FLSmidth (Figure 1.2), it is claimed that the use of the SMRt reactor is not mandatory for the activation to proceed, but it accelerates the process. The SMRt reactor can hold a smaller volume of feed concentrate slurry with respect to the CSTR, the dry solid equivalent contained in the SMRt is roughly the same as the CSTR. Bench-scale experiments with pure chalcopyrite, however, would usually contain less than 40% dry pure mineral in a 200 mL reactor. With the aid of a SMRt reactor, the chalcopyrite can be activated within minutes in these mildly reducing conditions. However, it should be clarified that in the activation studies of this work, the SMRt was not used.

The slurry redox potential during the metathesis reaction is controlled by the Fe$^{3+}$/Fe$^{2+}$ redox couple (Fe$^{2+}$ ions are added to the slurry initially, to obtain mildly reducing conditions), and the reactor is closed with a lid to prevent air oxidation of ferrous ions. During the course of the activation process, the slurry redox potential drops due to the release of Fe$^{2+}$, because the chalcopyrite particles function as both the reactive substrate and a reducing agent.$^6$

The activation reaction is found to comprise a partial conversion – not quite a metathesis – of chalcopyrite to a type of copper sulfide, most closely described as the binary Cu$_6$S$_6$ of covellite.$^6$ The suggested reaction is shown in Equation 17:

$$3CuFeS_2 + 3Cu^{2+} \rightarrow Cu_6S_6 + 3Fe^{2+}. \quad \text{(Equation 1.17)}$$

If the reaction was indeed metathetic, then it would be possible that the reaction sequence followed the type described by Pattrick, et al.$^{32}$ In their reaction sequence, Fe$^{3+}$ and Cu$^{2+}$ are reduced and the sulfide is oxidized:

$$3Cu^1+Fe^{3+}(S^{2-})_2 + 3Cu^{2+} \rightarrow Cu^3+_3Cu^2+_3(S^2_2-S^{*-})(S^{2-})_3 + 3Fe^{2+} \quad \text{(Equation 1.18)}$$

$$Cu^1+_3Cu^2+_3(S^2_2-S^{*-})(S^{2-})_3 \rightarrow Cu^1+_6(S^2_2-S^{*-})_2 \quad \text{(Equation 1.19)}$$

In order to maintain charge neutrality, point defects (namely, an electron hole designated as “•”) are created throughout the lattice. Such a metathesis product is startling because of its high concentration of point defects (16%), since typical point defect concentrations within an intrinsic semiconductor are significantly smaller ($\sim 10^{-13}$ per atom of silicon at room temperature).

The extent of the reaction is followed by the measuring of the concentration of soluble copper (Cu$^{2+}$) in the liquid phase as a function of time (see example in Figure 1.13). The Cu$^{2+}$ concentration in the leach solution can be measured in “real-time” (periodic collection of sample volume) by means of
UV/vis spectroscopy (absorbance at 810 nm), after centrifugation of the sample and filtration through a syringe filter.

The activation reaction is considered completed when the Cu$^{2+}$ concentration in the liquid phase has dropped close to zero (or below the detection limit). Then, this step follows with approximately 1 hour of dwell time (with heating and continuous stirring still turned on) before the slurry is transferred to the oxidative leaching step.

**Figure 1.13.** Measured copper concentration as a function of time in different bench-scale activation experiments conducted by FLSmidth. PD04 – PD07 refer to experiments using different chalcopyrite concentrates.

### 1.4.1.3 Oxidative leaching (Step 2)

Oxidative leaching of chalcopyrite particles is the second step, but it occurs after the activation (Step 1). Since leaching experiments were not performed as part of the study because the focus was on the former step, this description will suffice for the sake of presenting the full process. The reader may refer back to §1.2.2 for further details.

### 1.4.2 Characterization of the activated product prior to this study

The partial transformation of the chalcopyrite mineral (as described in Equation 1.17) is believed to influence the electron transport properties of the leaching particle. Initial characterization work was done by FLSmidth, and they identified a covellite-like (CuS) phase as the only detectable reaction product by XRD analysis. While the XRD pattern of the metathesis product is similar to covellite (CuS), the peak positions and relative peak heights do not match the nearest corresponding reference pattern for covellite in terms of peak positions and relative intensities. This is interpreted to suggest
that the activation product, while similar to covellite, is a novel, high-energy, and metastable transition state product that is best described as CuS. Electron diffraction measurements by HRTEM have indicated that the activation product has lattice parameters that differ from covellite (Table 1.2). Although not a complete match, the first and fourth parameters are close to that of covellite, still better than bornite, which was the next closest candidate and a copper-rich sulfide.

**Table 1.2.** Electron diffractograms (d-spacings) of activated chalcopyrite particles and reference minerals, reproduced from Chaiko, et al.⁶

<table>
<thead>
<tr>
<th>Pattern from XRD (Å)</th>
<th>Pattern from XRD (Å)</th>
<th>TEM activated chalcopyrite from FLSmidth (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covellite (CuS) Reference</td>
<td>Bornite (Cu₅FeS₄) Reference</td>
<td>TEM activated chalcopyrite from FLSmidth (Å)</td>
</tr>
<tr>
<td>3.287</td>
<td>3.267</td>
<td>3.28</td>
</tr>
<tr>
<td>2.319</td>
<td>2.179</td>
<td>2.24</td>
</tr>
<tr>
<td>2.099</td>
<td>2.107</td>
<td>2.22</td>
</tr>
<tr>
<td>2.045</td>
<td>1.956</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Figure 1.14 shows a CuFeS₂ particle (HRTEM image) with an activation product over-layer. The higher magnification image on the right hand side of Figure 1.14 shows grain boundaries and lattice dislocations, but notably absent is any evidence of major stress cracking or spalling. The rather smooth transition from a CuFeS₂ crystal lattice to a CuS crystal lattice is extraordinary as the individual unit cells are not congruent.⁶

**Figure 1.14.** HRTEM particle analysis of the activation product shows the presence of a surface layer (light area) covering an underlying chalcopyrite particle (dark area). Image on the right is a higher magnification showing grain boundaries and lattice dislocations. Notably absent are stress cracking and fracturing.⁶

1.4.2.1 **Features of the reductive activation step**

As opposed to other (mechano-chemical) leaching processes, the reductive activation step of the ROL process focuses on inducing lattice strain within the chalcopyrite particles as a means to increase
dissolution kinetics, rather than selectively and quantitatively extract iron. The chalcopyrite conversion through copper doping is purposefully limited to only a few percent, which is sufficient to increase dramatically the overall efficiency of copper recovery in the subsequent oxidative leach. A mole percentage of approximately 0.1% to 5.0% Cu$^{2+}$ in CuFeS$_2$ is typically used.

XRD analysis, as shown above, suggests that the activation product, while similar to covellite, is a novel, high-energy, and metastable transition-state product. The covellite-like phase is the only XRD-detectable reaction product, since X-ray analysis has determined that the peaks do not come from either Cu$_2$S or Cu$_{1.8}$S, which are parasitic reaction products observed in previous metathesis studies.

A linear relationship between the change in dissolved Cu and Fe concentrations and the square root of time has been found. This is a possible indication that the mechano-chemical activation reaction process is diffusion-controlled (see Figure 1.15).$^6$

Electron diffraction (TEM) measurements have been used to characterize accurately the metathesis product (Figure 1.16). The measurements indicate that the metathesis product has d-spacings that differ from covellite. The TEM images reveal an activation product (Cu$_6$S$_6$) over-layer on the chalcopyrite (CuFeS$_2$) substrate. Higher magnification shows grain boundaries and lattice dislocations. Notably, evidence of stress cracking and fracturing/spalling is absent. The rather smooth transition from a CuFeS$_2$ crystal lattice is extraordinary as the individual unit cells are not congruent.

![Graph showing kinetics of solid-state exchange of iron by Cu(II) in chalcopyrite with ferrous sulfate media](image)

**Figure 1.15.** Kinetics of solid-state exchange of iron by Cu(II) in chalcopyrite with ferrous sulfate media (adapted from Chaiko, et al.).$^6$
From the corresponding lattice image, the product layer appears to be highly crystalline. However, the d-spacings in this region do not exactly match any of the expected values for covellite, chalcocite, pyrite or the chalcocite/digenite series. While two of the d-spacings are quite similar to covellite, the two other observed spacings do not match covellite. This indicates a structure that differs from traditional covellite, and probably indicate a highly strained CuS lattice.

It is surmised that point defect induce lattice strain extends a significant distance ahead of the identifiable product layer boundary, and that this high-energy, metastable transition state catalyzes the dissolution of the underlying chalcocite phase.
Chapter 2. Characterization of Physical Changes

2.1 Background on diffraction
Diffraction is what occurs when a wave is bent around the edge of an object (see Figure 2.1). If a wave must pass through a three-dimensional periodic structure, as in a crystal, the outcome will be a diffraction pattern, an organized arrangement of spots that provides information about the studied structure. As long as the waves remain in phase with each other (see Figure 2.2), they will produce bright spots on the diffraction pattern, fulfilling Bragg’s Law:

\[ 2d \sin \theta = n\lambda \]  

(Equation 2.1)

Figure 2.1. Diffraction of a planar wave through a narrow slit. The two edges from the slit cause the wave to be fully curved.

Figure 2.2. Bragg’s law is fulfilled if the reflected (or diffracted) wave is in phase with the incident wave, e.g., the number of wavelengths marked at the blue line should equal an integer multiple, \( n \). Thus, the reflection will be seen at an angle \( 2\theta \) on the diffraction pattern. Otherwise, out-of-phase waves are destructive and show no indication on the pattern.
Special mention should be made about the distance, $d$, in Figure 2.2. This periodic distance is shown as an intense spot on diffraction patterns and is called the d-spacing because it relates to the space between atomic planes in a crystal lattice. It typically has a designation of the form $d_{hkl}$, where $h$, $k$, and $l$ are known as the Miller indices.$^{33}$ These indices are best described as planar directions in which a plane would be orthogonal to the inverse intercepts of the lattice vector. For example, the (111) plane would be extended across the three closest corners of a cube (or any hexahedron in general). For a second example, the (221) plane would be orthogonal at half the x- and y-axis directions (see Figure 2.3 below).

![Figure 2.3. Example of Miller index designation.](image)

Diffraction is convenient to understand for x-rays, since they are waves of electromagnetic radiation, and they are the most easily accessible tools for crystallography. Electrons may also be used, due to the wave-like nature of particles, as explained through quantum mechanics. The disadvantage of electrons for diffractions is that, as compared to x-ray photons, they have a mass and charge, which causes them to scatter inside the sample and unable to transmit beyond about 100 nm of thickness. Therefore, sample preparation is of key importance. The major advantage of electron diffraction, though, is the ability to target very small areas of a sample in selective area electron diffraction (SAED) mode during transmission electron microscopy (TEM). This is something unavailable with x-ray diffraction (XRD). The specificity of SAED allows for collecting information of phases that only occur in small parts of the sample, and that would be otherwise below the detection limit of XRD. These advantages of key importance in the study of the activation process, which converts $<5$ mol% of the mineral.

### 2.2 Activation experiments on pure chalcopyrite and copper concentrate

Early, activated chalcopyrite samples were prepared at FLSmidth, using the method described in §1.4.1.2. The exact details for sample preparation are as follows. Museum-grade chalcopyrite mineral was obtained from Excalibur Minerals, USA, and ground to minus 635 using a ring-and-puck mill (BICO, USA). Later samples were prepared at DTU using museum-grade chalcopyrite obtained from Ward’s Science, USA, and ground using mortar and pestle to similar mesh size. In both cases, a stirred
beaker containing 200 mL of deionized water with pH adjusted with sulfuric acid within the range of 1.0 to 4.0 and heated to 80 °C. To this was dissolved copper sulfate pentahydrate (CuSO₄·5H₂O, 4.08 g, from Alfa or Sigma-Aldrich) and iron sulfate heptahydrate (FeSO₄·7H₂O, 1.99 g, from Alfa or Sigma-Aldrich). The pH was again adjusted between 2.0 and 3.0. Then, 75.0 g of the chalcopyrite sample was added to the solution for the activation reaction to take place, and it would continue for a maximum of one hour.

Results from the initial activation experiments are listed on Tables 1.1 and 1.2, in which inductively coupled plasma - optical emission spectrometry (ICP-OES) was performed to calculate the concentrations of copper and iron in the solution. These are further summarized in Figure 2.4, which gives an indication of the rate of extraction as a diffusion-controlled process due to the root-time dependence.

**Table 2.1. ICP-OES data from pure chalcopyrite activation.**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>time</th>
<th>time</th>
<th>SQRT[time]</th>
<th>[Cu]</th>
<th>[Cu]</th>
<th>[Fe]</th>
<th>[Fe]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>hr</td>
<td>hr^½</td>
<td>g L⁻¹</td>
<td>M</td>
<td>g L⁻¹</td>
<td>M</td>
</tr>
<tr>
<td>A-1</td>
<td>5</td>
<td>0.083333</td>
<td>0.288675135</td>
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<td>0.040598</td>
<td>3.79</td>
<td>0.06786</td>
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<tr>
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<td>0.5</td>
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<td>4.91</td>
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<tr>
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<td>0.707106781</td>
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<tr>
<td>A-4</td>
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<td>1</td>
<td>1</td>
<td>4.54E-05</td>
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<td>0.109937</td>
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</tbody>
</table>

**Table 2.2. ICP-OES data from copper ore concentrate activation.**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>time</th>
<th>time</th>
<th>SQRT[time]</th>
<th>[Cu]</th>
<th>[Cu]</th>
<th>[Fe]</th>
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<tr>
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<td>0.083333</td>
<td>0.288675135</td>
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<td>0.5</td>
<td>5.14</td>
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</tr>
<tr>
<td>B-3</td>
<td>30</td>
<td>0.5</td>
<td>0.707106781</td>
<td>4.68</td>
<td>0.073643</td>
<td>7.77</td>
<td>0.139123</td>
</tr>
<tr>
<td>B-4</td>
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<td>1</td>
<td>1</td>
<td>3.91</td>
<td>0.061526</td>
<td>8.5</td>
<td>0.152193</td>
</tr>
<tr>
<td>B-5</td>
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<td>1.224744871</td>
<td>3.175</td>
<td>0.049961</td>
<td>8.95</td>
<td>0.160251</td>
</tr>
</tbody>
</table>
Figure 2.4. Change in the aqueous metal concentrations of Cu and Fe during the activation of chalcopyrite at 80 °C. The linear plots indicate that molar exchange of chalcopyrite iron by aqueous Cu$^{2+}$ occurs via a diffusion-controlled process.

Some important observation from these data are that the Cu/Fe ratios in both samples (pure chalcopyrite and copper concentrate) and FLSmidth paper are different. Chaiko, et al., calculated a ratio of 0.74 based on the linear correlation of their concentration vs. root-time data. However, we found that Sample A (pure chalcopyrite) has a Cu/Fe ratio of nearly 1.0 (corresponding to a metathesis reaction) and Sample B has a ratio of 1.74 (which happened due to an oversupply of copper ions, because the concentrate contains species other than chalcopyrite). Although the activation process can be seen ideally as a metathesis reaction, there have been observed inconsistencies in the Cu/Fe ratio both at the lab-scale setup at DTU and pilot plant at FLSmidth, so the reaction will be simply referred to as the activation reaction.

2.3 Investigating pure mineral chalcopyrite with electron microscopy
Scanning electron microscopy (SEM) of pure chalcopyrite (CuFeS$_2$) samples was performed at the Center for Electron Nanoscopy (CEN) at DTU using an FEI Quanta 200 ESEM with Field Emission Gun (FEG). Figure 2.5 shows the SEM image of a large number of chalcopyrite particles. Image analysis was performed with ImageJ software to find that the particle size ranges up to 30 μm.
Figures 2.6 – 2.8 have the x-ray energy dispersive spectroscopy (EDS) data along with back-scattered electron (BSE) images. Figure 2.6 was selected for a single point analysis with spectral information while Figure 2.7 was performed in mapping mode with area analysis giving spectral information. Initially, the quantitative data was collected in weight percent for Figure 2.6, so ImageJ was used to recalculate the data in mole percent, which is close to the expected 1:1:2 ratio of Cu:Fe:S for chalcopyrite. One interesting observation in Figure 2.7 is that there exist parts of the mineral sample that are high in sulfur content, according to the mapping. Furthermore, the spectra in Figure 5 indicate a concentration of zinc present within the particle. It is not uncommon to find some zinc sulfide (sphalerite in particular) as an impurity in chalcopyrite mineral samples, and this seems to be the case when observing the very center of Figure 2.7, where there is a black region in the copper and iron maps but not for sulfur.

![SEM image of pure chalcopyrite (lighter colored grains) on carbon tape.](image)

**Figure 2.5.** SEM image of pure chalcopyrite (lighter colored grains) on carbon tape.

**Figure 2.6.** (left) SEM image of pure chalcopyrite particles with point analysis at two different particles (not indicated in current image) and (right) the two corresponding spectra.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Weight %</th>
<th>Mol %</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>36.57</td>
<td>0.0114</td>
<td>2.21</td>
</tr>
<tr>
<td>Cu</td>
<td>34.03</td>
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</tr>
<tr>
<td>Fe</td>
<td>28.81</td>
<td>0.0052</td>
<td>1.00</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Weight %</th>
<th>Mol %</th>
<th>Ratio</th>
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<tbody>
<tr>
<td>S</td>
<td>36.58</td>
<td>0.0114</td>
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<tr>
<td>Cu</td>
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<td>0.0054</td>
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<tr>
<td>Fe</td>
<td>28.65</td>
<td>0.0051</td>
<td>0.99</td>
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</table>
Figure 2.7. SEM mapping using K-alpha radiation to identify total elements (above) along with individual maps (below).

Figure 2.8. Corresponding areal EDS spectra (read labels 7, 8, and 9) from Figure 2.7 above.
2.4 Investigating activated chalcopyrite with electron microscopy

Transmission electron microscopy (TEM) was used to look at the fine structural information of the finely ground activated chalcopyrite sample, using the FEI Tecnai T20 G² at DTU CEN. The samples were deposited onto a carbon film grid by dipping the grid into the powder. Initially imaging was difficult because of the large size of the particles relative to the typical electron transmission length of ~100 nm. However, a few details were spotted, as shown below.

The particle has identifiable crystallinity (Figure 2.9) and, as such, the bulk (yellow box) was investigated. The Fast Fourier Transform (FFT) shows two crystallographic spots. This is a result of periodic symmetry from the crystal lattice being observed in the TEM image. This periodicity can be determined by taking a Fourier transform of the observed data and redrawing it in reciprocal (Fourier) space:

\[
\hat{f}(\xi) = \int f(x)e^{-i\pi x \xi} dx \tag{Equation 2.2}
\]

where \(f(x)\) represents a point, coordinates of \((x_1, x_2)\), on a 2-dimensional image and \(\hat{f}(\xi)\) is the resulting transformed point in reciprocal space that might refer to a frequency (or crystallographic distance, referred to as d-spacing, in this case). In reality, an FFT is discretized, so the treatment is done through summation rather than integration.

By fitting for the maxima using ImageJ software, it was found that the corresponding d-spacings in the image are 2.94 and 3.08 Å. When comparing with a crystallography database, which defines chalcopyrite as having a d-spacing of 3.0387 Å for the first major peak (Table 2.3), it can be explained that the bulk particle has approximately the same d-spacing (averaging the two points yields 3.01 Å). It would be less likely to be covellite, for instance (Table 2.4). The reason for only a single diffraction spot is the low resolution, which highlights only the primary d-spacing (see Figure 2.9).
Then, the surface of the particles was investigated, and it has a considerably lighter color in TEM compared to bulk and appears amorphous. However, by selecting a large area with a polygon tool (Figure 2.10), it was possible to discern three different d-spacings from the FFT. These correspond closely with the crystallography database on covellite (CuS),\textsuperscript{1} which identifies these as 3.0503 Å, 2.8154 Å, and 2.7267 Å, associated with the first three (high intensity) reciprocal lattice planes: (102)
for copper-copper, (103) for copper-sulfur, and (006) for sulfur-sulfur, respectively (see Figure 2.11). Similar to the FLSmidth paper (Table 5), it was found that the d-spacings are overall larger compared to the database for covellite, indicating that the lattice is more strained on the surface of chalcopyrite. Something that requires further investigation is the discrepancy in hkl planes between the currently used database and the one used by FLSmidth (from AMCSD or ICSD), such as different lattice orientations being a possibility. This became the focus of the next section.

Table 2.3. Chalcopyrite (CuFeS$_2$) diffraction data from AMCSD.$^{37}$

<table>
<thead>
<tr>
<th>2-THETA</th>
<th>INTENSITY</th>
<th>D-SPACING</th>
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<th>K</th>
<th>L</th>
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<td>1</td>
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<td>1.2049</td>
<td>3</td>
<td>1</td>
<td>6</td>
</tr>
</tbody>
</table>
Figure 2.10. TEM of activated chalcopyrite particles with focus on the surface of the particle. Top inset: FFT of yellow polygonal area. Bottom inset: Results of maxima fitting in ImageJ (R in units of nm).
Table 2.4. Covellite (CuS) diffraction data (only showing first 13 peaks) from AMCSD.\textsuperscript{38}

<table>
<thead>
<tr>
<th>2-THETA</th>
<th>INTENSITY</th>
<th>D-SPACING</th>
<th>H</th>
<th>K</th>
<th>L</th>
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</tbody>
</table>

Figure 2.11. Crystal structure of covellite (CuS) showing sulfur atoms (yellow) and copper atoms (brown). Bond lengths between the first three (high intensity) nearest neighbors – copper-copper (102) plane, copper-sulfur in (103) plane, and sulfur-sulfur in (006) plane – are more easily seen in the low-resolution TEM results. Figure produced in Jmol.\textsuperscript{23}
2.5 X-ray and electron diffraction of activated chalcopyrite powder

X-ray diffraction (XRD) was performed on the unreacted, pure chalcopyrite powder used for activation experiments as well as the activated powder after drying at 80 °C for 16 hours. These results are summarized, respectively, in Tables 2.6 and 2.7. The d-spacings were matched very closely with the database reference for chalcopyrite, indicating that the bulk material is the same. Because the activated chalcopyrite has a small percentage of the surface that is converted and the x-rays can penetrate through the sample, the results closely match that of pure chalcopyrite (see Figure 2.12 for an overlay of the two spectra). Correspondence with FLSmidth indicates that these particles may have been able to relax, because the results from previous studies show that the d-spacings should be mismatched due to the large amount of lattice strain that the surface layer imparts.

Table 2.6. Peaks from XRD of pure chalcopyrite before activation.

<table>
<thead>
<tr>
<th>Chalcopyrite from database</th>
<th>Unreacted Pure Chalcopyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>Intensity</td>
</tr>
<tr>
<td>3.345</td>
<td>282.5017</td>
</tr>
<tr>
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<td>1.576</td>
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<td>1.069</td>
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Table 2.7. XRD of pure chalcopyrite after activation.

<table>
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<th>Activated Pure Chalcopyrite</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

Figure 2.12. Combined XRD patterns for pure and activated chalcopyrite samples. Crystallographic planes are labeled for the major peaks. Quartz peaks are labeled “Q.” Reprinted from Karcz, et al. 39
To better elucidate the nature of these particles, focused ion beam (FIB) secondary electron microscopy (SEM) was utilized to prepare a slab that is “electron-thin” (e.g., < 100 nm). This was performed at DTU CEN, as SEM before, with an FEI Helios EBS3 with Ga⁺ ion source (variable accelerating voltage 1 to 30 kV during these runs). An example of this process is shown in Figure 2.13.

Figure 2.13. a SEM image of the activated chalcopyrite particle before FIB milling. The green area indicates the region where platinum would be deposited and around which ions would mill away to remove a slab for study. b The slab after milling at 30 kV is attached to a TEM grid by depositing platinum. The layer of platinum on top is the remainder from the previous step. c The slab is still too thick so milling proceeded until the thickness was < 100 nm (1 – 5 kV). Fragile parts of the slab were broken away. d TEM image of the same slab after thinning, but with higher magnification (top section). Reprinted from Karcz, et al.³⁹
TEM images of some areas of interest were once again taken in bright field mode with a Tecnai T20 G² at 200 kV accelerating voltage. This time, select area electron diffraction (SAED) was used in noticeably different regions of the sample. Since platinum deposit was present, this allowed for calibration of the diffraction patterns (Figure 2.14).

<table>
<thead>
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</tr>
</thead>
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<td></td>
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</tr>
<tr>
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<td>13.896</td>
</tr>
<tr>
<td>[0 4 4]</td>
<td>14.431</td>
<td>14.267</td>
</tr>
</tbody>
</table>

Figure 2.14. (Left) Ring diffraction pattern of deposited platinum for use in FIB milling. Fitted ring pattern (using platinum reference AMCSD 0018006) is shown with lines indicating the associated lattice planes. (Right) Table showing the analysis from the fitting. Reprinted from Karcz, et al.39

The differences in regions can be more clearly seen in Figure 2.15, where two regions of interest are observed in the activated samples. The key features to take note of are those that appear to be either polycrystalline (as in the upper region of Figure 2.15a) or seemingly single-crystal region (as in the lower part of Fig. 6.3a). Further, these two areas were found to have significantly different diffraction patterns. In particular, the fitting methods for these two regions required separate schemes, explained later. It should be noted that this image comes from a region ~8 μm from the particle surface.

Even though the middle and lower regions of the slab sample in Figure 2.15 look qualitatively different by eye, further inspection of their diffraction patterns showed that their patterns were instead simply different crystallographic directions of the same chalcopyrite lattice (or a very close fit to them when analyzing the d-spacings calculated from fitting).

To guarantee that observed changes are consistent, the diffraction patterns were analyzed according to two different fitting schemes that yielded nearly identical results. The first scheme consisted of transforming the diffraction spots into a radial distribution profile (see Figure 2.16). Peak fitting was then performed to identify the major peaks of each of the profiles (Table 2.8). Based upon this analysis, it became possible to determine that there were overlaps between the spectra of the two
lower chalcopyrite regions (the areas labeled crystals A and B in Figure 2.15). Something to note, though, was that their peak signals did not have the same intensities, coming about from the understanding that diffraction must have been along different zone axes.

![Figure 2.15](image)

**Figure 2.15** a TEM image of the area over which the following diffraction patterns were taken. Circles on the image indicate the corresponding diffraction patterns to follow. b SAED pattern which is referred by the upper circle in the previous image and within a polycrystalline activated region. c SAED pattern which is referred by the middle circle and corresponds to a possible chalcopyrite region (denoted “crystal A”). d SAED pattern corresponding to a bulk chalcopyrite region, which is referred by the lower circle (denoted “crystal B”). Twinning was observed in c and d.

Another important observation that became evident from the analysis of diffraction patterns is that the d-spacings from the activated and non-activated regions are heavily mismatched. This observation was expected, since the activated regions are anticipated to be partially converted to a complex copper sulfide, as mentioned earlier (coming from previous work by Chaiko, et al.).

It is important to note that these regions, which are apparently not activated, also displayed very different crystallographic parameters, relative to their reference values, especially considering that
these values were initially found to have similar d-spacings with chalcopyrite reference data, according to XRD analysis.

The other scheme used for analysis relied on the crystallography toolbox software, known as CrysTBox.\textsuperscript{40–42} This software was utilized to find the best match for the observed diffraction patterns in comparison to reference data. Some examples of the analysis completed with CrysTBox can be seen in Figures 2.17 – 2.19 and Tables 2 and 3.

![Figure 2.16](image)

**Figure 2.16.** The radial distribution profile of the three diffraction spots indicated in Figure 2.15. Reprinted from Karcz, et al.\textsuperscript{39}

Regarding the chalcopyrite crystals A and B, which contained only a few crystallites with observable diffraction spots, it was simple to perform the fitting using few parameters in the CrysTBox software (see Figure 2.17). Since the product of the activation reaction was expected to have a covellite-like crystal structure, reference data for covellite\textsuperscript{43} was used during the fitting. Unfortunately, it was not simply a diffraction pattern for covellite, since the fitting did not get a good match with the reference pattern. Indeed, it was found to contain matches for lattice vectors that normally belong to forbidden planes of covellite. Even though this was a non-trivial fitting scheme because there was more than one crystal to fit, it was possible to focus on a single set of prominent crystal diffraction spots. By associating each observed spot to a lattice vector (Figure 2.17b), CrysTBox software was able to identify that the zone axis of crystal A was [0 -2 1]. Similarly, the zone axis of crystal B was identified as [1 -1 0]. These results support the earlier fitting method based on the radial intensity peak analysis, and align with the conclusion that the differences were due to different diffraction directions. Further information on and confirmation of the lattice vectors and associated planes can be seen in Figures 2.18 and 2.19. In particular, one may take note of intensities of the diffraction spots fit using CrysTBox related to lattice vectors A, B, and D (see Table 2.9). These planes also have approximate the same ratio for diffraction spot sizes in the pattern and simulation alike.
Figure 2.17. Simulated diffraction pattern with chalcopyrite reference data (AMCSD #0018623) for chalcopyrite crystal A. **A** Lattice vector was identified after spot-matching. **B** Zone axis was identified to be [0 -2 1] based on vectors above. Reprinted from Karcz, et al.\(^{39}\)

Table 2.9. Summarized results of lattice parameters and associated vectors from Figure 2.17.\(^{39}\)

<table>
<thead>
<tr>
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<th>d-spacing [Å]</th>
<th>d-spacing [nm]</th>
<th>Vector identification</th>
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<tr>
<td>B</td>
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</table>

Figure 2.18. **A** Unit cell generated in CrysTBox using chalcopyrite reference data (AMCSD #0018623) and the (1 -1 -2) and (2 0 0) lattice planes (blue on right and red on left, respectively). The atoms are as follows: iron in red, copper in blue, and sulfur in yellow. Reprinted from Karcz, et al.\(^{39}\)
Figure 2.19. The simulated diffraction pattern from Figure 2.17 along the [0 -2 1] zone axis with highlighting of the two planes (same color coding for planes). Note the similar ratio of spot sizes with Figure 2.17b. Reprinted from Karcz, et al.39

With regards to the activated region in which the diffraction pattern appears to have a high degree of polycrystallinity, a simulated ring diffraction scheme for fitting (Figure 2.20 and Table 2.10), commonly utilized for amorphous materials, was performed. In this area of the sample, which is located ~8 μm from the surface (and recurring throughout the particle), chalcopyrite reference data did not provide a good fit in relation to the XRD pattern, so covellite reference data were used instead. However, the validity of this fitting is questionable since Miller indices of 7 are found. These planes are considered forbidden in the crystal lattice, but the diffraction data provides a more suitable match for fitting of d-spacings associated with covellite than the chalcopyrite reference pattern (and with more precise results). In conclusion, it can be said that the activated region was more successfully identified using SAED within TEM, while powder XRD was not sensitive enough to provide this level of detail.
Figure 2.20. Ring pattern fitting against covellite reference data (AMCSD 0000534) for the polycrystalline activated region.

Table 2.10. Summary report of associated Figure 2.19. Reprinted from Karcz, et al.44

<table>
<thead>
<tr>
<th>Plane</th>
<th>Radius [1/nm]</th>
<th>d-spacing [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[0 1 6]</td>
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<td>2.10</td>
</tr>
<tr>
<td></td>
<td>4.622</td>
<td>2.16</td>
</tr>
<tr>
<td>[1 1 0]</td>
<td>5.272</td>
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<td>1.89</td>
</tr>
<tr>
<td>[0 2 7]</td>
<td>7.443</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>7.647</td>
<td>1.31</td>
</tr>
<tr>
<td>[1 2 6]</td>
<td>8.85</td>
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<td>1.12</td>
</tr>
<tr>
<td>[0 3 2]</td>
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</tr>
<tr>
<td></td>
<td>9.274</td>
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<tr>
<td>[1 3 7]</td>
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<td>0.85</td>
</tr>
<tr>
<td></td>
<td>11.956</td>
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</tr>
<tr>
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<tr>
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<td>12.155</td>
<td>0.82</td>
</tr>
<tr>
<td>[2 3 7]</td>
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<td>0.72</td>
</tr>
<tr>
<td></td>
<td>13.925</td>
<td>0.72</td>
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</table>

Important to mention is that the d-spacings that were calculated using the radial distribution profile and crystal lattice fitting were found to share the same deviations from reference data. Even though the simulated pattern was able to determine the associated crystal planes and the zone axis, the identified values for these d-spacings appear to have significant lattice distortions that lead to straining of the mineral particle because of copper doping due to activation. It is also noteworthy that there are d-spacing values, which are larger than expected, observed in the supposedly non-activated regions of chalcopyrite. They are consistently larger than the reference values of 3.04 Å for the (1 1 2) plane, 1.85 Å for the (0 2 4) plane, and 2.65 Å for (2 0 0) plane. Another point to mention is that ion milling has an unintended consequence of also increasing the d-spacing of the (1 1 2) plane.
even in pure, non-activated chalcopyrite mineral, but this is not observed in the other planes (see Figure 2.21 and Table 2.11). It is likely that this may be due to atoms in the lattice that are located at larger distances from one another, which then results in a lower atomic density. Since the particles have been ion-milled to a thickness <100 nm for electron transparency, it was anticipated that the chalcopyrite particles would no longer be strained. However, some strain seems to be native to these particles even before activation, but the effect of activation causes the particles to be even further strained, as the lattice d-spacings show changes in multiple planes.

**Figure 2.21.** a TEM image of a slab of pure mineral chalcopyrite after ion-milling with regions of interest highlighted in yellow. b Diffraction patten from region 1. Reprinted from supplementary information of Karcz, et al.44
Table 2.11. Calculated d-spacings from the three regions in Figure 2.21 using CrysTBox software. Region 2 differs from the other two regions in that it is highly polycrystalline, but otherwise shares d-spacings with the other regions. Reprinted from supplementary information of Karcz, et al.44

<table>
<thead>
<tr>
<th>VECTOR</th>
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<th>region 2</th>
<th>region 3</th>
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<tr>
<td>[0 1 3]</td>
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<td></td>
<td>2.83</td>
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</tr>
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<td></td>
</tr>
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<td></td>
</tr>
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<td>1.87</td>
<td></td>
</tr>
<tr>
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<td>1.68</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>1.32</td>
<td>1.32</td>
<td>1.31</td>
</tr>
<tr>
<td>[1 2 7]</td>
<td>1.26</td>
<td>1.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[0 4 4]</td>
<td>1.18</td>
<td></td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>[0 3 7]</td>
<td>1.14</td>
<td>1.15</td>
<td>1.12</td>
<td>1.14</td>
</tr>
<tr>
<td>[2 3 7]</td>
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<td></td>
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</tr>
<tr>
<td>[0 5 5]</td>
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<tr>
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<td>0.86</td>
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<td></td>
</tr>
<tr>
<td>[2 6 2]</td>
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</tr>
<tr>
<td>[3 7 0]</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>

The effects of activation outline above appear to have important contributions that lead to the promotion of enhanced reaction kinetics of chalcopyrite particles within the mechanochemical leaching system of the ROL process. Crystalline deformations in solids have previously been reported to affect chemical reaction kinetics and transport phenomena.45,46 Indeed, natural mineral chalcopyrite has been found to modify its structure to resemble other lattices.47 Thus, it is also anticipated that the lattice strain imparted by activation may be responsible for lowering the activation energy necessary for the dissolution of copper during leaching. It is possible that activation may be performed with a dopant other than copper. Although experimental work on alternatives did not fit within the scope of this study, some predictions are supported with atomistic calculations and presented later in Chapter 5.

Additionally, it is possible that the mineral chalcopyrite will be prone to fracturing in the presence of high mechanical energy imparted by the Stirred Media Reactor (SMRt) of the ROL process, since the amorphous, highly activated regions can be found throughout the particle, including the analysis of a region found 8 μm away from the surface. Even though the physical changes observed as a result of
the activation reaction do not present clear evidence as to their effect on the electrochemical properties, the significant strain in the mineral lattice still leads to a better understanding of one of the main mechanisms responsible for enhanced copper leaching. A thorough understanding of the electrochemistry needs to be established to support these insights, and that is the subject of the next chapter.
Chapter 3. Characterization of Chemical Changes

Pure chalcopyrite samples of the same source as in Chapter 2 were characterized using the K-Alpha™ X-ray Photoelectron Spectroscopy (XPS) system at DTU Danchip (now part of DTU Nanolab). This instrument uses aluminum Kα radiation as its source with an ion gun of 100 – 4000 eV range. For all characterization, a flood gun was used because of charging on the surface producing poor signal-to-noise ratio. An example of a full spectrum measured with the instrument on a sample of pure chalcopyrite mineral is presented in Figure 3.1, generated using Avantage software from Thermo Fisher. For peak fitting, a Powell fitting algorithm was used with convolved Gauss-Lorentz mixing. Activated chalcopyrite was also studied, and this was done with the same samples used in the diffraction studies.

Figure 3.1 Full XPS spectrum of pure mineral chalcopyrite. Green lines indicate background baseline fitting used when identifying major peaks with Avantage software.

3.1 Background on x-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive (typically within a few dozen nanometers) characterization technique, developed by Kai Siegbahn and his group in 1954, which is capable of determining the chemical composition of samples to the parts per thousand limit. It can also be used to identify chemical and electronic states of elements within that sample. The characteristic spectrum is generated by using (usually monochromatic) x-ray radiation directed as a
beam onto the surface under very high vacuum, and a detector collects information about the kinetic energy and the number of electrons. With this kinetic energy, $E_K$, one can then calculate the binding energy, $E_B$, of electrons using the equation associated with Rutherford’s work in 1914:

$$E_B = E_p - E_K - \phi$$

(Equation 3.1)

where $E_p$ is the energy of a photon, and as mentioned earlier, aluminum Kα is used, which has an energy of 1.487 keV, and $\phi$ is the work function, which is a correction factor dependent on the instrument.

The peaks found in an XPS spectrum are characteristic of the binding energies of electrons of different configurations, such as 1s, 2s, 2p, 3s, 3p, 3d, and so on. It is also not uncommon to find orbital splitting at p orbitals or higher (s orbitals only have a single spin angular momentum number, $j = \pm \frac{1}{2}$). The higher orbitals produce doublets, which have typical area ratios as follows in Table 3.1.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>j</th>
<th>Area Ratio</th>
</tr>
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<tbody>
<tr>
<td>p</td>
<td>1/2</td>
<td>3/2</td>
</tr>
<tr>
<td>d</td>
<td>3/2</td>
<td>5/2</td>
</tr>
<tr>
<td>f</td>
<td>5/2</td>
<td>7/2</td>
</tr>
</tbody>
</table>

3.2 Analysis of copper 2p binding energy

The 2p spectra of copper is the most prominent of this atom (see Figure 3.1), so it was closely studied. It can be seen in Figure 3.2 below that all of the unmodified chalcopyrite Cu-2p$_{3/2}$ peaks (red, pink, and orange) are centered on ~932 eV. The samples are labeled based on the location they were prepared, such as FLS for FLSmidth and DTU for locally prepared samples. The additional note of “10m” represents that the sample was finely ground in a planetary ball mill (Pulverisette 6 from Fritsch) for 10 min. The coloring scheme of the spectra was meant to separate pure mineral and activated samples by using red hues for the former and blue ones for the latter. The slight redshift observed can be attributed to freshly cleaved surfaces that reduce the area of oxidized surfaces.

The activated samples have the trend of blueshifting with respect to the pure mineral. The furthest shift is observed from the activated sample at FLSmidth (5% conversion, green). The next furthest is the sample with activation done at DTU (incomplete with <5% conversion, teal). Finally, the lowest degree of shifting is from the 10 min milled sample (blue), which, similar to the pure sample, has more surface area from the non-oxidized bulk exposed. This is why the shift is the least of the activated samples. The blueshift is important because it represents the oxidization of copper, such as a shift from Cu$^{1+}$ to Cu$^{2+}$ (see Figure 3.3), which is the expected change that occurs during activation, when Cu$^{2+}$ ions replace the Fe ions in chalcopyrite. It is also interesting to note, although not
surprising, that there seems to be a general shift, rather than a new peak, likely a result of the higher degree of activation on the surface.

**Figure 3.2.** XPS spectra of pure and activated chalcopyrite particles at the copper 2p\textsubscript{3/2} range.

**Figure 3.3.** XPS spectra of different Cu-bearing materials showing the shift in peaks due to oxidation state. Data included with Avantage software.
3.3 Analysis of iron 2p binding energy

The iron 2p range is also the most relevant for the element. Unfortunately, the spectra are difficult to discuss about trends since they tend to overlap. The comparison of FLSmidth samples (red and green) show a slight shift in the 2p\textsubscript{3/2} (from \~711 eV to \~713 eV) and 2p\textsubscript{1/2} (from \~724 eV to \~727 eV) ranges. However, there are no significant differences in the other sets.

![Figure 3.4. XPS spectra of pure mineral and activated samples in the Fe-2p range.](image)

3.4 Analysis of sulfur 2p binding energy

Similar to the previous two elements, sulfur’s range of interest belongs also to the 2p range. In particular, the changes that occur in the sulfide range (around 160 – 166 eV) are the most relevant (see Figure 3.5), since metal-sulfur bonds are the ones associated with chalcopyrite. With the same color convention as in the previous sections, it can be once again observed that a shift to higher energy with respect to pure mineral sample occurs. Such an effect is also observed in the oxidation of sulfite (SO\textsubscript{3}) to sulfate (SO\textsubscript{4}), as shown in Figure 3.6. The sulfur in sulfate has an oxidation state of +6, while in sulfite it has an oxidation state of +4. Indeed, we can see a similar shift in the sulfate range of the spectra (Figure 3.7 includes the full range with the FLSmidth samples isolated for clarity), where there appears to be oxidation of the chemical state to a higher number.

Of particular interest in the sulfide range, there is the appearance of multiple peaks. As can be from Figure 3.7 and fitting results in Figure 3.8, the pure mineral chalcopyrite is best described when considering three oxidation states. Since chalcopyrite is known to have a major peak (161.8 eV)\textsuperscript{48} close to that of Cu\textsubscript{2}S (161.6 eV),\textsuperscript{49} this peak has been attributed with a S\textsuperscript{2-} oxidation state. The next peak lies close to that of CuS,\textsuperscript{43} which has a formal charge of -1, so the peak was designated S\textsubscript{2}\textsuperscript{2-}, since that would satisfy the charge per atom (recall Equations 1.18 and 1.19 for proposed oxidation
states of sulfur in covellite). Following this, the third peak should be at a lower charge per atom ratio, so it has been designated a polysulfide, $S_n^{2-}$, like that of elemental sulfur, $S_8$, which has a peak around 163.7 eV. The original of this peak is not very clear, but it may be a result of sulfur-rich species on the surface of the particles. Computational studies of chalcopyrite have shown that sulfur tends to prefer reorganizing to the surface, even when metal atoms had initially been the termination on the surface.

When looking at the activated samples, it is clear that the monosulfide, $S^{2-}$, is highly diminished. The peaks are shifted to a higher energy where the polysulfides begin to dominate. This is important when considering that covellite may be forming on the surface, since the structure contains sulfur-sulfur bonds (see Figure 2.11), which may be the reason for the shift. Another reason, related to the presence of covellite, is that presence of electron holes that are expected to exist in that mineral (Equations 1.18 and 1.19) may also affect the charge per atom ratio, since their effect is oxidative. These two points together show that XPS can be used to validate the effect of activation in the mineral chalcopyrite, producing a copper sulfide phase.

![Figure 3.5](image_url)

**Figure 3.5.** XPS spectra of pure and activated chalcopyrite particles at the sulfur 2p range. Colors are assigned the same as previous cases.
Figure 3.6. XPS spectra of different sodium sulfates showing the shift in peaks due to oxidation state. Data included with Avantage software.

Figure 3.7. XPS spectra of FLSmidth samples in the full sulfur 2p range (sulfides and sulfates).
A concern when using a sulfate solution to activate chalcopyrite with copper (sulfate) is that sulfates may influence the sulfide range of the spectra. For this reason, activation was also performed with a chloride solution (HCl substituted for HSO₄) and CuCl₂ in place of CuSO₄. The resulting spectra can be found below in Figure 3.9, which is shown alongside the activated spectrum from Figures 3.5, 3.7, and 3.8. As one can see, the blueshift is still observed in this system, and the sulfate peak is replaced with what may be described as hydrogen sulfide, since the peak is located close to that chemical state (170.7 eV). Because the peak is much broader than the sulfate system, a fourth polysulfide was included, S₉⁻, which is further oxidized with a lower charge per atom ratio. It is also a possibility that all the peaks are shifted to higher energies, since it was possible to fit the broad peak with either three or four fitted curves. To confirm that chlorine was no longer on the surface, the chlorine spectrum was found to have no observable peaks (Appendix A).
It becomes clear that the activation process has the effect of increasing the oxidation numbers of copper and sulfur. The former is due simply to the replacement of Cu$^{2+}$ for Fe$^{3+}$ in chalcopyrite, and the latter appears to be the result of a new phase that contains sulfur with decreased charge per atom, either because of the formation of polysulfide or presence of electron holes. The latter supports the hypothesis that covellite is present on the surface of particles.
Chapter 4. Quantum Mechanical Calculations

4.1 Background on Density Functional Theory

Density functional theory (DFT) is a computational modelling method (for which Walter Kohn received a Nobel Prize in Physics in 1998) used to predict the physical properties of systems based on the quantum mechanical principles. Primarily, it can compute these properties based on the electron density, $n(r)$, where $r$ is the position of an electron, of a given system. It is usually the case that the calculations require finding the minimum (ground state) energy, $E_0$, of the system. From there, other physical properties are calculated. These calculations are based on the Hohenberg-Kohn (HK) theorem, which states that the system (described by a Hamiltonian, $\hat{H}$) is completely determined by the external potential, $V_{\text{ext}}$, which is derived from the ionic potential of the nucleus, such that:

$$\hat{H} = \hat{T}_e + \hat{U}_{ee} + \hat{V}_{\text{ext}}$$

(Equation 4.1)

where $\hat{T}_e$ is the electron kinetic energy (one-body term), $\hat{U}_{ee}$ is the coulomb interaction of electrons (two-body term). Both of these terms, $\hat{T}_e$ and $\hat{U}_{ee}$, can be approximated to their non-interacting or classical forms plus the contribution of an exchange-correlation (XC) term, i.e., $E_{xc}$, arising from the remaining contributions to the real system. The exchange part relates to the Pauli Exclusion Principle, while the correlation part relates to Coulombic repulsion.

$$\hat{H} = \hat{T}^{\text{class.}}_e + \hat{U}^{\text{class.}}_{ee} + E_{xc} + \hat{V}_{\text{ext}}$$

(Equation 4.2)

The ground state energy, $E_0$, is calculated from the minimum eigenvalue of the Hamiltonian, and the total energy is considered a functional of the electron density, i.e., $E_i[n(r)]$. The eigenvalue is calculated with respect to an eigenfunction (vectorized form of a function), which in this case is the wave function, $|\psi_i\rangle$, so that we need to solve the following expression.

$$\hat{H} |\psi_i\rangle = E_i |\psi_i\rangle$$

(Equation 4.3)

In FHI-aims DFT code (eponymously named after the Fritz Haber Institute and the ab initio molecular simulations it uses), the wave function $|\psi_i\rangle$ is matrix-represented through numerical atom-centered orbitals (NAO’s), $\varphi_i(r)$, which include the numerically tabulated radial shape $u_i(r)$ and the complex spherical harmonics $Y_{lm}(\Omega)$ of the wave function.
\[ |\psi_i \rangle \Rightarrow \varphi_i(r) = \frac{u_i(r)}{r} Y_{lm}(\Omega) \]  

(Equation 4.4)

The radial shape is fully flexible and determined by a chosen basis set (for each \( l,m \) quantum number). A representation of these orbitals is given in Fig. A1. The basis sets in FHI-aims are labeled as “light,” “tight,” or “really-tight,” as examples, which differentiate by how many orbital shapes are included in their descriptions.

**Figure 4.1.** Atomic orbitals using radial function and spherical harmonic representation. The letters \( n, l, \) and \( m \) are the electron energy principal quantum number, angular momentum quantum number, and magnetic quantum number. The values of \( l \) and \( m \) are +/-, so they are not reproduced twice in this table. Orbitals were generated using Orbital Viewer (www.orbitals.com/orb/ov.htm).

This requires an iterative calculation loop (known as the self-consistent field, SCF) for DFT, represented in Figure 4.2.

**Figure 4.2.** Pictorial representation of a self-consistent field (SCF) iteration.
Using the approximations explained above, the ground state density using individual atoms is provided as a starting point with which the HK theorem calculates the ionic potential and corresponding effective potential (which includes XC energy):

\[ v_R(r) = \int \frac{n(r')}{|r - r'|} dr' + v_{\text{ion}}(r) + \frac{\delta E_{\text{xc}}[n]}{\delta n} \]  
(Equation 4.5)

From this potential, the wave function described above can be used to solve, in the simplest case, the single-particle equation (using only the one-body Hamiltonian terms):

\[ \left( -\frac{\hbar^2}{2m} \nabla^2 + v_R(r) \right) \phi_i(r) = \varepsilon_i \phi_i(r) \]  
(Equation 4.6)

Finally, the last step is the calculation of a new electron density:

\[ n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 \]  
(Equation 4.7)

The new electron density is inserted back into the calculation of the potential and iterated until the energy is minimized. This is used to relax the geometry of a system, i.e., the atomic spacings of a crystal lattice; calculate the electronic structure, i.e., energy band diagram and density of states (DOS); and so on. However, geometry optimization tends to converge more efficiently when the first and second derivatives of the energy with respect to nuclear coordinates are used. This requires solving an unconstrained nonlinear optimization problem that needs to be done iteratively, as in the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm\textsuperscript{55–59} used in all calculations in this work.

The XC term in Equation 4.5 can be approximated in a number of ways, and these are typically classified in four (or more) categories, listed in order of increasing tier (of higher complexity and lower error):

- Local-density approximation (LDA),

\[ E_{\text{xc}}^{\text{LDA}}[n(r)] = \int d^3r \cdot \xi_{\text{xc}}(n(r)) \cdot n(r) \]  
(Equation 4.8)
• Generalized gradient approximation (GGA),

\[ E^{\text{GGA}}_{\text{xc}}[n] = \int \{ d^3r \cdot \varepsilon_x(n, |\nabla n|, \ldots) \cdot n(r) \} + E_c[n, |\nabla n|, \ldots] \]  
(Equation 4.9)

• Meta-GGA, and

\[ E^{\text{MGGA}}_{\text{xc}}[n] = \int \{ d^3r \cdot \varepsilon_x(n, |\nabla n|, \tau(r), \ldots) \cdot n(r) \} + E_c[n, |\nabla n|, \tau(r), \ldots] \]  
(Equation 4.10)

• Hybrid functionals, e.g., B3LYP.

\[ E^{\text{B3LYP}}_{\text{xc}}[n] = E^{\text{LDA}}_{\text{xc}} + c_1 (E^\text{exact}_x - E^{\text{LDA}}_x) + c_2 E^{\text{GGA}}_x + c_3 E^{\text{GGA}}_c \]  
(Equation 4.11)

The main distinctions are as follows. In the LDA method, the XC energy is derived solely from the electron density (like that of a homogeneous electron gas), which is where its name comes from. In the equation above, this is colored in red to show where the important term is found. In the second tier, which is the GGA approach, the name also explains the major difference from the LDA, since it is apparent that gradients (colored in blue) are now included in the description of the energy. Another set of functionals, which becomes a tier higher, is the meta-GGA group, which takes GGA further by including the kinetic energy, \( \tau(\mathbf{r}) \), found through the Laplacian of the density (colored in purple). Finally, the fourth tier of hybrid functionals is aptly named because they contain a combination of the first two tiers along with the exact energy (colored green), often calculated from the Hartree-Fock (HF) method. \(^{60-62} \) The HF method predates DFT for calculation of atomic energies, and where the DFT method uses the electron density in its scheme, HF instead uses a determinant of single-electron wavefunctions. However, it is not able to take into account correlation, which is why only the x-term is used in the equation above.

It is expected that the computational time increases as one moves into higher tiers of approximation, although it tends to be that accuracy in the calculation is gained.

### 4.2 Density functional theory calculations of pure mineral chalcopyrite

#### 4.2.1 Calculating structural relaxation and electronic properties

As noted above, DFT calculations were performed using FHI-aims. \(^{53,54} \) A standard routine for calculation requires a control file, which contains information about the types of calculations that should be run, important parameters which affect the description of the calculation (including choice
of XC functional), and the basis sets for the atoms used in the run. An example of a control file is included in Appendix B. The second necessary input is the geometry file, which defines the positions of atoms and possibly extra characteristics like the initial spin moment (the difference in total electron spin, \( N^\uparrow - N^\downarrow \), on that site). Geometry files for a Cu-doped input file and reconstructed structures are included in Appendix C. The initial geometry file for chalcopyrite was prepared using CIF data from AMCSD #0018622, and it was converted into an aims input file with CIF2Cell from Bjorkman. The geometry input file can be seen in Table 4.1.

**Table 4.1.** Geometry data used for chalcopyrite in FHI-aims.

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>atom_frac</th>
<th>initial_moment</th>
<th>atom_frac</th>
<th>initial_moment</th>
<th>atom_frac</th>
<th>initial_moment</th>
<th>atom_frac</th>
<th>initial_moment</th>
<th>atom_frac</th>
<th>initial_moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.29000</td>
<td>0.00000</td>
<td>1.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
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<td>0.50000</td>
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<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
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<td>2.64500</td>
<td>0.50000</td>
<td>0.50000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
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<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
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<td></td>
<td>0.25000</td>
<td>0.75000</td>
<td>0.50000</td>
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<tr>
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<td></td>
<td>0.13540</td>
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<td>0.25000</td>
<td>0.25000</td>
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<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.86460</td>
<td>0.75000</td>
<td>0.75000</td>
<td>0.00000</td>
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<td>0.00000</td>
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<tr>
<td></td>
<td></td>
<td>0.61460</td>
<td>0.62500</td>
<td>0.25000</td>
<td>0.25000</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.87500</td>
<td>0.38540</td>
<td>0.75000</td>
<td>0.75000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

Literature has shown to give reasonable results of the bandgap energy \((E_g \approx 0.5 \text{ eV})^{64-69}\) of chalcopyrite based on the GGA functionals, as shown in Figure 4.3. The choice of k-points in the x-axis of this and future band diagrams comes from the tetragonal unit cell of chalcopyrite, and these points are chosen to describe as many vectors that would describe the electronic structure (see Figure 4.4 and associated Table 4.2). The k-points come about from the reciprocal space of the primitive unit cell, also known as the Bravais lattice, in the same manner as Fourier transforms described in §2.4. Since the planes are periodic in the crystal unit cell, these would be transformed into points in reciprocal space. Just like there exists a primitive unit cell that defines the crystallography, an analogue exists in reciprocal space as the Brillouin zone (Figure 4.4 for a tetragonal system). The points in the Brillouin zone are closely related to the Miller indices, which are also defined in reciprocal space. The symmetry elements of the unit cell can be completely described by the first Brillouin zone, which contains all the k-points, and these points are used to create pathways when designing the electronic band structure for calculations, since it should then capture its full description.
Figure 4.3. Chalcopyrite band structure from de Oliveira, et al.\textsuperscript{70}

Figure 4.4. The k-points are unique to the tetragonal crystal system. The wire-frame model is the Brillouin zone of the tetragon unit cell. The vectors comprise a partial set, since the complete set would contain vectors along all the outside edges, but the partial set is sufficient for description.

The bandgap is determined from the closest distance between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). In the band diagram of Figure 4.3, these two orbitals are separated by the Fermi energy level ($E_F$ or $\mu$), included as a dashed line in the figure. Known also as the electrochemical potential and named after Fermi-Dirac statistics, which show a distribution of the form:

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \quad \text{(Equation 4.12)}$$
It is especially pronounced at absolute zero, which also happens to be the temperature that DFT calculations are assumed to occur, there is a sharp change between the probability of finding electrons above or below the Fermi level, e.g. \( f(E) = 1 \) at energies below it. The Fermi energy is also the level, which at thermodynamic equilibrium, has a 50/50 probability of being occupied by an electron. Thus, bandgap arises when electrons are unable to move freely between the HOMO and LUMO because the Fermi level lies between them, and this leads to semiconductors and insulators. The difference between these two classes of materials depends on the size of the bandgap. Typically, semiconductors are those that have a bandgap less than 6 eV, since larger energies than that make it difficult to excite electrons from the HOMO to the LUMO. For instance, the solar spectrum varies up to a little over 3 eV, which gives a design requirement in the selection of solar cell materials. However, when the HOMO and LUMO bands intersect, this allows electrons to move freely and gives rise to metallic/conducting properties. The way that semiconductors are described as low bandgap insulators is the reason why they have been sometimes called “semi-insulators.”

Table 4.2. The k-points of interest of the tetragonal system above.

<table>
<thead>
<tr>
<th>k-point</th>
<th>Reciprocal space point</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma )</td>
<td>((0, 0, 0))</td>
</tr>
<tr>
<td>( Z )</td>
<td>((0, 0, \frac{1}{2}))</td>
</tr>
<tr>
<td>( X )</td>
<td>((\frac{1}{2}, 0, 0))</td>
</tr>
<tr>
<td>( R )</td>
<td>((\frac{1}{2}, 0, \frac{1}{2}))</td>
</tr>
<tr>
<td>( M )</td>
<td>((\frac{1}{2}, \frac{1}{2}, 0))</td>
</tr>
<tr>
<td>( A )</td>
<td>((\frac{1}{2}, \frac{1}{2}, \frac{1}{2}))</td>
</tr>
</tbody>
</table>

Since the real system is dependent on the XC energies, \( E_{xc} \), these energies need to be approximated a number of ways by different functionals, such as the commonly used PBE\(^{71,72} \) and PW91\(^{73,74} \) XC functionals. De Oliveira and Duarte\(^{70} \) have been able to calculate reasonable results of the band gap (~0.8 eV) of chalcopyrite based on the latter functional. However, it has been a challenge to reproduce these results using these XC functionals in FHI-aims. The reason for this is the use of a Hubbard U parameter (proposed by Liechtenstein, et al., \(^{75} \) and Dudarev, et al.\(^{76} \)), which adds a user-defined energy to a chosen atomic orbital (e.g., iron 3d in chalcopyrite) to account for Coulomb interactions in a simplified manner. Implementation of the Hubbard U value into FHI-aims has not led to converging results (despite varying U value and Petukhov mixing factor\(^ {77} \)), as in the paper referenced (see Appendix D).

Personal attempts at reproducing the band structure of de Oliveira, et al., instead displayed band mixing, indicating metallic properties (Figures 4.5 and 4.6). The potential reason for this is that FHI-aims uses the wavefunction approximation of NAO’s, while the other work uses pseudo-waves. Further literature review on this subject led to the finding based on a paper which tested different XC
functionals on semiconductor systems\textsuperscript{78}. They found that generally PBE and PW91 under-predicted the electronic bandgap as metallic (~0 eV), while hybrid functionals (e.g., B3LYP, B3PW91, and PBE0) were closer to experimental values. Upon close inspection of Figure 4.3, it is evident that their bandgap is approximately 0.1 eV, which is well below the experimental value.

**Figure 4.5.** Chalcopyrite band structure with FHI-aims using PW91 functional in “really-tight” basis. Fermi level is the red line.

**Figure 4.6.** Chalcopyrite density of states using PW91 in “really-tight” basis. Dashed line included for the Fermi level.
Furthermore, an analysis of many different functionals was performed to determine the ones, which would provide the most accurate representation of the physical structure of chalcopyrite, not just the electronic structure. A summary of this analysis is captured in Table 4.3, where it can be seen that BLYP and B3LYP gave the smallest change in structure (for comparison, thermal expansion to 0 K would yield about -1% reduction in unit cell volume). However, BLYP produced an electronic structure similar to PW91 above, so it was abandoned.

Table 4.3. Comparison of XC functionals for chalcopyrite. L represents a “light” basis, and T represents “tight.”

<table>
<thead>
<tr>
<th>XC Functional</th>
<th>Unit Cell Vol. (Å³)</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.³⁷</td>
<td>291.642</td>
<td>–</td>
</tr>
<tr>
<td>PBE(L)</td>
<td>268.936</td>
<td>-8%</td>
</tr>
<tr>
<td>PBE(T)</td>
<td>266.004</td>
<td>-9%</td>
</tr>
<tr>
<td>PBEint</td>
<td>259.39</td>
<td>-11%</td>
</tr>
<tr>
<td>PBEsol</td>
<td>not converged</td>
<td>n/a</td>
</tr>
<tr>
<td>revPBE</td>
<td>275.462</td>
<td>-6%</td>
</tr>
<tr>
<td>rPBE</td>
<td>277.834</td>
<td>-5%</td>
</tr>
<tr>
<td>PW91</td>
<td>265.726</td>
<td>-9%</td>
</tr>
<tr>
<td>BLYP</td>
<td>286.342</td>
<td>-2%</td>
</tr>
<tr>
<td>TPSS</td>
<td>267.184</td>
<td>-8%</td>
</tr>
<tr>
<td>revTPSS</td>
<td>262.114</td>
<td>-10%</td>
</tr>
<tr>
<td>PBE0(L)</td>
<td>not converged</td>
<td>n/a</td>
</tr>
<tr>
<td>PBE0(T)</td>
<td>not converged</td>
<td>n/a</td>
</tr>
<tr>
<td>HSE03(L)</td>
<td>268.342</td>
<td>-8%</td>
</tr>
<tr>
<td>HSE03(T)</td>
<td>265.9</td>
<td>-9%</td>
</tr>
<tr>
<td>B3LYP(L)</td>
<td>283.256</td>
<td>-3%</td>
</tr>
<tr>
<td>B3LYP(T)</td>
<td>280.57</td>
<td>-4%</td>
</tr>
</tbody>
</table>

As mentioned earlier, the real system is dependent on the exchange-correlation energies, $E_{xc}$. These energies are approximated in many numbers of ways by different groups, such as the commonly used PBE⁷¹,⁷² and PW91,⁷³,⁷⁴ which belong to the GGA tier of XC functionals. For example, Xiao, et al, have performed a detailed study,⁷⁸ which does not rely on the Hubbard parameter, for the parent minerals of copper indium gallium selenide (CIGS) semiconductors, copper indium selenide, CuInSe₂, and copper gallium selenide, CuGaSe₂. This has direct correlation to chalcopyrite, since all of these minerals belong in the I-III-VI₂ family of semiconductors. In the study, Xiao, et al., tested different XC functionals on these two crystal structures. They found that generally PBE and PW91 (without the Hubbard U parameter) under-predicted the bandgap as being electronically metallic (~0 eV), while hybrid functionals, such as B3LYP, B3PW91, and PBE0, were much closer to experimental values. Upon close inspection of Figure 4.3, it is evident that their bandgap is approximately 0.1 eV, which is well below the experimental value of ~0.5 eV.
As shown above, the GGA functionals did not provide accurate descriptions, so, as a result, calculations using the B3LYP functional were performed with satisfactory results. Where the PW91 functional predicts metallic nature, the B3LYP functional correctly determines that there is a band gap. Comparing the DOS of the two functionals (Figures 4.5 – 4.8), it is evident that PW91 estimates the densities to be shifted by about +3 eV, since the curves look roughly the same otherwise. Calculations during this study have been able to reproduce a band gap similar to the experimental values when using the B3LYP functional\cite{79,80} with spin-relativistic effects included,\cite{53} as shown in Figures 4.7 and 4.8. Because the Fermi level is located between the HOMO and LUMO (marked on the band diagram of Figure 4.7), it means that the system is semiconducting, which accurately represents the natural mineral. From the DOS of Figure 4.8, it is also possible to identify that the major contribution to the HOMO comes from the sulfur p-orbital and the major contributor to the LUMO is the iron d-orbital. Furthermore, it can be seen that the band gap has been calculated to be approximately 0.52 eV, in good agreement with experimental results.

**Figure 4.7.** Band structure of chalcopyrite with B3LYP functional with spin effects included. The HOMO and LUMO are indicated on the graph, and the red line represents the Fermi level, to which the system is normalized. The position of the Fermi level between the HOMO and LUMO indicates semiconducting properties.
Figure 4.8. Density of states of chalcopyrite with B3LYP functional in “really-tight” basis with spin effects included. The dashed line at the origin represents the Fermi level, to which the system is normalized. The location of the Fermi level lies in a region of no electron density, indicating semiconducting properties. It can be seen here that the sulfur p-orbital and iron d-orbital are the major contributors to the HOMO and LUMO, respectively.

The unfortunate consequence is that the B3LYP functional requires much larger resources. In FHI-aims calculations, typically, 500 GB of RAM is necessary for the complex matrix calculations involved, and it requires about 10 days, while distributed over 192 nodes. The computation time can be reduced by changing from a “tight” basis set (related to the amount of wavefunctions included) to a lighter one, which results in about an order of magnitude decrease in time, while RAM usage is only reduced about 20%. Fortunately, DTU’s high-performance computing (HPC) center is very accommodating for these calculations, but because of the long calculation times, strategies to reduce computation time were attempted. The choice of basis set became the initial focus, since the electron density is described by how many orbital shapes are included. For that purpose, the full calculations of structural relaxation and band structures were compared with the “light” and “really-tight” basis sets. However, the features of the HOMO and LUMO gaps were significantly different (Figure 4.9), since the “light” basis set showed a larger bandgap (Figure 4.10) and appears to be an indirect-gap semiconductor rather than direct-gap as in the “really-tight” basis set (Figure 4.9).
Figure 4.9. Band diagram of pure chalcopyrite using B3LYP functional with “really-tight” basis set (left) and “light” basis set (right), for both relaxation and band calculations. The major difference is that chalcopyrite under really-tight basis is closer to a direct-gap semiconductor with a more accurate bandgap prediction.

Figure 4.10: Density of states for pure chalcopyrite using B3LYP in light basis. Axis labels are same as Fig. 4.8. However, the x-axis direction is reversed compared to that figure. It can be seen here again that the sulfur p-orbital and iron d-orbital are the major contributors to the HOMO and LUMO, respectively.

Fortunately, however, the calculated band diagram for the “light” relaxed structure is effectively the same as the one calculate with the “really-tight” basis set for structural relaxation (Figure 4.11). This provides significant computational savings, since relaxation is the most time-intensive step.
Figure 4.11. Band diagram of pure chalcopyrite using B3LYP functional with “really-tight” basis set for band calculation but “really-tight” basis for relaxation (left) and “light” basis set for relaxation (right).

Using the light basis with B3LYP, the 3D plots of the total electron density and HOMO and LUMO were generated (see Figure 4.12). What can be seen in the plot of total electron density is that copper (central atom in all diagrams of Figure 4.12) does not share electron density with sulfur (atoms surround each of the metal atoms) as readily as iron (cf. Figure 4.12a with the other figures). This is observed again in the HOMO/LUMO plots where the orbitals of iron and sulfur are mixing. This gives one the impression that copper is not strongly bound in the chalcopyrite structure, and should be easy to remove. The fact that this is not the case indicates that surface chemistry must play an important role in preventing efficient leaching. Therefore, modeling of the surface with copper activation became of high interest to determine how the surface structure changes. Fortunately, there has been other work done one surface structure of pure chalcopyrite, which can be used as a comparison. The surface calculations are described later in §4.3.2.

Some further interesting observations from the HOMO/LUMO are the shapes of the orbitals. For instance, sulfur has the expected 3p shape (cf. Figure 4.1). In the HOMO plot, copper orbital resembles 3d(m=1,2) while iron has representations of 3d(m=0,1,2) with mainly 3d(m=0) iron atomic orbitals mixing with sulfur. Surprisingly, the orbital mixing of iron with sulfur switches to different iron atoms in the LUMO plot. The iron orbitals seems to be exclusively 3d(m=0) while copper is now a mixture of 3d(m=0,1,2). It should be noted that 3d(m=1) and 3d(m=2) are difficult to differentiate because their shapes are the same but rotated (cf. Figure 4.1).
Figure 4.12. a Ball-and-stick diagram of the chalcopyrite crystal structure generated with Jmol software. b Total electron density plot with iso-value of 0.6. c Plot of the HOMO with iso-value +0.01 for symmetric orbital (red) and -0.01 for anti-symmetric (blue). d Plot of the LUMO with iso-value +0.01 for symmetric orbital (orange) and -0.01 for anti-symmetric (cyan). The latter three were generated in PyMOL Viewer after calculation in FHI-aims with B3LYP in light basis.
Additionally, Mulliken charge analysis was performed in FHI-aims to help determine the oxidation states of copper and iron in chalcopyrite mineral. Table 4.4 shows the results from a B3LYP calculation. Copper and iron have approximately fully filled \( s \) and \( p \) orbitals. Copper has nearly 10 electrons in the \( d \) orbital, indicating a +1 oxidation state, while iron has over 6 electrons, giving it a +4 oxidation number (an unrealistically high value). This supports previous literature that reports +1 for copper and +3 for iron (if it can be assumed that the analysis under-estimates the number of \( d \)-orbital electrons). Sulfur shows \(-10\) electrons in \( p \) \((l = 1)\), representing a \(-2\) charge, as expected. Although the charge analysis only gives fractional numbers, the ratio of charge is approximately correct. Mulliken analysis should be taken with some care, since the charges are commonly ill defined.

Table 4.4. Mulliken charge and population analysis of chalcopyrite with B3LYP in “really-tight” basis with spin effects included. The \( f \) and \( g \) orbitals are excluded from the table since they had values below 0.03.

<table>
<thead>
<tr>
<th>atom</th>
<th>electrons</th>
<th>charge</th>
<th>( s )</th>
<th>( p )</th>
<th>( d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>28.680</td>
<td>0.320</td>
<td>6.317</td>
<td>12.537</td>
<td>9.795</td>
</tr>
<tr>
<td>Cu</td>
<td>28.679</td>
<td>0.321</td>
<td>6.316</td>
<td>12.536</td>
<td>9.795</td>
</tr>
<tr>
<td>Fe</td>
<td>24.874</td>
<td>1.126</td>
<td>6.276</td>
<td>12.460</td>
<td>6.119</td>
</tr>
<tr>
<td>Fe</td>
<td>24.874</td>
<td>1.126</td>
<td>6.276</td>
<td>12.460</td>
<td>6.119</td>
</tr>
<tr>
<td>S</td>
<td>16.723</td>
<td>-0.723</td>
<td>5.895</td>
<td>10.676</td>
<td>0.127</td>
</tr>
<tr>
<td>S</td>
<td>16.723</td>
<td>-0.723</td>
<td>5.895</td>
<td>10.676</td>
<td>0.127</td>
</tr>
<tr>
<td>S</td>
<td>16.723</td>
<td>-0.723</td>
<td>5.895</td>
<td>10.676</td>
<td>0.127</td>
</tr>
<tr>
<td>S</td>
<td>16.723</td>
<td>-0.723</td>
<td>5.895</td>
<td>10.676</td>
<td>0.127</td>
</tr>
<tr>
<td>Total</td>
<td>174.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3 Density functional theory calculations of activated chalcopyrite

4.3.1 Effect of doping the chalcopyrite lattice

In an attempt to mimic doping of the unit cell, additional B3LYP calculations were done by substituting half of the iron atoms with copper, e.g., \( \text{Cu}_{1.5}\text{Fe}_{0.5}\text{S}_2 \). Since the DFT calculations of a unit cell require 8 atoms (2 copper, 2 iron, and 4 sulfur), one out of the two iron atoms in the geometry file was replaced with a copper, and a calculation was performed. Since the ROL activation process introduces copper (II) into the chalcopyrite structure, this results in a negatively charged system (\( \text{Fe}^{3+} \rightarrow \text{Cu}^{2+} \)), and this was included as a net \(-1\) charge in the control file. As can be seen from the results in Figures 4.13 and 4.14, the system behaves metallically since the Fermi level is situated between orbitals. The shape of the HOMO (sulfur 2p) in the pure chalcopyrite is reproduced as the “HOMO” in the doped system (also the sulfur 2p), but the Fe-3d LUMO is shifted down, closer to the “HOMO,” when it appears as the “LUMO.” Regardless, both of these are above the Fermi level, giving rise to metallic behavior.
Figure 4.13. Band structure and of 50% copper-doped chalcopyrite, Cu$_{1.5}$Fe$_{0.5}$S$_2$, with B3LYP functional with spin effects included. The possible HOMO and LUMO are indicated on the graph, and the red line represents the Fermi level, to which the system is normalized. The net charge is $-1$.

Figure 4.14. Density of states of 50% copper-doped chalcopyrite, Cu$_{1.5}$Fe$_{0.5}$S$_2$, with B3LYP functional with spin effects included. The possible HOMO and LUMO are indicated on the graph, and the dashed line at the origin represents the Fermi level, to which the system is normalized.
4.3.2 Modelling a solvated surface of chalcopyrite

As a consequence of the heavy computations required for using the B3LYP functional and because a surface calculation with water molecules requires at least 22 atoms, the PBE functional was employed to produce desirable results at a lighter computational workload, which could be later validated with a longer B3LYP calculation. In a first set of calculations, water molecules were placed on a chalcopyrite (001) surface to mimic solvation (built with Virtual Nanolab\textsuperscript{86,87}). The (001) cleavage was chosen because it has the most interesting features to observe, since it is the most likely to reconstruct with disulfide dimers\textsuperscript{88} and has two distinct terminations: sulfur-rich and metal-rich. There are a number of locations that these molecules can be deposited onto the surface; however, the orientations in which water was placed over a sulfur atom were able to converge the fastest (or at all) in calculations, so the water molecules were located with oxygen in the same horizontal position as sulfur atoms. The orientation of the water molecules with respect to the surface is important, so two configurations were compared: water with hydrogen atoms directed toward and away from the surface (see Table 4.5). The absorption energies of the different solvated surfaces was calculated as:

\[
E_{\text{Abs}} = E_{\text{CuFeS}_2 + n \cdot H_2O} - E_{\text{CuFeS}_2} - E_{n \cdot H_2O}
\]  

(Equation 4.12)

The calculated absorption energy is given as per unit surface area (chalcopyrite has 5.289 Å × 5.289 Å in the (001) plane) and per surface water molecules (two can fit within this surface). Little change in the absorption energy was observed, and since the away direction was lower in energy, that orientation was kept.

Table 4.5. Comparison of initial water molecule orientations on sulfur-terminated surface with two water molecules above chalcopyrite (001) surface. Absorption energy is shown normalized per surface area and per surface water molecule.

<table>
<thead>
<tr>
<th>Hydrogen orientation</th>
<th>Absorption energy (eV/nm\textsuperscript{2})</th>
<th>Absorption energy (eV/molec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Away from surface</td>
<td>-2.67889</td>
<td>-0.37483</td>
</tr>
<tr>
<td>Toward surface</td>
<td>-2.64406</td>
<td>-0.36996</td>
</tr>
</tbody>
</table>

The two different surface terminations were compared, one which was sulfur-terminated (Figures 4.15 and 4.16), and the other was metal-terminated (Figures 4.17 and 4.18). What is obvious from these calculations is that water does not bind to sulfur on the surface, and the sulfur bridge is evidenced as has been seen in literature.\textsuperscript{51} Interestingly enough, in the case of a metal-terminated surface, an iron atom was bound to oxygen of the water molecule and moved much further from the surface compared to copper. What this initial calculation seems to indicate is that sulfur on the surface of chalcopyrite produces a hydrophobic environment, while metal-rich surfaces would open a pathway for leaching, but not favorably for copper. This gives some small insights into why copper leaching is difficult for pure mineral chalcopyrite.
Figure 4.15. Sulfur-terminated surface calculation with PBE function and spin-treatment with initial structure. Hydrogen is white, oxygen is red, sulfur is yellow, iron is orange, and copper is brown. Unit cell is expanded 3×3 for better view of the surface. Image generated in Jmol.23

Figure 4.16. Sulfur-terminated surface calculation with PBE function and spin-treatment with final structure after relaxation. Hydrogen is white, oxygen is red, sulfur is yellow, iron is orange, and copper is brown. Notice the new position of water molecules. Unit cell is expanded 3×3 for better view of the surface. Image generated in Jmol.23
Figure 4.17. Metal-terminated surface calculation with PBE function and spin-treatment with initial structure. Hydrogen is white, oxygen is red, sulfur is yellow, iron is orange, and copper is brown. Unit cell is expanded $3 \times 3$ for better view of the surface. Image generated in Jmol.\textsuperscript{23}

Figure 4.18. Metal-terminated surface calculation with PBE function and spin-treatment with final relaxed structure. Hydrogen is white, oxygen is red, sulfur is yellow, iron is orange, and copper is brown. Notice the iron atom bound to one of the water molecules and being displaced from the surface. Unit cell is expanded $3 \times 3$ for better view of the surface. Image generated in Jmol.\textsuperscript{23}

In order to understand better the effect of solvation, a more accurate picture of the chalcopyrite surface was produced by performing surface reconstructions prior to inclusion of water molecules. An
example of the geometry file for this calculation is shown in Table 4.5. The bottom two CuFeS₂ molecules were frozen (designated with “constrain_relaxation” as true in the table), and the top two were allowed to relax (no designation). In this calculation, a vacuum of 20 Å was left above the surface to avoid periodic effects.

**Table 4.6. Geometry file for reconstruction of the sulfur-terminated chalcopyrite surface.**

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>5.289</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
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<td>0.044956</td>
</tr>
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<td>.true.</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.75</td>
<td>0.044956</td>
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<td></td>
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<tr>
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<td>0.5074</td>
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</tr>
<tr>
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<td>.true.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>atom_frac</td>
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<td>0.9926</td>
<td>0.089912</td>
</tr>
<tr>
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<td>.true.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>atom_frac</td>
<td>0.7574</td>
<td>0.25</td>
<td>0.134869</td>
</tr>
<tr>
<td>constrain_relaxation</td>
<td>.true.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>atom_frac</td>
<td>0.2574</td>
<td>0.75</td>
<td>0.134869</td>
</tr>
<tr>
<td>constrain_relaxation</td>
<td>.true.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>atom_frac</td>
<td>0.0148</td>
<td>0</td>
<td>0.179825</td>
</tr>
<tr>
<td>constrain_relaxation</td>
<td>.true.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>atom_frac</td>
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<td>0.5</td>
<td>0.179825</td>
</tr>
<tr>
<td>constrain_relaxation</td>
<td>.true.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>atom_frac</td>
<td>0.257398</td>
<td>0.250002</td>
<td>0.218306</td>
</tr>
<tr>
<td>atom_frac</td>
<td>0.757401</td>
<td>0.749999</td>
<td>0.223464</td>
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<tr>
<td>atom_frac</td>
<td>0.494156</td>
<td>0.037131</td>
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<td>0.263924</td>
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<tr>
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<td>0.30524</td>
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<tr>
<td>atom_frac</td>
<td>0.257396</td>
<td>0.75</td>
<td>0.308405</td>
</tr>
<tr>
<td>atom_frac</td>
<td>-0.10616</td>
<td>-0.07644</td>
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<td>atom_frac</td>
<td>0.620977</td>
<td>0.576458</td>
<td>0.341543</td>
</tr>
</tbody>
</table>

The result of a reconstruction for a sulfur-terminated structure with the geometry from Table 4.5 is shown in Figure 4.19. It can be seen that the sulfur bridges occur once more. This was performed with a metal-terminated surface, and it can be seen in Figure 4.20. In this surprising case, sulfur atoms are rearranged to appear on the surface and the metal atoms are pushing inside the unit cell, creating a dense structure, which has been similarly observed by de Oliveira, et al.\textsuperscript{51} These results seem to indicate that sulfur is the preferred end-termination for chalcopyrite, and it might be a reason why sulfur passivation happens readily during leaching.
Afterwards, solvation was simulated by applying six molecules of water above each of the reconstructed surfaces (three pairs of molecules stacked above). The initial and final structures for sulfur-terminated surfaces are presented in Figures 4.21 and 4.22, respectively. The results of this calculation are quite similar to that of the non-reconstructed surface calculation of Figures 4.15 and 4.16. Water molecules move away from the sulfur surface and form hydrogen bonds between each other (dashed lines in the figures). A similar effect was seen with the metal-terminated, reconstructed surface (Figures 4.23 and 4.24), which is less surprising this time, since the reconstructed surface has sulfur atoms on the surface instead of metals. Once again, water molecules were repelled from the surface and formed hydrogen bonds between themselves.
Figure 4.21. Initial geometry for calculation of sulfur-terminated surface. Hydrogen is white, oxygen is red, sulfur is yellow, iron is orange, and copper is brown. Hydrogen bonds are shown as dashed lines (none are present in this case). Unit cell is expanded 3×3 for better view of the surface. Background in black to make hydrogen bonds visible. Image generated in Jmol.23

Figure 4.22. Final geometry after calculation of sulfur-terminated surface. Hydrogen is white, oxygen is red, sulfur is yellow, iron is orange, and copper is brown. Hydrogen bonds are shown as dashed
lines. Unit cell is expanded 3×3 for better view of the surface. Background in black to make hydrogen bonds visible. Image generated in Jmol.\textsuperscript{23}

\textbf{Figure 4.23.} Initial geometry for calculation of metal-terminated surface. Hydrogen is white, oxygen is red, sulfur is yellow, iron is orange, and copper is brown. Hydrogen bonds are shown as dashed lines (none are present in this case). Unit cell is expanded 3×3 for better view of the surface. Background in black to make hydrogen bonds visible. Image generated in Jmol.\textsuperscript{23}

\textbf{Figure 4.24.} Final geometry after calculation of metal-terminated surface. Hydrogen is white, oxygen is red, sulfur is yellow, iron is orange, and copper is brown. Hydrogen bonds are shown as dashed
The results for the different terminations and reconstructions above are given in Table 4.7, calculated in the same manner as Table 4.5, using Equation 4.12. What can be found here is that the metal-terminated surface without reconstruction has a much higher energy that a sulfur-terminated one, while this is reverse for reconstructed surfaces. The way that the reconstructed metal-terminated surface behaves gives some insight into the difficulty of leaching, since sulfur is already repelling the water molecules.

Table 4.7. Calculated absorption energies for solvated chalcopyrite, shown normalized to the unit surface area and per surface water molecules.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Termination</th>
<th>Absorption Energy (eV/nm²)</th>
<th>Absorption Energy (eV/molec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified Sulfur</td>
<td>-1.71038</td>
<td>-0.23923</td>
<td></td>
</tr>
<tr>
<td>Unmodified Metal</td>
<td>3.07467</td>
<td>0.43005</td>
<td></td>
</tr>
<tr>
<td>Reconstructed Sulfur</td>
<td>0.32512</td>
<td>0.04547</td>
<td></td>
</tr>
<tr>
<td>Reconstructed Metal</td>
<td>-5.37745</td>
<td>-0.75213</td>
<td></td>
</tr>
</tbody>
</table>

Because reconstructed surfaces are more likely to be the naturally observed situations of the mineral surface, it gives an understanding for the mineral’s hydrophobic nature. During leaching, some metal ions may be removed from the surface layers, but if these calculations are to be understood correctly, then it is very likely that a dense sulfur layer would form, preventing further leaching from occurring, except in solutions that can attack the sulfur as well. Although the behavior of the surface-terminated metal atoms sinking below the surface, leading to the exposure of sulfur atoms on the surface, would seem anomalous, similar observations were made by de Oliveira, et al., with PW91 functional. This behavior happens despite the fact that sulfur at either of the reconstructed surfaces has dangling bonds, which prefer not to bond with water molecules, regardless of the orientation of the water molecule (Table 4.5 above).
Chapter 5. Conclusions

5.1 Insights gained from the body of this work

The major accomplishment of this work concerns the combination of different characterization techniques with supporting theoretical basis to understand the effect of chalcopyrite activation in the Rapid Oxidative Leaching (ROL) process.

The physico-chemical changes of activation were elucidated through the merger of information gathered from diffraction studies with transmission electron microscopy (TEM) and binding energy analysis from x-ray photoelectron spectroscopy (XPS). As the preliminary investigations done by FLSmidth had found, phase changes occur on the surface of the particle that result in covellite-like structure, as TEM results from Chapter 2 have been able to support. However, an important observation, which was made in the present work, was that these changes extend beyond the surface and cause bulk changes as well. These bulk changes were evidenced by expanded lattice parameters during electron diffraction. The implications of this observation is that diffusion of ions through the bulk would be enhanced, due to an enlarged unit cell. It was also found that regions of amorphous covellite-like phase were present through the bulk, and these would provide pathways for ions to diffuse, much like grain boundary diffusion is quicker compared to bulk.

Chemical changes were then identified with XPS, and the most relevant information gained from the spectra was the oxidation of copper and sulfur. It was discovered that activation causes the binding energies of these atoms to increase, which is typical of oxidation of a species. In the case of copper, this can be relegated to the increase of oxidation state due to incorporation of Cu$^{2+}$ ions that are replacing Fe in chalcopyrite. For the sulfur binding energy, an increase is correlated to a decrease in charge per atom, which may be due to a change from monosulfide character to disulfide or polysulfide. Another possibility is that this may be due to the presence of holes on sulfur atoms, but both of these scenarios allude to the formation of a covellite-like phase, since these are both features common to it. The spectroscopy results enforce the conclusions from TEM.

Density functional theory (DFT) calculations were used since they can provide a theoretical basis for understanding the role of activations from first principles. A number of remarks can be made from the calculations performed. First, the electronic properties of chalcopyrite were reproduced by using an appropriate exchange-correlation functional, B3LYP, to find an energy gap that fits with experimentally determined values and retains the best unit cell volume of those tested in this work. Following this, doping of the mineral was devised by substituting half the iron atoms with Cu$^{2+}$, resembling a highly activated system. It was found that doing so causes the electronic nature to become metallic. Such a change can be interpreted to improve the electrochemistry of the mineral by facilitating the flow of ions. Secondly, the solvation of chalcopyrite was studied by calculating the surfaces of the mineral with different terminations (sulfur or metal). The calculations show that the surface prefers to have sulfur atoms, which also results in a hydrophobic surface. Because the metal atoms tend to recede from the surface, it can be assumed that leaching of chalcopyrite leads to the formation of a sulfur-dense surface, which would be non-conducting and passivate further leaching, as is observed in nature. Fresh metal-terminated surfaces give a possibility of leaching, since they
produce a high-energy surface that could lower the activation energy for further leaching, which gives a basis for the success of the stirred media reactors (SMRt) in the ROL process.

5.2 Future outlook and endeavors

5.2.1 Activation beyond copper
Since there is interest in activation of chalcopyrite using alternative ions, and because access may be dictated by the customer’s stock or geo-economics, calculations were performed in a manner as in §4.3.1. Calculations were performed to dope the crystal lattice with other atoms than copper, since the change of electrochemistry due to the formation of a conductive phase gives an important property to single out for predictions. The results of atoms that hold an oxidation state of +2 are included in Table 5.1. Firstly, there was a question regarding the reality of a net negative charged structure, so an energy calculation was repeating using copper but with zero net charge. What can be seen is that the crystal still has a very small gap, which would constitute conductive properties. Hence, it was suitable to use a net negative charge for the other candidates. The most promising of these were chromium, nickel, and silver, although the former two did not have converging calculations. Since silver activation converged, it was recalculated with zero net charge to confirm the results of copper, and it was found to have little change in the outcome. It would be interesting to support these results with experimental work with silver activated chalcopyrite. Furthermore, it would also be interesting to apply this methodology to another mineral system to determine its applicability in a general sense.

Table 5.1. Estimated band gap energies for activation candidates. * indicates that the calculation did not converge, but the last band gap calculation was extracted.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Net charge</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-1</td>
<td>0.034</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>0.051</td>
</tr>
<tr>
<td>Ca</td>
<td>-1</td>
<td>1.624</td>
</tr>
<tr>
<td>Cr</td>
<td>-1</td>
<td>0.000*</td>
</tr>
<tr>
<td>Mn</td>
<td>-1</td>
<td>0.988</td>
</tr>
<tr>
<td>Co</td>
<td>-1</td>
<td>1.031</td>
</tr>
<tr>
<td>Ni</td>
<td>-1</td>
<td>0.007*</td>
</tr>
<tr>
<td>Zn</td>
<td>-1</td>
<td>1.127</td>
</tr>
<tr>
<td>Ag</td>
<td>-1</td>
<td>0.002</td>
</tr>
<tr>
<td>Ag</td>
<td>0</td>
<td>0.003</td>
</tr>
</tbody>
</table>

5.2.2 Improved solvation model
An important factor that should be considered is the inclusion of solvation models, such as the Stern- and finite-ion-size-modified Poison-Boltzmann (SMPB) model. This model modifies the standard Poisson-Boltzmann theory by introducing a solvent Stern layer that separates the solute from the
diffuse ions, which are treated as roughly rigid in their size. This model is implemented in FHI-aims, although it requires the building of appropriate clusters and tuning of parameters that are necessary to run the calculation. The relevance of including solvation models is that the solvent can be modified in a computationally efficient manner to account for salts and acids in the solution. Once established, it could be used to compare a chalcopyrite cluster with an activated one.

5.2.3 Business benefits for FLSmidth
For FLSmidth the benefits of this project were related to the expansion of sales opportunities in copper processing, such as initiation of the next generation of Rapid Oxidative Leaching (ROL), brownfield opportunities, and services with regard to modeling, calculations, and troubleshooting.

5.2.3.1 Next Generation of Rapid Oxidative Leaching
Traditionally strong in copper concentrator equipment sales, FLSmidth will be expanding its existing market for tanks, agitators, solvent extraction and electrowinning equipment by bringing the ROL process to market. FLSmidth will be leveraging process-know-how in copper leaching to be more competitive in copper hydrometallurgy and to open up entirely new hydrometallurgical markets. Environmental and economic concerns are beginning to change the landscape of copper processing, and the ability to offer solution beyond smelting is necessary to be competitive in this sector. Better understandings of the mechanisms at play during the activation stage (which has been reported by FLSmidth to half the leaching time) in the leaching process will yield reproducible results so that a new generation of ROL can be brought to market. This will also bring about improved efficiencies in terms of decreased processing time, lower energy requirements, and/or fewer necessary tanks for leaching, which will lead to lower CAPEX and/or OPEX.

Based on the results of characterization and modeling of activated chalcopyrite leaching in different conditions, improved and new process design rules can be established for copper recovery processes. Activation will be an additional step in the process flow that significantly reduces time and energy. This will allow for:

1. **Fewer necessary stirred tank reactors (CSTRs)**: Because the activation stage significantly improves the copper leaching rates, the total number of CSTRs can be reduced because the residence time and overall processing time needed for extraction will be much smaller.

2. **Lower energy costs**: As mentioned above, the total time for leaching will be greatly reduced, which decreases the total energy costs of the leach circuit per kg of copper produced. Furthermore, the inclusion of the SMRt reactors, which supply a high energy mixing in a small volume rather than applying to a whole tank reactor, allow for reduced energy consumption.

5.2.3.2 Brownfield Opportunities
Further understanding into the benefits and limitations of the activation of chalcopyrite can expand brownfield applications of the ROL process. Through better understanding of the technology, FLSmidth will be well positioned to identify business opportunities and solutions for their customers. Retrofitting existing operations to improve copper recovery and throughput will provide avenues for equipment and process sales for FLSmidth.
5.2.3.3 Services (Modeling/Calculations/Troubleshooting)

The modeling work done during this project was performed in order to understand the physical mechanisms at play during activation and leaching. The expertise generated in the modeling allows for better customer service and troubleshooting for clients. This can be provided for both FLSmidth and outside customers. An example of such services could include an expansion of the predictions performed in §5.2.1.
References


Leaching or Dissolving Metal and Enhancing Electrorefinery and Smelting Operations. 36 (2017).


31. Spencer, W. D. & Topley, B. Chemical kinetics of the system Ag 2 CO 3 ⇔ Ag 2 O + CO 2. J.


43. Perry, D. L. & Taylor, A. J. X-ray photoelectron and Auger spectroscopic studies of CuzS and CuS.


Appendix B. Chlorine 2p spectra of activated chalcopyrite.

Figure A.1. XPS spectra of CuCl$_2$ activated chalcopyrite particles in the chlorine 2p range.
Appendix C. Control input file for DFT calculation in FHI-aims

C.1 Example of control file for geometry relaxation

#----------------------------------------
# Config Parameters
#----------------------------------------
relativistic atomic_zora scalar 1e-9
k_grid 6 6 6
xc b3lyp
sc_accuracy_eev 0.001
sc_accuracy_rho 1e-05
sc_accuracy_etot 1e-05
sc_accuracy_forces 1E-3
sc_iter_limit 200
hf_version 0
RI_method LVL_fast
charge -1
mixer pulay
n_max_pulay 8
empty_states 1000
charge_mix_param 0.1
occupation_type gaussian 0.2
spin none
#include_spin_orbit non_self_consistent
relax_geometry bfgs 1.e-2
max_atomic_move 0.2
relax_unit_cell full
#----------------------------------------
# End Config Parameters
#----------------------------------------

species S
# global species definitions
nucleus 16
mass 32.065
# l_hartree 4
#
cut_pot 3.5 1.5 1.0
basis_dep_cutoff 1e-4
# radial_base 44 5.0
radial_multiplier 1
angular_grids specified
division 0.4665 110
division 0.5810 194
division 0.7139 302
# division 0.8274 434
# division 0.9105 590
# division 1.0975 770
# division 1.2028 974
# outer_grid 974
outer_grid 302

# Definition of "minimal" basis
#

# valence basis states
valence 3 s 2.
valence 3 p 4.
# ion occupancy
ion_occ 3 s 1.
ion_occ 3 p 3.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Constructed for dimers: 1.6 A, 1.9 A, 2.5 A, 3.25 A, 4.0 A
#
# "First tier" - improvements: -652.81 meV to -45.53 meV
ionic 3 d auto
hydro 2 p 1.8
# hydro 4 f 7
ionic 3 s auto
# "Second tier" - improvements: -30.20 meV to -1.74 meV
# hydro 4 d 6.2
# hydro 5 g 10.8
# hydro 4 p 4.9
# hydro 5 f 10
# hydro 1 s 0.8
# "Third tier" - improvements: -1.04 meV to -0.20 meV
# hydro 3 d 3.9
# hydro 3 d 2.7
# hydro 5 g 12
# hydro 4 p 10.4
# hydro 5 f 12.4
# hydro 2 s 1.9
# "Fourth tier" - improvements: -0.35 meV to -0.06 meV
# hydro 4 d 10.4
# hydro 4 p 7.2
# hydro 4 d 10
# hydro 5 g 19.2
# hydro 4 s 12

# FHI-aims code project
# VB, Fritz-Haber Institut, 2009
#
# Suggested "light" defaults for Fe atom (to be pasted into control.in file)
# Be sure to double-check any results obtained with these settings for post-processing,
# e.g., with the "tight" defaults and larger basis sets.
#
species Fe
# global species definitions
nucleus 26
mass 55.845
#
l_hartree 4
#
cut_pot 3.5 1.5 1.0
basis_dep_cutoff 1e-4
#
radial_base 51 5.0
radial_multiplier 1
angular_grids specified
division 0.4337 50
division 0.8154 110
division 1.1046 194
division 1.3713 302
# division 1.5424 434
# division 1.7365 590
# division 1.9587 770
# division 1.9990 974
# division 2.4139 1202
# outer_grid 1202
outer_grid 302

# Definition of "minimal" basis
#
# valence basis states
valence 4 s 2.
valence 3 p 6.
valence 3 d 6.
# ion occupancy
ion_occ 4 s 1.
ion_occ 3 p 6.
ion_occ 3 d 5.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Constructed for dimers: 1.45 A, 1.725 A, 2.25 A, 3.00 A, 4.00 A
#
# "First tier" - improvements: -300.53 meV to -10.50 meV
hydro 4 f 9.4
hydro 2 p 2.2
# hydro 5 g 12.4
hydro 3 d 3.1
ionic 4 s auto
# "Second tier" - improvements: -16.31 meV to -0.65 meV
# hydro 3 d 6.2
# hydro 6 h 19.2
# hydro 4 f 15.2
# hydro 4 f 6.6
# hydro 3 p 3
# hydro 5 g 13.2
# hydro 1 s 0.65
# "Third tier" - improvements: -1.60 meV to -0.10 meV
# hydro 4 d 7.8
# Hydro 4 p 19.6
# Hydro 4 d 10.4
# Ionic 4 p auto
# Hydro 6 h 17.6
# Hydro 5 f 27.2
# Hydro 4 s 4.8
"Fourth tier": improvements -0.13 meV and below
# Hydro 5 f 12
# Hydro 5 g 10.4
# Hydro 5 p 8.4
# Hydro 4 d 14.8
# Hydro 2 s 1.9

# FHI-aims code project
# VB, Fritz-Haber Institut, 2010
#
# Suggested "light" defaults for Cu atom (to be pasted into control.in file)
# Be sure to double-check any results obtained with these settings for post-processing,
# e.g., with the "tight" defaults and larger basis sets.
#
species Cu
#
   nucleus 29
   mass   63.546
#
   l_hartree 4
#
   cut_pot 3.5 1.5 1.0
   basis_dep_cutoff 1e-4
#
   radial_base 53 5.0
   radial_multiplier 1
   angular_grids specified
      division 0.5231 50
      division 0.8642 110
      division 1.1767 194
      division 1.5041 302
      division 1.9293 434
      division 2.0065 590
      division 2.0466 770
      division 2.0877 974
      division 2.4589 1202
   outer_grid 302

# Definition of "minimal" basis
#
valence basis states
   valence 4 s 1.
   valence 3 p 6.
   valence 3 d 10.
#
ion occupancy
   ion_occ 4 s 0.
   ion_occ 3 p 6.
   ion_occ 3 d 9.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
# Constructed for dimers: 1.8, 2.2, 3.0, 4.0 Ang
#
# "First tier" - improvements: -211.42 meV to -9.17 meV
#  ionic 4 p auto
#  hydro 4 f 7.4
#  hydro 3 s 2.6
#  hydro 3 d 5
#  hydro 5 g 10.4
# "Second tier" - improvements: -2.49 meV to -1.08 meV
#  hydro 4 p 5.8
#  hydro 3 d 2.7
#  hydro 6 h 15.2
#  hydro 5 s 10.8
#  hydro 4 f 16
# "Third tier" - improvements: -0.50 meV to -0.21 meV
#  hydro 4 d 6
#  hydro 3 p 2.4
#  hydro 4 f 6.4
#  hydro 3 s 6.8
#  hydro 5 g 11.2
# "Fourth tier" - improvements: -0.13 meV to -0.05 meV
#  hydro 4 p 7
#  hydro 4 s 4
#  hydro 6 h 14
#  hydro 4 d 8.6
#  hydro 5 f 15.2

## C.2 Example of control file for band structure calculation

```bash
# Config Parameters
relativistic atomic_zora scalar 1e-9
k_grid 8 8 8
xc b3lyp
sc_accuracy_eev 0.001
sc_accuracy_rho 1e-05
sc_accuracy_etot 1e-05
sc_accuracy_forces 1E-3
sc_iter_limit 200
hf_version 0
RI_method LVL_fast
charge -1
mixer pulay
n_max_pulay 8
empty_states 1000
charge_mix_param 0.1
occupation_type gaussian 0.2
spin collinear
include_spin_orbit non_self_consistent
exx_band_structure_version 1
# output species-projected DOS
```
output species_proj_dos -18. 0. 500 0.05
dos_kgrid_factors 12 12 12

# output total DOS
output dos -18. 0. 500 0.05
dos_kgrid_factors 12 12 12

# output band structure
output band 0.5 0.0 0.5 0.0 0.0 0.5 100 R Z
output band 0.0 0.0 0.5 0.0 0.0 0.0 100 Z Gamma
output band 0.0 0.0 0.0 0.5 0.0 0.0 100 X M
output band 0.5 0.0 0.0 0.5 0.5 0.0 100 M Gamma

#----------------------------------------
# End Config Parameters
#----------------------------------------
# Suggested additional basis functions. For production calculations, uncomment them one after another (the most important basis functions are listed first).
# Constructed for dimers: 1.6 A, 1.9 A, 2.5 A, 3.25 A, 4.0 A
#
# "First tier" - improvements: -652.81 meV to -45.53 meV
  ionic 3 d auto
  hydro 2 p 1.8
  hydro 4 f 7
  ionic 3 s auto
#
# "Second tier" - improvements: -30.20 meV to -1.74 meV
  hydro 4 d 6.2
  hydro 5 g 10.8
  hydro 4 p 4.9
  hydro 5 f 10
  hydro 1 s 0.8
#
# "Third tier" - improvements: -1.04 meV to -0.20 meV
  hydro 3 d 3.9
  hydro 3 d 2.7
  hydro 5 g 12
  hydro 4 p 10.4
  hydro 5 f 12.4
  hydro 2 s 1.9
#
# "Fourth tier" - improvements: -0.35 meV to -0.06 meV
  hydro 4 d 10.4
  hydro 4 p 7.2
  hydro 4 d 10
  hydro 5 g 19.2
  hydro 4 s 12
#
# For methods that use the localized form of the "resolution of identity" for the two-electron Coulomb operator (RI_method LVL), particularly Hartree-Fock and hybrid density functional calculations, the highest accuracy can be obtained by uncommenting the line beginning with "for_aux" below, thus adding an extra g radial function to the construction of the product basis set for the expansion. See Ref. New J. Phys. 17, 093020 (2015) for more information, particularly Figs. 1 and 6.
#
# for_aux hydro 5 g 6.0
#
# FHI-aims code project
# Volker Blum, Fritz Haber Institute Berlin, 2009
#
# Suggested "tight" defaults for Fe atom (to be pasted into control.in file)
# 2016/05/03, VB:
# Added d and p function from tier2 to list of functions that are included in tight / really_tight by default.
# This is done in analogy to Co and Ni. In the case of Fe, the change was triggered by specific tests that indicated that the total energy of bulk Fe is decreased by ~50 meV using these changes. The impact on total energy differences between bonded structures is likely much smaller.
# This change is a borderline case, though, since it makes "tight" calculations
# with Fe much more expensive for a relatively small gain. This is particularly
# challenging for hybrid functionals.
# For any calculations where time is critical - especially hybrid functionals,
# but also LDA / GGA - it would seem to be very safe to use only the radial
# functions in tier1, i.e., comment out the additional d and p function of tier2.
#
species Fe
# global species definitions
nucleus 26
mass 55.845
#
1_hartree 6
#
cut_pot 4.0 2.0 1.0
basis_dep_cutoff 1e-4
#
radial_base 51 7.0
radial_multiplier 2
angular_grids specified
  division 0.2739 50
  division 0.5898 110
  division 0.9223 194
  division 1.1267 302
  division 1.3186 434
  division 1.5125 590
  division 1.7365 770
  division 1.9990 974
  division 2.7593 1202
  outer_grid 1202
  outer_grid 434

# Definition of “minimal” basis
#
# valence basis states
valence 4 s 2.
valence 3 p 6.
valence 3 d 6.
#
# ion occupancy
ion_occ 4 s 1.
ion_occ 3 p 6.
ion_occ 3 d 5.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Constructed for dimers: 1.45 A, 1.725 A, 2.25 A, 3.00 A, 4.00 A
#
# “First tier” - improvements: -300.53 meV to -10.50 meV
hydro 4 f 9.4
hydro 2 p 2.2
hydro 5 g 12.4
hydro 3 d 3.1
ionic 4 s auto
# “Second tier” - improvements: -16.31 meV to -0.65 meV
hydro 3 d 6.2
# hydro 6 h 19.2
# hydro 4 f 15.2
# hydro 4 f 6.6
# hydro 3 p 3
# hydro 5 g 13.2
# hydro 1 s 0.65
# "Third tier" - improvements: -1.60 meV to -0.10 meV
# hydro 4 d 7.8
# hydro 4 p 19.6
# hydro 4 d 10.4
# ionic 4 p auto
# hydro 6 h 17.6
# hydro 5 f 27.2
# hydro 4 s 4.8
# "Fourth tier": improvements -0.13 meV and below
# hydro 5 f 12
# hydro 5 g 10.4
# hydro 5 p 8.4
# hydro 4 d 14.8
# hydro 2 s 1.9

# FHI-aims code project
# Volker Blum, Fritz Haber Institute Berlin, 2010
# # Suggested "tight" defaults for Cu atom (to be pasted into control.in file)
# #
#species        Cu
# #
nucleus      29
mass         63.546
#
l_hartree    6
#
cut_pot      4.0  2.0  1.0
basis_dep_cutoff    1e-4
#
radial_base    53 7.0
radial_multiplier 2
angular_grids    specified
division  0.3478  50
division  0.6638  110
division  0.9718  194
division  1.1992  302
division  1.5920  434
division  1.8557  590
division  2.0466  770
division  2.0877  974
division  2.4589 1202
outer_grid   434

# Definition of "minimal" basis
#
# valence basis states
valence      4  s   1.
valence      3  p   6.
valence      3  d  10.
# ion occupancy
ion_occ      4  s   0.
ion_occ      3  p   6.
ion_occ      3  d   9.
# Suggested additional basis functions. For production calculations, uncomment them one after another (the most important basis functions are listed first).
# Constructed for dimers: 1.8, 2.2, 3.0, 4.0 Ang
#
# "First tier" - improvements: -211.42 meV to -9.17 meV
  ionic 4 p auto
  hydro 4 f 7.4
  hydro 3 s 2.6
  hydro 3 d 5
  hydro 5 g 10.4
# "Second tier" - improvements: -2.49 meV to -1.08 meV
#  hydro 4 p 5.8
#  hydro 3 d 2.7
#  hydro 6 h 15.2
#  hydro 5 s 10.8
#  hydro 4 f 16
# "Third tier" - improvements: -0.50 meV to -0.21 meV
#  hydro 4 d 6
#  hydro 3 p 2.4
#  hydro 4 f 6.4
#  hydro 3 s 6.8
#  hydro 5 g 11.2
# "Fourth tier" - improvements: -0.13 meV to -0.05 meV
#  hydro 4 p 7
#  hydro 4 s 4
#  hydro 6 h 14
#  hydro 4 d 8.6
#  hydro 5 f 15.2

C.3 Example of surface reconstruction control file

#----------------------------------------
# Config Parameters
#----------------------------------------
relativistic atomic_zora scalar 1e-9
k_grid 12 6 1
xc pbe
#vdw_correction_hirshfeld
sc_accuracy_eev 0.001
sc_accuracy_rho 1e-05
sc_accuracy_etot 1e-05
sc_accuracy_forces 1E-3
sc_iter_limit 200
charge 0
mixer pulay
n_max_pulay 8
empty_states 1000
charge_mix_param 0.1
occupation_type gaussian 0.2
spin none
#include_spin_orbit non_self_consistent

  relax_geometry bfgs_textbook 1.e-2
max_atomic_move 0.2
# relax_unit_cell full
#----------------------------------------
# End Config Parameters
#----------------------------------------

Species S
# global species definitions
nucleus 16
mass 32.065
#
l_hartree 4
#
cut_pot 3.5 1.5 1.0
basis_dep_cutoff 1e-4
#
radial_base 44 5.0
radial_multiplier 1
angular_grids specified
division 0.4665 110
division 0.5810 194
division 0.7139 302
# division 0.8274 434
# division 0.9105 590
# division 1.0975 770
# division 1.2028 974
# outer_grid 974
# outer_grid 302

Definition of "minimal" basis
#
valence basis states
valence 3 s 2.
valence 3 p 4.
#
ion occupancy
ion_occ 3 s 1.
ion_occ 3 p 3.

Suggested additional basis functions. For production calculations,
uncomment them one after another (the most important basis functions are
listed first).
#
Constructed for dimers: 1.6 A, 1.9 A, 2.5 A, 3.25 A, 4.0 A
#
"First tier" - improvements: -652.81 meV to -45.53 meV
ionic 3 d auto
hydro 2 p 1.8
# hydro 4 f 7
ionic 3 s auto
#  "Second tier" - improvements: -30.20 meV to -1.74 meV
#     hydro 4 d 6.2
#     hydro 5 g 10.8
#     hydro 4 p 4.9
#     hydro 5 f 10
#     hydro 1 s 0.8
#  "Third tier" - improvements: -1.04 meV to -0.20 meV
#     hydro 3 d 3.9
#     hydro 3 d 2.7
#     hydro 5 g 12
#     hydro 4 p 10.4
#     hydro 5 f 12.4
#     hydro 2 s 1.9
#  "Fourth tier" - improvements: -0.35 meV to -0.06 meV
#     hydro 4 d 10.4
#     hydro 4 p 7.2
#     hydro 4 d 10
#     hydro 5 g 19.2
#     hydro 4 s 12

#  FHI-aims code project
#  VB, Fritz-Haber Institut, 2009
#  Suggested "light" defaults for Fe atom (to be pasted into control.in file)
#  Be sure to double-check any results obtained with these settings for post-processing,
#  e.g., with the "tight" defaults and larger basis sets.
#
species Fe
#  global species definitions
nucleus 26
mass 55.845
#
  l_hartree 4
#
cut_pot 3.5 1.5 1.0
basis_dep_cutoff 1e-4
#
  radial_base 51 5.0
radial_multiplier 1
angular_grids specified
  division 0.4337 50
  division 0.8154 110
  division 1.1046 194
  division 1.3713 302
  division 1.5424 434
  division 1.7365 590
  division 1.9587 770
  division 1.9990 974
  division 2.4139 1202
  outer_grid 1202
outer_grid 302

#  Definition of "minimal" basis
#
#  valence basis states
valence 4 s 2.
valence 3 p 6.
valence 3 d 6.

# Ion occupancy
ion_occ 4 s 1.
ion_occ 3 p 6.
ion_occ 3 d 5.

# Suggested additional basis functions. For production calculations, uncomment them one after another (the most important basis functions are listed first).
#
# Constructed for dimers: 1.45 A, 1.725 A, 2.25 A, 3.00 A, 4.00 A
#
# First tier" - improvements: -300.53 meV to -10.50 meV
# hydro 4 f 9.4
# hydro 2 p 2.2
# hydro 5 g 12.4
# hydro 3 d 3.1
# ionic 4 s auto
# "Second tier" - improvements: -16.31 meV to -0.65 meV
# hydro 3 d 6.2
# hydro 6 h 19.2
# hydro 4 f 15.2
# hydro 4 f 6.6
# hydro 3 p 3
# hydro 5 g 13.2
# hydro 1 s 0.65
# "Third tier" - improvements: -1.60 meV to -0.10 meV
# hydro 4 d 7.8
# hydro 4 p 19.6
# hydro 4 d 10.4
# ionic 4 p auto
# hydro 6 h 17.6
# hydro 5 f 27.2
# hydro 4 s 4.8
# "Fourth tier": improvements -0.13 meV and below
# hydro 5 f 12
# hydro 5 g 10.4
# hydro 5 p 8.4
# hydro 4 d 14.8
# hydro 2 s 1.9

# FHI-aims code project
# VB, Fritz-Haber Institute, 2010
#
# Suggested "light" defaults for Cu atom (to be pasted into control.in file)
# Be sure to double-check any results obtained with these settings for post-processing, e.g., with the "tight" defaults and larger basis sets.
#
# species Cu
# nucleus 29
# mass 63.546
# l_hartree 4
# cut_pot 3.5 1.5 1.0
# basis_dep_cutoff 1e-4
# radial_base 53 5.0

C-14
radial_multiplier 1
angular_grids specified
division 0.5231  50
division 0.8642 110
division 1.1767 194
division 1.5041 302
# division 1.9293  434
# division 2.0065  590
# division 2.0466  770
# division 2.0877  974
# division 2.4589 1202
outer_grid  302

# Definition of "minimal" basis
#
# valence basis states
# valence  4 s   1.
# valence  3 p   6.
# valence  3 d  10.
# ion occupancy
# ion_occ  4 s   0.
# ion_occ  3 p   6.
# ion_occ  3 d  9.

# Suggested additional basis functions. For production calculations, uncomment them one after another (the most important basis functions are listed first).
#
# Constructed for dimers: 1.8, 2.2, 3.0, 4.0 Ang
#
# "First tier" - improvements: -211.42 meV to -9.17 meV
# ionic 4 p auto
# hydro 4 f 7.4
# hydro 3 s 2.6
# hydro 3 d  5
#  hydro 5 g 10.4
# "Second tier" - improvements: -2.49 meV to -1.08 meV
#  hydro 4 p  5.8
#  hydro 3 d  2.7
#  hydro 6 h 15.2
#  hydro 5 s 10.8
#  hydro 4 f 16
# "Third tier" - improvements: -0.50 meV to -0.21 meV
#  hydro 4 d  6
#  hydro 3 p  2.4
#  hydro 4 f  6.4
#  hydro 3 s  6.8
#  hydro 5 g 11.2
# "Fourth tier" - improvements: -0.13 meV to -0.05 meV
#  hydro 4 p  7
#  hydro 4 s  4
#  hydro 6 h 14
#  hydro 4 d  8.6
#  hydro 5 f 15.2

# FHI-aims code project
# VB, Fritz-Haber Institut, 2009
#
# Suggested "light" defaults for H atom (to be pasted into control.in file)
# Be sure to double-check any results obtained with these settings for post-processing,
# e.g., with the "tight" defaults and larger basis sets.
#
# species        H
#     global species definitions
nucleus             1
mass                1.00794
#
  l_hartree           4
#
cut_pot             3.5  1.5  1.0
basis_dep_cutoff    1e-4
#
radial_base         24  5.0
radial_multiplier   1
angular_grids specified
  division   0.2421   50
  division   0.3822   110
  division   0.4799   194
  division   0.5341   302
#  division   0.5626   434
#  division   0.5922   590
#  division   0.6542   770
#  division   0.6868  1202
#  outer_grid  770
outer_grid  302
#
# Definition of "minimal" basis
#
# valence basis states
valence      1  s   1.
# ion occupancy
ion_occ      1  s   0.5
# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Basis constructed for dimers: 0.5 A, 0.7 A, 1.0 A, 1.5 A, 2.5 A
#
# "First tier" - improvements: -1014.90 meV to -62.69 meV
hydro 2 s 2.1
hydro 2 p 3.5
# "Second tier" - improvements: -12.89 meV to -1.83 meV
# hydro 1 s 0.85
# hydro 2 p 3.7
# hydro 2 s 1.2
# hydro 3 d 7
# "Third tier" - improvements: -0.25 meV to -0.12 meV
# hydro 4 f 11.2
# hydro 3 p 4.8
# hydro 4 d 9
# hydro 3 s 3.2
#
# FHI-aims code project
# VB, Fritz-Haber Institut, 2009
# Suggested "light" defaults for O atom (to be pasted into control.in file)
# Be sure to double-check any results obtained with these settings for post-processing,
# e.g., with the "tight" defaults and larger basis sets.
#
species 0
  global species definitions
    nucleus 8
    mass 15.9994
#
    l_hartree 4
#
    cut_pot 3.5 1.5 1.0
    basis_dep_cutoff 1e-4
#
    radial_base 36 5.0
    radial_multiplier 1
    angular_grids specified
      division 0.2659 50
      division 0.4451 110
      division 0.6052 194
      division 0.7543 302
#      division 0.8014 434
#      division 0.8507 590
#      division 0.8762 770
#      division 0.9023 974
#      division 1.2339 1202
#    outer_grid 974
    outer_grid 302
#
# Definition of "minimal" basis
#
# valence basis states
#    valence 2 s 2.
#    valence 2 p 4.
#
# ion occupancy
#    ion_occ 2 s 1.
#    ion_occ 2 p 3.
#
# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Constructed for dimers: 1.0 A, 1.208 A, 1.5 A, 2.0 A, 3.0 A
#
# "First tier" - improvements: -699.05 meV to -159.38 meV
#    hydro 2 p 1.8
#    hydro 3 d 7.6
#    hydro 3 s 6.4
# "Second tier" - improvements: -49.91 meV to -5.39 meV
#    hydro 4 f 11.6
#    hydro 3 p 6.2
#    hydro 3 d 5.6
#    hydro 5 g 17.6
#    hydro 1 s 0.75
# "Third tier" - improvements: -2.83 meV to -0.50 meV
#    ionic 2 p auto
#    hydro 4 f 10.8
# hydro 4 d 4.7
# hydro 2 s 6.8
# "Fourth tier" - improvements: -0.40 meV to -0.12 meV
# hydro 3 p 5
# hydro 3 s 3.3
# hydro 5 g 15.6
# hydro 4 f 17.6
# hydro 4 d 14
# Further basis functions - -0.08 meV and below
# hydro 3 s 2.1
# hydro 4 d 11.6
# hydro 3 p 16
# hydro 2 s 17.2
Appendix D. Geometry input file for DFT calculation with FHI-aims

D.1 Example geometry for Cu-doped chalcopyrite

#************************************************************************************
#*                  Generated by cif2cell 1.2.10 2018-01-09 11:43                   *
#*                                                                                  *
#*                                   (Chalcopyrite)                                 *
#*  Knight K S et al., The Canadian Mineralogist 49, 1015-1034 (2011)              *
#************************************************************************************

lattice_vector    5.290000000000000   0.000000000000000   0.000000000000000
lattice_vector    0.000000000000000   5.290000000000000   0.000000000000000
lattice_vector    2.645000000000000   2.645000000000000   5.210850000000000

atom_frac    0.000000000000000   0.000000000000000   0.000000000000000  Cu
initial_moment 1.000000
# initial_charge +1

atom_frac    0.750000000000000   0.250000000000000   0.500000000000000  Cu
initial_moment 1.000000
# initial_charge +1

atom_frac    0.500000000000000   0.500000000000000   0.000000000000000  Cu
initial_moment 1.000000
# initial_charge +2

atom_frac    0.250000000000000   0.750000000000000   0.500000000000000  Fe
initial_moment 4.000000
# initial_charge +3

atom_frac    0.135400000000000   0.125000000000000   0.250000000000000  S
initial_moment 2.000000
# initial_charge -2

atom_frac    0.375000000000000   0.864600000000000   0.750000000000000  S
initial_moment 2.000000
# initial_charge -2

atom_frac    0.614600000000000   0.625000000000000   0.250000000000000  S
initial_moment 2.000000
# initial_charge -2

atom_frac    0.875000000000000   0.385400000000000   0.750000000000000  S
initial_moment 2.000000
# initial_charge -2

D.2 Example geometry of solvated, reconstructed sulfur-terminated chalcopyrite surface

# Configuration exported from Virtual NanoLab
atom_frac   0.2574     0.25 0.032231 Cu
initial_moment 1
constrain_relaxation .true.
atom_frac   0.7574     0.75 0.032231 Fe
initial_moment 4
constrain_relaxation .true.
atom_frac   0.0074   0.5074 0.0644621 S
initial_moment 2
constrain_relaxation .true.
atom_frac   0.5074   0.9926 0.0644621 S
initial_moment 2
constrain_relaxation .true.
atom_frac   0.7574     0.25 0.0966931 Cu
initial_moment 1
constrain_relaxation .true.
D.3 Example geometry of solvated, reconstructed metal-terminated chalcopyrite surface

# Configuration exported from Virtual NanoLab
atom_frac 0.2574 0.25 0.032231 S
initial_moment 2
constrain_relaxation .true.
atom_frac 0.7574 0.75 0.032231 S
initial_moment 2
constrain_relaxation .true.
atom_frac 0.0074 0.5074 0.0644621 Fe
initial_moment 4
constrain_relaxation .true.
atom_frac 0.5074 0.0074 0.0644621 Cu
initial_moment 1
constrain_relaxation .true.
atom_frac 0.7574 0.25 0.0966931 S
initial_moment 2
constrain_relaxation .true.
atom_frac 0.5148 0.407775 0.29514 H
initial_moment 0
atom_frac 0.606149 -0.089699 0.294434 H
initial_moment 0
atom_frac 0.416675 0.11548 0.293985 H
initial_moment 0
atom_frac -0.078508 0.612309 0.29288 H
initial_moment 0
atom_frac 0.00737379 0.492532 0.279544 O
initial_moment 0
atom_frac 0.507468 0.00737379 0.279544 O
initial_moment 0
atom_frac 0.110908 0.407775 0.29514 H
initial_moment 0
atom_frac 0.00737379 0.492532 0.279544 O
initial_moment 0
atom_frac 0.507468 0.00737379 0.279544 O
initial_moment 0
atom_frac 0.416675 0.11548 0.293985 H
initial_moment 0
atom_frac 0.606149 -0.089699 0.294434 H
initial_moment 0
atom_frac 0.2574 0.25 0.0966931 Fe
initial_moment 4
constrain_relaxation .true.
atom_frac 0.0074 0.5074 0.0644621 Fe
initial_moment 4
constrain_relaxation .true.
atom_frac 0.5074 0.0074 0.0644621 Cu
initial_moment 1
constrain_relaxation .true.
atom_frac 0.7574 0.25 0.0966931 S
initial_moment 2
constrain_relaxation .true.
atom_frac 0.2574 0.75 0.0966931 S
initial_moment 2
constrain_relaxation .true.
atom_frac 0.0148 0 0.128924 Cu
initial_moment 1
constrain_relaxation .true.
atom_frac 0.5 0.5 0.128924 Fe
initial_moment 4
atom_frac 0.2574 0.75 0.161155 S
initial_moment 2
atom_frac 0.0074 0.193386 Fe
initial_moment 4
atom_frac 0.0074 0.4926 0.193386 Cu
initial_moment 1
atom_frac 0.7574 0.25 0.225617 S
initial_moment 2
atom_frac 0.2574 0.75 0.225617 S
initial_moment 2
atom_frac 0 0.0074 0.257848 Fe
initial_moment 4
atom_frac 0.5148 0.5 0.257848 Cu
initial_moment 1
atom_frac -0.0785082 0.612309 0.29288 H
initial_moment 0
atom_frac 0.00737379 0.492532 0.279544 O
initial_moment 0
atom_frac 0.110908 0.407775 0.29514 H
initial_moment 0
atom_frac 0.606149 -0.0896994 0.294434 H
initial_moment 0
atom_frac 0.507468 0.00737379 0.279544 O
initial_moment 0
atom_frac 0.416675 0.11548 0.293985 H
initial_moment 0
#
# unit cell
#
lattice_vector 5.289 0 0
lattice_vector 0 5.289 0
lattice_vector 0 0 40.423
Appendix E. Calculations with Hubbard U parameter

DFT calculations were performed in FHI-aims with PBE and PW91 XC functionals and using different values for U (accounting for Coulomb interactions) and the Petukhov mixing factor (PMF, between 0 to 1). More information about the mixing factor can be found in the original paper. A value of PMF = 0 relates to complete treatment with the Around Mean Field contribution while a value of 1 selects the Fully Localized Limit. It can also be unspecified to vary and converge self-consistently. The results are below, and the reason for U = 1.3 eV being used often is due to reference papers.51,70

![Figure C1. Calculation with PBE and U = 0 eV.](image1)

![Figure C1. Calculation with PBE and U = 0 eV.](image2)
Figure C2. Calculation with PBE and $U = 1.3$ eV, PMF = 0.

Figure C3. Calculation with PBE and $U = 1.3$ eV, PMF = 1.

Figure C4. Calculation with PW91 and $U = 1.3$ eV, PMF = 0.
Figure C5. Calculation with PW91 and $U = 1.3$ eV, PMF = 1.

Figure C6. Calculation with PW91 and $U = 1.3$ eV, PMF = unspecified. Result resembles Figure A4.
Figure C7. Calculation with PW91 and $U = 2.6$ eV, PMF = 1.

Figure C8. Calculation with PW91 and $U = 3.9$ eV, PMF = 1.