A FUNDAMENTAL INVESTIGATION OF THE HIGH TEMPERATURE OXIDATION OF GOLD ORES
THAT CONTAIN SULFIDES AND CARBONACEOUS MATERIALS

by
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ABSTRACT

As the dollar value per ounce of gold has hit a downward trend in the last few years, there is more pressure within a gold operation to reach the highest percent recovery, no matter what kind of ore is presented for treatment. For double refractory gold ores, the most crucial unit operation is performed by the roaster by creating a high temperature oxidation of the ore. An efficient roasting operation creates a leachable ore in the next unit operation by extracting gold in an aqueous solution. A fundamental knowledge of how particular ores behave in this oxidation step is crucial to the overall understanding of a large scale roasting operation. This thesis has focused on the fundamental chemical aspects of three different ore stockpiles from a gold roasting operation by determining how each responds to batch roasting in a laboratory tube furnace. Fundamental aspects evaluated in this project will be mineralogical phases before and after roasting using XRD and MLA, surface area before and after by BET, and chemical analyses including: sulfur and carbon analysis, cyanide solubility and chemical compounds at different roast temperatures.
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Gold is a metal with a rich history to say the least. Having significance in human history dating back to thousands of years B.C., it was one of the first mined metals due to its high nobility, or tendency to occur in its original form. Its uses today include everything from jewelry to medicine to electronics. The metal also holds value as a medium of exchange for much of western civilization, especially as a holding device when forms of currency begin to lose their value. The gold price in history has always shown a cyclical rise and fall and the dollar per ounce price of the metal saw a rapid increase in the early 2000s. This price peaked at above $1800/ounce around 2011, but the years from 2012 to the present has seen the price drop to below $1100/ounce for certain periods. This drop in gold price, and the metal’s overall volatility in the market, has been the driving force for improving recoveries in a gold processing operation, along with processing new types of ores.

New demands to extract gold value from “double refractory” ores in the mid to late 20th century changed how mill engineers looked at the overall recovery process. Not only was it crucial to get the most out of existing unit operations in the mill, but it also meant adding in new operations in order to improve overall gold recovery. Double refractory gold ore, meaning significant gold is locked in sulfides and being “preg-robbed” by carbonaceous material, presented a new challenge in which pretreatment by oxidation was a necessary step. The best type of oxidation for double refractory ore, especially due to dealing with the carbon component, is high temperature oxidation, or roasting. Figure 1.1 shows where roasting lies in the process for a typical gold operation using oxidative pretreatment.
In a flowsheet similar to the one pictured above, roasting as a unit operation may be the single most important step. Lack of efficiency in oxidation of double refractory ores will lead to very low gold recoveries at the end of the process, and is the reason why gold companies are constantly trying to improve this part of the operation. It is a set up process for another crucial operation, cyanide leaching, and is the reason why it is called a pretreatment step. Key parameters for effective oxidation by roasting include temperature of the furnace, retention time, and percent oxygen in the system. Finding a good balance of all three in the roaster creates a product containing gold that is highly amenable to the cyanide leach in the next step of the operation.

Many gold companies today are focusing in on the last ten percent of gold that is not being recovered and how it relates to the fundamental chemistry of high temperature oxidation. In other words, many operations are achieving around 85 to 90 percent recovery of gold but where the last 10 to 15 percent is going is still a mystery. This thesis project will focus on this problem and where possible inefficiencies in the roasting process are occurring from a fundamental perspective. A few theories exist related to how and why the gold occlusion is occurring. These include using more retention time of feed in the roast, incomplete oxidation product formation that occludes gold, and how composition of the feed aids in occluding gold. With state-of-the-art lab tools to provide analyses, the goal of this project is to be able to provide some validity to these theories while also coming up with new theories as to what is keeping gold extraction down due to roasting.
CHAPTER 2
LITERATURE REVIEW

Literature regarding the roasting of double refractory gold ore was reviewed. It is a subject that has been studied for much of the second half of the 20th century up until present day. The main subjects reviewed for this thesis include characteristics of double refractory gold ore, reaction chemistry involving high temperature oxidation of this ore, and a review of roasting in an operational setting and how it is applied in present times.

In order to know why a study of roasting of double refractory ore is necessary, it is important to first understand the flowsheet of a typical roasting operation. Interpreting where roasting lies as a unit operation in the overall process is critical to being able to pinpoint possible contributions using fundamentals. Figure 2.1 illustrates a simple mill and roaster flowsheet.

![Figure 2.1. Simplified Mill and Roaster Flowsheet (2)](image)

The research for this thesis is based around the left and middle side of this flowsheet. If improved efficiencies in roasting can be achieved then this leads to better recovery of gold in the cyanidation step and more gold bullion produced in the final step. Depending on the size of the
operation, and gold’s dollar value per ounce in the economy, an improvement of even 1% efficiency can mean millions of dollars per year in profit gains for a gold mining company. Despite only being considered a pre-treatment step for gold recovery, roasting holds huge value in the overall process if efficient oxidation of the ore can be achieved.

2.1 Refractory Gold Ore

Gold occurs in many different forms in all different types of minerals. Refractory refers to how the gold is arranged within these minerals, and came about due to low gold recoveries in a conventional leach process, also known as cyanidation. These ores produce low recoveries for many gold mining operations, even when the ore is ground to a fine size, and have been the focus of much research in the last 50 years. Refractory gold occurs in two different forms, one as gold that is locked in sulfides and the other as gold occurring within ores containing carbonaceous materials. The combination of both of these refractory forms in an ore is sometimes referred to as “double refractory”.

Gold locked in sulfides is usually referred to as “invisible gold”. Its name comes from the fact that it is very difficult to detect by optical microscopy or scanning electron microscopy (SEM). Pyrite (FeS₂) is the main gold-bearing sulfide of these ores and is a lot of times found in the forms of arsenian pyrite (FeS₂) and arsenopyrite (FeAsS). The association with arsenic is another contributor to the refractoriness of the ore, considering arsenic is difficult to deal with downstream in the gold extraction process because of potential environmental concerns(3). Figure 2.2 shows an example of gold encapsulation in sulfides that contributes to the refractoriness of the ore. Invisible gold occurs in this form but at a much smaller scale that is very difficult to detect by SEM.

![Figure 2.2. Gold encapsulation in sulfides pyrite and chalcopyrite](image-url)
In a paper by Robinson, two theories are suggested for gold occurrence in sulfides not detected by a scanning electron microscope. One is that the invisible gold is finely spread throughout the surface area of the sulfide mineral. The other is that the gold forms a solid solution within the mineral and is hard to detect as a result. The paper reveals that no direct evidence was found to confirm these theories(5).

Another theory by Swash is suggested for gold occurrence in South African ores containing high arsenic levels. He explains, in a suggestion by Boyle, that gold occurrence in arsenopyrite is common due to the favorable atomic spacing and crystal chemistry of the structure, but that when these ores are formed at an elevated temperature in the Earth’s crust they form largely in a solid solution. When the solution is cooled, the gold in the structure alters the sulfide lattice of arsenopyrite, making extraction using conventional processes very difficult. Not only does the structure of arsenopyrite get altered but gold can migrate to grain boundaries and fractures within the mineral when these high temperature events occur. Understanding gold movement within a mineral due to these geological occurrences gives some indication as to the refractoriness ores associated with arsenic can create(6). In another experiment conducted on a high arsenic (>1.5%) Carlin ore, results showed a significant trend between arsenic content of roasted calcines and percent gold extracted. Bottle roll tests showed that the more arsenic in each sample the less gold extracted, confirming structural differences associated with gold in arsenopyrite do have an effect on leachability(7).

Gold ores containing high amounts of carbonaceous materials are called “preg-robbbing” ores. These ores are the opposite of free-milling ores, or ores that need no pretreatment step prior to leaching, and the name comes from the naturally occurring carbon’s tendency to rob a gold cyanide solution by capturing the gold. The organic carbon components contained in the ore remove the gold cyanide complex (Au(CN)_{2—}) from solution, making it unavailable for subsequent recovery from the aqueous phase. Rather than adsorbing onto the surface of the activated carbon placed in the leach, the naturally occurring carbon materials in the ore capture the gold. These materials may include wood chips, organic carbon and impurities like elemental carbon. The ore can also contain its own “active” carbon that inhibits the leaching process. Preg-robbbing carbon is responsible for a significant amount of gold loss that can be calculated at the end of the process(8).

In a paper by Helm et al, three different components are identified in preg-robbbing carbonaceous ores that could be responsible for significant gold loss. The authors describe an activated carbon type material seen in the ore, high molecular weight hydrocarbons that coat activated carbon in the adsorption process, and organic acids with functional groups that have an ability to disrupt the gold cyanide complex during leaching. The paper also tries to correlate degree of disorder in structure to preg-robbbing capabilities using Raman spectroscopy. The more ordered the crystalline structure of the carbon in the ore, or the more similar it is to activated carbon, the higher the preg-rob value. Despite these theories,
and results indicating a strong correlation, it is still acknowledged that the carbonaceous components in preg-robbing ore is poorly understood overall(9).

The findings became clear in the late 20\textsuperscript{th} century that there was significant enough gold in these ores to justify research on a method to improve recoveries. The carbonaceous matter in the ore was turning out to be a big problem for many gold companies and they needed to find a solution.

2.2 Chemistry of Pyrometallurgical Oxidation

The typical treatment process for getting better gold recovery from refractory ores is oxidation of the ore prior to the leach process. Depending on the mineralogical components of the ore, there are many different oxidation reactions that play a role in overall process considerations for a gold circuit. The sulfide component of a refractory ore needs to be oxidized in order to expose gold values at the surface of the ore and to limit reagent consumption due to lack of gold in solution in the subsequent leach process. The carbonaceous component needs the same oxidation treatment in order to prevent the preg-robbing of gold in solution. This naturally occurring carbon in the ore will not allow adsorption of gold onto activated carbon if not oxidized off by roasting prior to the carbon-in-leach process that occurs in most operations. The fundamental reactions occurring in the oxidation process can affect everything from hematite formation (desired in a gold circuit) to creation of sulfuric acid that is sold as a byproduct or used in other unit processes in the operation(3).

2.2.1 Iron Sulfide Oxidation

The first order of business when using oxidative pretreatment of a double refractory ore is oxidation of the sulfides that contain gold particles. The sulfides can occur in many different mineral forms, with the most common being pyrite and marcasite. Oxidation of these sulfides to an intermediate magnetite (Fe\textsubscript{3}O\textsubscript{4}) form and then eventually on to hematite (Fe\textsubscript{2}O\textsubscript{3}) is the goal. The reactions proceed as follows:

\[ 3\text{FeS}_2 + 8\text{O}_2(\text{g}) \rightarrow \text{Fe}_3\text{O}_4 + 6\text{SO}_2(\text{g}) \]
\[ 3\text{FeS} + 5\text{O}_2(\text{g}) \rightarrow \text{Fe}_3\text{O}_4 + 3\text{SO}_2(\text{g}) \]
\[ 4\text{Fe}_3\text{O}_4 + \text{O}_2(\text{g}) \rightarrow 6\text{Fe}_2\text{O}_3 \]

In the intermediate phase, as magnetite is being oxidized to the desired porous hematite, pyrite (or marcasite) will decompose to pyrrhotite (FeS). The following reaction is shown below:

\[ \text{FeS}_2 \rightarrow \text{FeS} + \text{S}(\text{g}) \]
Under oxidizing conditions, this volatilized sulfur is quickly converted to sulfur dioxide (SO$_2$) in a highly exothermic reaction. This first oxidation stage of a sulfidic ore creates heat for a roaster in a commercial operation and allows for savings on costs of fuel required to heat it.

\[ S + O_2(g) \rightarrow SO_2(g) \]

Ideally, and usually through a two-stage roasting process, pyrite is converted to magnetite and the majority of your magnetite is converted to hematite. Gold in hematite is more amenable to leaching in the next stage due to hematite having higher porosity and surface area, allowing free cyanide ions in solution access to the gold particles. Sometimes an intermediate, gold-occluding product can form in the oxidation of pyrite to hematite and can cause recovery problems in the overall process. Maghemite is discussed in more detail in section 2.2.4(3).

### 2.2.2 Organic Carbon Oxidation and Decomposition of Carbonate Carbon

The second step to oxidative pretreatment of a double refractory ore is oxidation of the carbon and carbon containing minerals contained in the ore. This process usually occurs at a higher temperature than sulfide oxidation. Organic carbon in the ore, along with organics found in coal and oil in the roaster, oxidize to carbon dioxide (CO$_2$) by the following reaction:

\[ C + O_2(g) \rightarrow CO_2(g) \ (3) \]

Similar to the intermediate phase produced with oxidation of sulfides, many times in organic carbon combustion an intermediate carbon monoxide (CO) phase is formed if complete oxidation does not occur. Like most processes, 100% efficiency of oxidation to CO$_2$ does not occur in roasting and therefore carbon monoxide is dealt with and removed by a CO incinerator on site to avoid reactive gas build-up. This intermediate phase is shown below along with its full oxidation step.

\[ 2C + O_2(g) \rightarrow 2CO(g) \]

\[ 2CO(g) + O_2(g) \rightarrow 2CO_2(g) \ (2) \]

Carbon in the form of carbonate minerals such as dolomite (CaMg(CO$_3$)$_2$), calcite (CaCO$_3$), and siderite (FeCO$_3$), to name a few, create a good portion of the makeup of double refractory gold ores as well. Upon high temperature oxidation, these minerals in the ore react in a few different ways. Depending on the conditions of the roast (temperature, % oxygen, retention time) carbonates can decompose, creating carbon dioxide gas and also further react with sulfur dioxide gas and oxygen to form
calcium and magnesium sulfates (CaSO₄ or MgSO₄) (3). Some examples of these reactions and the temperature at which they occur are shown in the table below:

<table>
<thead>
<tr>
<th>Carbonate species</th>
<th>Reaction</th>
<th>Temperature range (°C)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO₃ → CaO + CO₂</td>
<td>900 - 1000</td>
<td>43.97</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂ → CaCO₃ + MgO + CO₂</td>
<td>550 - 765</td>
<td>23.86</td>
</tr>
<tr>
<td></td>
<td>CaCO₃ → CaO + CO₂</td>
<td>900 - 1000</td>
<td>43.97</td>
</tr>
<tr>
<td></td>
<td>CaMg(CO₃)₂ → CaO + MgO + 2CO₂</td>
<td>550 - 1000</td>
<td>47.77</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃ → FeO + CO₂</td>
<td>450 - 550</td>
<td>37.99</td>
</tr>
</tbody>
</table>

Figure 2.3. Carbonate Carbon decomposition temperatures (10)

Carbonates in the ore can also react with the sulfur dioxide gas created by oxidation of the sulfides to form metal sulfates, usually calcium sulfate. This reaction is referred to as sulfur dioxide fixation and can be seen below.

$$2\text{CaCO}_3 + 2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{CaSO}_4 + 2\text{CO}_2(g)$$

### 2.2.3 Arsenic Sulfide Oxidation

In some cases sulfides are not found strictly as pure pyrite or marcasite, but are associated with arsenic. This mineral usually occurs in the form of arsenopyrite or arsenian pyrite and presents another challenge for a roasting operation due to the oxidation of arsenic. Environmental concerns with arsenic as a solid and as an oxidized gas make dealing with it difficult after roasting. The roasting chemistry of these sulfides associated with arsenic proceeds as follows:

$$\text{FeAsS} + 3\text{O}_2(g) \rightarrow \text{FeAsO}_4 + \text{SO}_2(g)$$
$$2\text{As}_2\text{S}_3 + 11\text{O}_2(g) \rightarrow 2\text{As}_2\text{O}_5 + 6\text{SO}_2(g)$$
$$2\text{As}_2\text{S}_2 + 9\text{O}_2(g) \rightarrow 2\text{As}_2\text{O}_5 + 4\text{SO}_2(g)$$
$$4\text{FeS}_2 + 2\text{As}_2\text{O}_5 + 11\text{O}_2(g) \rightarrow 4\text{FeAsO}_4 + 8\text{SO}_2(g)$$

In a largely oxidizing environment these reactions occur simultaneously and the arsenic sulfides can take on intermediate forms depending on the ore type. These forms include orpiment (As₂S₃) and realgar (AsS). Nearly all of the arsenic is converted to either to a solid ferric arsenate (FeAsO₄), arsenic pentoxide (As₂O₅), calcium arsenate (Ca₃(AsO₄)₂), or magnesium arsenate (Mg₃(AsO₄)₂) and these
products are dealt with further along in the process in the tailings or baghouse, to ensure a clean waste material is released into the environment.

The second stage oxidation process occurs just the same as the normal iron sulfide oxidation mentioned in section 2.2.1, with partial oxidation of pyrite to pyrrhotite (Fe\textsubscript{7}S\textsubscript{8} here) and then eventual oxidation to the desired hematite product.

\[
7\text{FeS}_2 + 6\text{O}_2(g) \rightarrow \text{Fe}_7\text{S}_8 + 6 \text{SO}_2(g) \\
4\text{Fe}_7\text{S}_8 + 53\text{O}_2(g) \rightarrow 14\text{Fe}_2\text{O}_3 + 32\text{SO}_2(g) \tag{2}
\]

In a paper by Grimsey and Aylmore, a high temperature reaction of arsenopyrite takes place with an intermediate pyrrhotite forming. The authors describe this step as an endothermic decomposition that consumes energy in the system and would need to be accounted for in terms of providing energy to the roaster. The reaction is shown below:

\[
4 \text{FeAsS} + 3\text{O}_2(g) \rightarrow 4\text{FeS} + \text{As}_2\text{O}_6(g) \\
3\text{FeS} + \text{SO}_2(g) \rightarrow \text{Fe}_3\text{O}_4 + 3\text{SO}_2(g)
\]

The authors also describe a scenario where, depending on composition of the feed, arsenic can be retained in the calcine product as calcium arsenate or ferric arsenate. The formation of these products has been linked to an increase in volume of the particle that blocks gold extraction. The many forms that arsenic can take, either as a solid or a gas, along with its effect on gold extraction, are the reasons why it is so difficult to deal with in the roasting process(11).

### 2.2.4 Oxidation Products that Contribute to Refractoriness

A subject of much research, now and in the future, is on products formed in the roast that contribute to gold occlusion upon leaching. Two of these products are maghemite (Fe\textsubscript{2}O\textsubscript{3}) and calcium sulfate (CaSO\textsubscript{4}). Both contain significant residual gold in high temperature oxidation products and will be described in detail in this section.

The production of maghemite occurs as an intermediate phase when magnetite transitions to hematite in the roast(12). It is mentioned above but the chemistry can be seen below again.

\[
4\text{Fe}_3\text{O}_4 + \text{O}_2(g) \rightarrow 6\text{Fe}_2\text{O}_3
\]
Maghemite has been described as essentially being hematite with magnetic properties, but because of the low porosity bands that form in this phase, maghemite tends to occlude a lot more gold than a porous hematite would. It is a different crystal form of hematite and can be distinguished by methods that include x-ray diffraction and Raman spectroscopy. The low porosity characteristic of maghemite keeps the cyanide from getting to the gold in the particle upon leaching. Figure 2.4 shows visually the differences between maghemite and hematite(13).

Figure 2.4. Low porosity maghemite (left) and high porosity, leachable hematite (right)

Many theories on why and how maghemite forms exist, with most centering around conditions of the roast (temperature, retention time, % oxygen). Maghemite occludes enough gold from the extraction process to warrant big concerns for process engineers on how to optimize the roast to reduce formation of this product. In a good gold extraction process, calcines from roasting should be:

1) Highly porous
2) Fractured and permeable
3) High in magnetite and lack impervious bands of maghemite in iron oxides
4) Largely hematite (14)

Calcium sulfate, another product of oxidation of sulfides in roasting, can occlude small amounts of gold as well, although typically not as much as maghemite. It results from the decomposition of calcium and magnesium carbonates, usually in the form of dolomite, at high temperatures. The reactions for CaSO₄ formation are shown below.

1. \[ \text{CaCO}_3/\text{MgCO}_3 = \text{CaO/MgO} + \text{CO}_2 \]
2. \[ \text{CaO/MgO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 = \text{CaSO}_4/\text{MgSO}_4 \]
Original evaluations of this reaction in the roast were positive due to the fact that its formation results in a reduction of sulfur dioxide in the off-gas. Upon further examination though, it has been found that, in some ores, calcium sulfate formation inhibits gold extraction by occluding gold in the leach process(15).

2.3 The Roasting Process

The two main methods for oxidative pretreatment in a mining operation are hydrometallurgical and pyrometallurgical and many times what is chosen is based on the composition of the ore. Hydrometallurgical routes for oxidation of sulfidic gold ores have been popular in the past. These routes include use of an autoclave or bioleaching to oxidize the sulfur and create a product that is more amenable to the subsequent cyanide leach. The problem with using these methods is that they do not deal with the preg-robbing carbon component of the ore. Oxidation of the carbon is equally important to the gold recovery at the end of the process and for that reason a roaster is typically used to ensure carbon burn-off(3). Another reason a roaster is typically chosen is because it is quicker and cheaper than the other methods. Roasting takes only minutes while an autoclave can take hours and bioleaching days to achieve oxidation of the ore(16). For these reasons a roaster is a popular oxidation step for treatment of double refractory gold ores.

Roasting as an oxidative pretreatment step on a commercial scale has evolved tremendously in the past one hundred years. The four main processes used, starting with the earliest and ending with what is now used today are:

- Rotary Kiln and Multiple Hearths
- Fluidized Bed (single and multi-stage)
- Circulating Fluidized Bed (CFB)
- Oxygenated Fluidized Bed

2.3.1 Edwards Roaster

Pre-1940s developments saw the use of rotary kilns and multiple hearth roasters for the oxidation of refractory gold ores. The one seen the most was the Edwards roaster, also known as a rabble roaster. At that time it was most popular because it provided better temperature control in the bed than other roasters. The roaster was made up of an enclosed hearth that was brick lined and typically had dimensions of 40 meters long by 3.6 meters wide. The ore (typically a concentrate) was progressed down the hearth by rabble arms that proceeded to rotate upon ore entering the furnace. The cross-sectional view in Figure 2.5 helps to visualize this process(2).
2.3.2 Fluidized Bed Roaster

In order to address inadequacies with the Edwards roaster, in particular a need for more throughput, a fluidized bed roaster was developed in the 1940s. It works by pushing air into the furnace at a sufficient velocity so that it may “fluidize” these particles. Air enters the roaster through a nozzle grate in the wind box at the bottom of the roaster. The velocity of the air required to fluidize the particles will vary from ore to ore based on density. The fluidization of these particles ensures better mixing, allowing for more efficient oxidation of pyrite to hematite(2). The fluidized bed design also allows for a more uniform temperature across the reactor along with increased heat and mass transfer rates in the system(17).

Along with better mixing of particles, the fluidized bed also provided for a higher throughput per unit area, better temperature control, and better control of gas composition than the Edwards roaster. All of these improvements from an Edwards roaster allowed for a more streamlined and efficient process when applied to a commercial operation(2). Giant Yellowknife, Campbell Red Lake, and Jerritt Canyon all provide examples of fluidized bed roaster operations in North America. All of these sites operated for a period before being shut down for various reasons, including emissions issues(3). A diagram of the fluid-bed roaster can be seen in Figure 2.6.
2.3.3 Circulating Fluidized Bed (CFB)

The 1960s brought along the development of the Circulating Fluidized Bed (CFB) by Lurgi, together with Vereinigte Aluminumwerke A.G. in Germany. The CFB was a furnace that used the same principles as a normal fluidized bed but improved upon it by implementing a recirculating load to the process. A process originally developed for the alumina industry, and not applied by major gold companies until the late 1980s, it had major implications for the extraction of gold from refractory ores. Some of these advantages include:

- lower capital and operating costs
- great efficiency in oxidation of sulfur and carbon
- better throughput as operations continued to get bigger
- even better process control than a normal Fluidized Bed

The circulating fluidized bed also enabled gold companies, for the first time, to roast whole ore and not just concentrates. Concentrates could be blended with whole ore to create fuel value, but this was the first instance where a previously untreated ore could go directly into the roast on its own. At the time of its introduction, with the particular ore that was being used in the system, the CFB addressed concerns about sulfur and carbon oxidation in a whole ore. High gold recoveries were being achieved without a sulfide concentration step (flotation) prior to roasting.

In a gold mining operation where a CFB is used, the whole crushed and dry, ground ore is stored in the roaster feed bin. Upon entering, the ore is roasted with air or oxygen-enriched air (achieves better sulfur and carbon burnoff in some cases) that is introduced at the bottom of the roaster along with fuel to
heat the system. The circulating process comes in when a quantity of the roasted product (calcine) collected by the cyclone in the next step is recycled back to the roaster. The remaining quantity of the calcine goes on to the leaching step. The recirculation step provides for major improvements in the percentage of gold recovered due to its ability to improve overall oxidation. Figure 2.7 shows a typical CFB roasting operation.

![Figure 2.7. Circulating Fluidized Bed gold operation](image)

The CFB technology by Lurgi was utilized in a single roaster at Cortez in Nevada and is also used for two parallel roaster trains by Newmont, also in Nevada. The Cortez ore going into the roaster contained 1-2% sulfide sulfur and 1-3% organic and carbonate carbon, along with having a throughput of 1820 tonnes per day(2).

### 2.3.4 Oxygenated Fluidized Bed Roasting in a Two-Stage System

In the 1980s, spawned by the need to address preg-robbing carbon components found in Nevada’s Carlin Trend, fluidized bed roasting with pure oxygen was developed. In order to increase recovery, better oxidation of this type of carbon needed to be achieved. From previous research on roasting with air, it was found that sulfide sulfur is roasted below 650°C and carbon at temperatures above 730°C. Finding a balance for this was always an issue, and engineers needed to find a way to achieve oxidation at lower temperatures, especially for carbon. Roasting of whole ore with a CFB roaster
created good sulfur burnoff but did not create an oxidizing atmosphere sufficient enough to make preg-robbing carbon inert in the ore, or at least all of it. The solution to this problem was inserting pure oxygen into the system as an oxidizing supplement. Not only does it help achieve oxidation at lower temperatures but it also negates the need to use an alternative fuel source with air in the system to utilize available heat. With a heavily oxidizing atmosphere, more heat is made available when CO$_2$ and SO$_2$ are formed than there would be if just using air. In this atmosphere the sulfur and carbon components in the ore are the only fuel needed to keep the roaster at a specific operating temperature.

Barrick Goldstrike began operation, using Freeport McMoran Inc technology, of an oxygenated roasting circuit in 2000. It began as a way to increase overall gold recovery of these double refractory, preg-robbing ores. The operation feeds dry ore, crushed to 80% passing 74 micron, into two separate, two-stage oxygen roasters. Figure 2.8 highlights the roasting circuit along with the crushing and grinding flow sheet.

Roasting in a second stage, set at different operating conditions than the first, allows for a more complete oxidation of preg-robbing carbon components. This idea was crucial to creating better recovery of gold in the leach tank. Key elements to the Barrick Goldstrike roaster operation that aid in better oxidation include:

- First-stage bed operating temperature in the range of 525$^\circ$C-595$^\circ$C
- Second-stage bed operating temperature in the range of 525$^\circ$C-620$^\circ$C
• Use of low-pressure, high-purity oxygen (99.5%, (v/v))
• An ore fuel value equation that is correlated with the % OC and % sulfide sulfur
• Dry grinding in Double Rotator mills for flexibility with hardness of feed ores entering the roaster

The two-stage system begins as the fluidizing medium enters the cold windbox at the bottom of the second stage reactor in the form of pure oxygen. From here, hot exhaust gas flows up through the reactor and the hot windbox (in between the 1st and second stage reactors) to create fluidization for the bed in the first reactor. The hot, oxygen-rich gas is introduced into the 2nd reactor in order to initiate this fluidization in the first stage, but more importantly to complete the oxidation of organic carbon and sulfur in the 2nd stage. The design of the two-stage roasting system in this manner allowed for Barrick Goldstrike to improve their reported oxidation numbers in the calcined ore leaving the system tremendously. As of 2005, based on an assumed ore-composition of 1.9% sulfide sulfur, 1.2% organic carbon, and 5.5% carbonates, reported numbers for overall oxidation in the system was 99% for sulfide sulfur and 88.5% for organic carbon. Figure 2.9 shows the two stage system in more detail below.
Two-stage roasting with pure oxygen is the best system to date for oxidation of double refractory gold ores. Its ability to create optimum conditions for roasting of both sulfidic components and preg-robbing carbon components are what sets it apart, allowing for a calcine that is as amenable to cyanide leaching as possible in the next unit operation(2).

2.3.5 Dealing with Roaster Off-Gas

With increasing environmental regulations in the United States in the past 50 years, handling roaster off-gas in order to release clean air back into the environment has become extremely important. Stricter environmental legislation has been the biggest obstacle for gold companies trying to commission new roasters for oxidative pretreatment of their ore. This process involves treatment of particulate material, sulfur dioxide, arsenic trioxide, and mercury.

Particulate material is important in a roasting operation in order to not release extremely small particles into the environment and to also recover any gold contained in them. The use of cyclones, dust chambers, and baghouses are all integral parts of recovering particles contained in the off-gas. In the typical operation, the underflow from each of these systems is quenched and pumped back in with the roaster calcine, while the overflow containing residual particles is recovered by electrostatic precipitation.

Depending on the amount of sulfide sulfur in the feed going into the roaster, sulfur dioxide produced from the roast can be dealt with in a few different ways. When sulfide sulfur is high, many times sulfur dioxide is converted into sulfuric acid to be sold or used in another unit operation on the mine site (autoclave, etc)(3). In this process, sulfur dioxide that is produced in the process is converted to sulfur trioxide using oxygen in air and then absorbed in either water or a diluted sulfuric acid solution. This process moves along with the help of a vanadium oxide catalyst in the acid plant(18).

When the sulfide sulfur content in the feed is low and sulfur dioxide production in the off-gas is low, different methods are used, both involving reaction with lime. The first method involves roaster off-gas passing through a scrubber containing lime slurry. The reaction chemistry is shown below:

\[ 2\text{Ca(OH)}_2 + 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{CaSO}_4 + 2\text{H}_2\text{O} \]

This reaction works to cancel out sulfur dioxide’s effects by forming gypsum, which is inert. The second method uses limestone that is added to roaster feed to “fix” sulfur dioxide in the bed as it goes through oxidation. This method works to remove almost 75% of the sulfur dioxide and also provides a way to control the temperature in the bed. This reaction produces calcium sulfate and carbon dioxide by the following reaction:
Sometimes this method is a problem due to CO₂ gas forming a blanket over the roaster bed and decreasing roasting efficiency(3). In some regions of the globe though, there is a market for calcium sulfate and it can be sold as a by-product. Calcium sulfate is used as an additive for cement and gypsum, referring to the previous reaction, and can be used in everything from plaster to road building. If a by-product of a reaction can be sold for a profit, it definitely makes the process that much more appealing(19).

When roasting ores containing arsenic, the main compound formed in the off-gas is arsenic trioxide. It is a gas that is naturally corrosive and causes problems in the plant, so it is dealt with in a few different ways. The first method, usually for when arsenic in the feed is greater than 2%, is to condense As₂O₃ and recover it by lowering the off-gas temperature down to 120°C and collecting it in the baghouse. This way produces a fairly pure form but is very maintenance intensive within the plant. Off-gases containing lower arsenic levels are treated by wet-scrubbing with lime(3). Another relatively new procedure for arsenic removal involves co-precipitation of arsenic oxides with ferric ions. A solution containing ferric iron ions can be neutralized, forming a ferric oxyhydroxide phase that has adsorptive properties, especially for arsenic. Chemistry for the reaction is seen below:

\[
\text{FeO(OH)(H}_2\text{O)}_{1+x} + \text{AsO}_4^{3-} = \text{AsO}_4^{3-} \cdot \text{FeO(OH)(H}_2\text{O)}_{1+x}
\]

Arsenic can be relatively unstable in oxide form, so the stable ferric iron in this form helps to stabilize the arsenic and remove it from solution. Much like products formed from dealing with sulfur dioxide, As₂O₃ in pure form can be marketed for sale. It also has big concerns if left untreated due to its affinity for biological components such as proteins and lipids in the environment, making neutralizing it in the roaster off-gas procedure a very important process(20).

Due to the toxicity of the element mercury, any amount that is in the roaster feed must be dealt with in the off-gas safely. High levels of mercury are removed by scrubbing with mercuric chloride, in what is called the Boliden-Nor zinc process. The reaction proceeds as follows:

\[
\text{HgCl}_2(\text{aq}) + \text{Hg}_2^{(v)} \rightarrow \text{HgCl}_2
\]

The solid mercurous chloride is handled by two different methods. A fraction of it is shipped to a mercury producer while the remainder is chlorinated with chlorine gas to be used with the scrubbing process to neutralize more mercury coming into the system(2).
2.4. Additional Roaster Operations

This section will provide additional operational examples of fluidized bed systems operating today. Flowsheets and detailed descriptions of operating parameters will be given, including ore feed content, roasting temperatures, and percent gold recoveries for each operation.

2.4.1. Gidji Plant – Kalgoorlie, Australia

The first commissioned circulating fluidized bed operation was in Kalgoorlie, Australia at the Gidji Plant in June 1989. Now shut down, the plant roasted sulfide gold concentrates as oppose to whole ore and had a throughput of 360-640 tonnes per day of ore. The retention time for solids in the roaster, at a given feed rate, can be estimated by the differential pressure between the top and bottom of the furnace. A key specification of the Gidji plant roaster was its recycle cyclone that recirculates calcine upon reaction completion in the roaster. The recycle cyclone loop provides a stability in process and homogeneity in calcine product that ensures no ore is under- or over-roasted in the furnace. This process design eliminates the need for two stages of roasting and increases chances for maximum gold recovery in the plant. According to 2005 data, the plant operated at an average roasting temperature of 640°C and had around 95% gold extraction efficiency. The unit operations that were involved in the Gidji plant are seen in Figure 2.10(21).

![Figure 2.10. CFB Roaster at the Gidji Plant](image-url)
2.4.2. Newmont CFB Plant – Carlin, Nevada, USA

In 1993 Newmont Gold Company began operation of a circulating fluidized bed roaster, with option for oxygen enrichment, in Nevada. The main unit operations of the plant include ore pre-heating, roasting, gas cleaning, and sulfuric acid production. Data from 2005 indicates that the roaster operates with a throughput of 7800 tonnes per day and produces 90.5% recovery of gold at a head grade of 8.8 grams per tonne.

The main function of the ore pre-heater is to drive off any residual moisture in the ore prior to it entering the fluidized bed furnace. Having the ore enter dry makes the roasting process more efficient in that it takes less time to get to a completely oxidized product. The pre-heater has a design operating temperature capacity of 435°C but operates at no higher than 420°C in order to prevent partial oxidation of sulfides. The typical retention time for ore in the pre-heater is between two and five minutes.

The roasting operation at Newmont consists of two trains in an integrated system that has two cyclones, a fluidizing air blower, oxygen pre-heater, an induct burner and two calcine coolers. The roaster has a retention time of ten minutes and operates at 550°C on average. Depending on the composition of ore feed entering the roaster, sometimes liquid sulfur is injected into the system to maintain temperature and heat balance. If the feed is high in sulfur, this may not be necessary and the roaster becomes semi-autogeneous. Hot calcine product from the CFB is cooled in the calcine cooler by direct and indirect heat exchange and then quenched and neutralized with lime before going on to the leach tanks. Roaster off-gas is cooled in a waste heat boiler down to 375°C and then proceeds to the electrostatic precipitator for removal of dust. The flowsheet is shown in Figure 2.11.

![Figure 2.11. Newmont CFB Roaster](image-url)
The gas cleaning operation begins with the part of the gas stream that is not recycled back into the roaster. The gas enters at 380°C at the bottom of the wash tower, where an evaporation process proceeds to cool the gas to 70°C. While cooling, the gas is saturated with moisture and absorption of SO$_3$ gas, combined with condensing of volatile impurities, occurs. After this step, the gas enters into a combination of 2 two-stage gas coolers to be brought down to a final temperature of 30°C. Upon exit, the cooled gas enters the first of two wet electrostatic precipitators for removal of acid mist and fine dust. Fluorine removal occurs between the two electrostatic precipitators in a fluorine-removal tower while mercury is removed in a tower of its own by mercuric chloride scrubbing. It is crucial that both of these impurities be removed prior to the gas entering the sulfuric acid plant to avoid contamination.

The sulfuric acid plant has three primary operations that include drying/adsorption, SO$_2$ conversion and tail gas scrubbing. It uses a 3 + 1 double absorption system and operates in four production modes. The final product converts SO$_2$ gas to 99.8% sulfuric acid to be sold to market or to be used in other leaching operations on the mine site(21).
CHAPTER 3
EXPERIMENTAL PROCEDURES

Procedures used to prepare, roast, and analyze samples that were received for testing will be explained in this chapter. These procedures were used for both characterization of ore feed and post-roast calcines and will be detailed fully. All procedures in this chapter are used to provide fundamental analysis of three different stockpiles roasted in a laboratory batch tube furnace.

3.1 Testwork Samples

Coarse ore from three different stockpiles that feed a North American roasting circuit in a gold operation were received in August 2014. A high sulfide material ("Hot"), a low sulfide material ("Cold"), and a low sulfide/high organic carbon material ("Troublesome") each were received in separate 55 gallon drums. Table 3.1 summarizes the samples received along with initial weights of each. Each stockpile was dried on a hot plate at 140°F for 24 hours prior to crushing and splitting in order to limit moisture content problems in sample preparation.

Table 3.1. Overall Weights of Samples Received

<table>
<thead>
<tr>
<th>Stockpile</th>
<th>Overall weight (Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot</td>
<td>156.36</td>
</tr>
<tr>
<td>Cold</td>
<td>177.10</td>
</tr>
<tr>
<td>Troublesome</td>
<td>188.02</td>
</tr>
</tbody>
</table>

3.2 Sample Preparation and Grind Study

After the three samples were dried on a hot plate at original coarse size, they were shoveled into separate five gallon plastic buckets for easier mobility and recording of weights. Each sample was stage crushed, first using an Essa jaw crusher set at approximately 19 mm for coarse rock and then a ROCKLABS® jaw crusher set at approximately 3.5 mm apart to get the material to minus 2 mm. Rather than splitting the coarse material from the start, all of the sample received was crushed and then split in order to make sure the samples were representative of the stockpile as a whole. Stage crushing consisted of taking jaw crushed material and screening it in a 457 mm Sweco Vibro-Energy® Separator at 2 mm screen size and re-crushing plus material until all the material comes out in the minus portion. From here sample was split into approximately 1 kilogram charges using a 12 pan Rotary splitter. 12 charges
were placed into another 5 gallon bucket and labeled while the rest of the sample (retain) was placed in a plastic bag and set in a bin. The 12 charges were then taken and split to 500 grams for the grind study. Because the 12 charges were not exactly 1 kilogram, a weight was taken first and then it was placed in a ROCKLABS® Bench Top Rotating Sample Divider and split out based on the percent of that weight needed to make 500 grams. Figure 3.1 shows a picture of the coarse sample received prior to crushing.

The importance of a grind study, if a specific micrometer size is needed for a test, cannot be underestimated because all ores are different. The goal here was to establish a grind time that would ensure 80% passing ($P_{80}$) 74 µm for the roasting tests. To simulate the grinding on site, a dry grind was done. Also, to ensure a narrow particle size range, a Sepor laboratory size batch rod mill was used. Each 500 gram sample was rolled at approximately 74 rpm with a rod charge of nine 19 mm, nine 16 mm, and seven 13 mm diameter by 229 mm long hardened steel rods, with a total weight of 20 pounds. For each stockpile, a minus 2 mm, 500 gram charge was rolled at three different times (sometimes four) and particle size analysis was performed for each grind time. From the particle size analysis, the data was fit to a regression equation used to target a specific $P_{80}$ of 74 µm for each stockpile. Figure 3.2 shows the set-up for dry grinding. Figure 3.3 shows the grind curve for the Cold stockpile with the blue vertical line indicating 74 µm on the curve.
The particle size analysis procedure involves the use of different screen sizes set in a stack and Ro-tapped to determine the size ranges in which particles lie after grinding. The full metallurgical procedure is detailed below:

1) Wet screen the 500 gram ground sample using a 500 mesh Tyler Standard screen on a sieve shaker.
2) Filter the plus and minus portions of the screen and dry each overnight.
3) Place the plus 500 mesh dried sample on to a sieve stack containing 65, 100, 150, 200, 270, 325, 400, and 500 mesh Tyler Standard Sieves. These sizes represent 212, 150, 105, 75, 53, 45, 38, and 25µm sizes respectively. Ro-tap the stack for 15 minutes.
4) Transfer each plus portion of the stack along with the combined minus 500 mesh material from the stack and from the wet screening to a tared bowl and record weights at each size.
5) Enter these weights into a MS Excel sheet with a specific formula to determine a Pₘₐₜ for each time.

Sample preparation and the grind study were key parameters that needed to be done correctly in order to ensure accurate sample representation and particle size. Initial issues arose with the grind study due to lingering moisture in the minus 2 mm sample. The moisture in the samples was affecting the dry grind in a significant enough way so that a consistent regression line with an R-squared value close to one could not be produced. The minus 2 mm samples were then dried overnight prior to each grind at 60°C to evaporate the residual moisture. Just drying the samples on a hotplate as coarse rock is not enough, and a lesson was learned as a result of this initial error in the procedure.

3.3. Mineralogical and Analytical Methods

Methods performed to produce mineralogical and analytical results with both feed and roasted samples are described in detail in the following sections.

3.3.1. X-Ray Diffraction for Semi-Quantitative Mineral Composition

X-ray diffraction was the main tool of use for quantifying minerals in the feed samples and in the roasted calcines from each stockpile. The XRD process involves the use of a micronizing mill for sample prep, a Panalytical X’Pert Pro machine for scanning of samples, and MDI Jade software for processing.

Prep for each sample involved the use of a McCrone micronizing mill to get the samples down to less than 10µm. The sample prep process involved weighing out of approximately 1.5 grams of sample and grinding for five minutes in a slurry of isopropyl alcohol. Grinding media in the mill consisted of 48 corundum grinding pellets. The micronizer produces a product of a more uniform particle size without damaging the crystallites in the sample. It also provides for better sulfide mineral quantification, which was of huge importance in this project. Once samples were ground in the mill, they were dried in an oven and sample was packed into an XRD disc to be loaded into the machine.

Once samples were packed into the discs, they were loaded onto racks and placed into the Panalytical X’pert Pro with X’celerator detector for scanning. Instrument settings for the scans were a
5.00° start angle, 75.020° end angle, and 34.925 seconds per step. A Cobalt tube for X-ray diffraction, as opposed to a Copper tube, was used in order to get better peak resolution. Figure 3.4 shows the XRD setup.

Figure 3.4. Panalytical X’pert Pro with X’celerator detector and Cobalt tube

Phase identification of peaks was done with MDI Jade software. Quantities were identified using Rietveld refinement and whole pattern fitting and no internal standard was used with this data to determine amorphous material. All results greater than 2% were rounded to whole numbers, resulting in all crystalline phases totaling exactly 100%. Individual results for each feed sample and its subsequent roasted sample at a given temperature will be discussed in Chapters 4 and 5.

3.3.2 MLA – Mineral Liberation Analysis

In order to look at gold deportment of roaster feed and calcines of certain stockpiles from the tube furnace, Mineral Liberation Analysis (MLA) by scanning electron microscope (SEM) was used. Backscatter electron images of samples were taken in order to see where potential gold occlusion was occurring. Figure 3.5 shows the setup used for analysis of gold deportment.
For sample analysis, backscattered electron (BSE) imaging using MLA software V3.1 was used along with EDAX genesis software for EDS measurements of arsenic. Sample preparation included mounting, polishing and carbon coating of each feed and calcine chosen prior to running on the MLA.

### 3.3.3 Raman Spectroscopy

Another tool used to examine differences in the outer rim versus the center of certain iron oxide particles was Raman spectroscopy. Raman works by using vibrational spectroscopy, or monitoring molecule bond vibration behavior when laser excitation is used. It is an instrument that becomes very useful when needing to identify minerals with the same chemical composition but different chemical structure, a distinction that cannot be made by SEM or XRD. For uses of this project, distinguishing the formation of hematite versus maghemite in iron oxide particles was very important and findings will be shown in the results chapter. Figure 3.6 shows the Raman setup.
Sample preparation for the Raman was the same as for MLA. Samples were made into epoxy pucks and polished prior to scanning by the instrument. A point-and-shoot method was employed for examining particular particles and identification was made by using internal standards provided by the software.

3.3.4 BET - Surface Area and Pore Volume Analysis

BET analysis is another tool that helps to provide insight into how effective a roast is. Roaster products with high surface area and pore volume are important to the next step in the flowsheet, the cyanide leach. How amenable samples are to gold extraction by leaching is possibly the single most important measurement parameter for a gold operation. For purposes of this project, a Microtrac Belsorp-mini II was used to provide these results. Figure 3.7 shows the instrument.

![Figure 3.7. Microtrac Belsorp-mini II for BET analysis](image)

The BET method works by measuring the amount of gas, in this case nitrogen, that is adsorbed onto a surface. From the amount of gas measured, a surface area and pore volume can be determined(22). The Belsorp Mini-II uses the volumetric method for adsorption analysis. Volumetric method is preferred to gravimetric because sample handling is easier in most cases. The adsorption measurement by volumetric method for this instrument is characterized by four steps that include sample pretreatment, dead volume measurement, adsorption measurement, and lastly desorption measurement.

Pretreatment is a lengthy step to begin the BET process that is extremely important to ensuring accurate adsorption measurement later in the procedure. It takes place in a heated vacuum environment
in order to remove any residual adsorbed gases or water on the sample. Removing gases and water in this step also ensures an accurate sample weight when the actual measurement takes place. For purposes of this experiment, samples were pretreated for approximately 90 minutes at 300°C.

Dead volume measurement is the second step in this process that works by accounting for empty space in the cell that holds the sample. Any dead volume that is not accounted for would produce inaccuracies in the final results. For this instrument the dead volume change was measured using reference cell dead volume data in comparison with the dead volume in each sample that was run. This reference cell data was already saved to a file on the software from a previous measurement in a liquid nitrogen atmosphere and therefore was not measured in this process. Dead volume data for each sample was measured prior to the adsorption measurement and after the pretreatment step.

The adsorption amount in the Belsorp-mini II is calculated based on a difference in pressures before and after adsorption in the system and is the basis of the volumetric method. Pressure sensors at the top and sides of the apparatus help to provide key information on pressure differences, and a bath of liquid nitrogen provides an inert atmosphere that ensures constant temperature in the system. Figure 3.8 shows a diagram of the sample holder setup that is immersed in a 3 liter liquid nitrogen bath during measurement.

![Figure 3.8. Microtrac Belsorp-mini II setup](image)

Highly reproducible and precise adsorption data is achieved in this instrument by the advanced free space measurement method (AFSM), invented by BEL. This method allows the user to not have to control the liquid nitrogen level in the system, whereas in other adsorption instruments this is not
case. The adsorption volume onto a sample is calculated based on the ideal gas law. This equation is shown in Equation 1.

\[ PV = nRT \]

Where \( P \)=pressure in the system, \( V \)=volume, \( n \)=moles of substance, \( R \)=ideal gas constant, and \( T \)=absolute temperature.

The final step, desorption measurement, is calculated the same as an adsorption measurement and an adsorption-desorption isotherm is provided with the surface area and pore volume information for quality assurance purposes. The desorption and adsorption plots should be very similar to ensure that the test was run properly. Figure 3.9 shows an example of an adsorption-desorption isotherm of nitrogen at 77 K.

![Figure 3.9. Adsorption-desorption Isotherm](image)

Bel-Mini Software was used to operate the instrument and enter all weights and operating parameters. BELMaster software was used for data analysis that included surface area, pore volume, and adsorption-desorption isotherms for all samples measured(23).
3.3.5 **LECO Analysis of Carbon and Sulfur**

A LECO Model # 620-400-100 instrument was used for total carbon, total sulfur, sulfide sulfur, and organic carbon measurements. Each stockpile feed along with calcine samples from roasting were analyzed by LECO.

Total carbon and sulfur were determined by analyzing off-gas in the form of sulfur dioxide and carbon dioxide. A known amount of sample was burned in the LECO and off-gas was analyzed by IR in the instrument.

Sulfide sulfur and organic carbon were determined in the same way as total carbon and sulfur but with a hydrochloric acid digestion step prior to burning. The HCl digestion works to dissolve out all carbonates and sulfates in the sample, leaving behind organic carbon and sulfide sulfur respectively. Upon burning, it is known that whatever CO$_2$ and SO$_2$ formed is due to organic carbon and sulfide sulfur(24).

3.3.6 **Preg-Rob Test**

A method similar to the Standard Preg-Rob Test (SPRT) used by Barrick Goldstrike corporation was used to measure the ability of feed samples to preg-rob cyanide soluble gold. The method involves the use of a gold-spike, of known parts per million, added to a slurry of ore and cyanide solution. A specific preg-rob formula, based on the amount of gold still in solution, is used to indicate if the sample has minimal, moderate, or high preg-robbing capacity(24).

3.3.7 **Cyanide Amenability Analysis**

A cyanide shake test was used to analyze gold extraction in roasted samples. A similar method to an Alaska Assay Laboratories procedure for gold cyanide amenability was used, in which a known amount of sample is combined with a hot, 1% NaCN solution and agitated for one hour at a constant temperature. The gold in solution, in parts per million, is then determined by atomic absorption spectroscopy (AAS)(25).

3.4. **Metallurgical Methods of Roasting**

Instruments used to roast samples in a batch setting are described in this section. Batch testing was done in order to provide fundamental analyses of each stockpile at different conditions of roasting.
3.4.1 TGA/DSC with FTIR Evolved Gas Analysis

Thermogravimetric analysis (TGA) was utilized to measure the change in mass of sample as a function of increasing temperature. Differential scanning calorimetry (DSC) is coupled with TGA to provide a measurement of heat flow versus temperature. These two measurements combined can help to predict when and where certain elements or compounds are burning off during the roasting process. Speculation on what is burning off is confirmed when these measurements are combined with an FTIR instrument to provide off-gas analysis. FTIR, or Fourier Transform Infrared Spectroscopy, provides information on peaks coming off at a certain intensity and wavenumber during the roast that, when compared with an internal standard provided by the software, can be matched with a certain gas compound.

The TGA/DSC 1 from Mettler Toledo was used for thermal analysis. The Nicolet 6700 FT-IR with a TGA/FT-IR interface system from Thermo Scientific was used for evolved gas analysis of heated samples. Both instruments are shown in Figures 3.10 and 3.11.

![Figure 3.10. TGA/DSC 1](image-url)
The full metallurgical procedure for TGA/DSC with FTIR is detailed below:

1) Obtain 150µl alumina crucible with cap and use Weigh-In Auto function on TGA software.
2) Get a tare weight of the crucible by setting crucible with cap in the tray and selecting "Weigh Pan" option from software.
3) Once the tare is performed in the system, fill alumina crucible with sample. A ¾ full crucible will hold about 50mg.
4) Ensure FTIR instrument and OMNIC software are on and that the gas line connecting TGA and TGA/FTIR interface is heated up to 200°C for exchange of off-gas between the two instruments. You do not want cold gas flowing into the FTIR.
5) With crucible full of capped sample and in holder, now select “Weigh Sample” option from software.
6) Once a weight is recorded in the software, select measurement program (temperature, gas type, flow rate parameters) in the Method window and hit start. Methods for individual experiments can be created prior to running the experiment.
7) While the TGA is getting up to temperature, select Experiment→TGA experiment in the OMNIC software.
8) Once the TGA gets up to temperature and Weight vs Temperature and Temperature vs. Heat Flow graphs clearly begin to record, go over to the FTIR and hit start for it to begin to analyze. Important to have no delay here or results as far as at what time peaks occurred will not be accurate.
9) Once the sample has run to completion, cool down gas line on FTIR and remove sample from the TGA instrument.
The one drawback to the TGA/FTIR instrument is its small crucible size. Despite being able to provide valuable weight loss and heat flow information, it was difficult to take these samples and run them for analytical and mineralogical tests due to lack of sample size. For this reason, after getting baseline information from the TGA/FTIR, the roasting process was transferred to the tube furnace, an instrument that can handle more sample, and XRD, cyanide soluble gold, and surface area tests were performed on these larger roasted calcines.

3.4.2 Tube Furnace

Tube furnace runs for each stockpile were conducted in a Lindberg Tube Furnace with a Bacharach Oxor® III Oxygen Sensor attached to the off gas line to measure for oxygen consumption in the system. Off gas was scrubbed in 500mL of caustic solution to account for SO₂ forming upon oxidation in the system. A steel vessel with two attached Type K thermocouples was used to hold the 12ml ceramic combustion boat upright inside the furnace. Initially, without the holder, samples were likely to tip over upon entering and being pulled out of the furnace. One thermocouple was used for furnace temperature and sat just outside of the boat, while the other thermocouple sat at the bottom of the boat to measure temperature of the packed sample bed. It was found, through trial and error, that 7.5 grams of sample could sit comfortably in the boat with the thermocouple without losing any sample out of the top during the roast. Temperature as a function of time in the furnace was tracked using the Omega® DP1001AM Automatic Temperature Scanner. This function was plotted using the instrument’s software on the PC and then subsequently transferred into MS Excel for data analysis once the roast was complete. Percent oxygen was written down by hand in a lab notebook to track oxygen consumption at each interval. Figure 3.12 shows the tube furnace set up.

Figure 3.12. Lindberg Tube Furnace
The full procedure for batch roasting in the tube furnace is listed below:

1) Turn on water line and warm up furnace. Temperature will be set manually on front of furnace and may take up to 45 minutes, depending on temperature needed for roast.

2) The tube furnace setting runs about 10-15°C higher than actual temperature in the furnace, so the setting will have to be constantly adjusted during the roast to achieve the desired temperature in the furnace.

3) Once the furnace is up to the desired temperature, turn on the O$_2$ sensor to warm it up for reading and place 7.5 gram pre-weighed sample into the boat and into the furnace and seal the furnace tight. You will know it is tight when bubbles start to flow into the caustic solution column. Make sure the clamp from the O$_2$ sensor is down on the line to ensure pressure into the system.

4) Once sample is sealed in the furnace, immediately go over to the PC and turn on temperature scanner to take the reading.

5) After temperature scanner is on, take your first O$_2$ reading. Release the clamp on the line to get air flow into the sensor. It will take about 15 seconds for the reading to stabilize. Once you have your reading, clamp stopper back down on the line to re-pressurize the system and get air flow back into the furnace. O$_2$ readings will take place every three minutes and a warm up for the instrument will need to happen every time. Have a timer ready for readings.

6) O$_2$ readings will be recorded until the oxygen reading gets back up to 20.7 or 20.8 percent (minus 0.1 % error in the instrument). Once this happens, the roast is complete and the furnace should be turned off and sample removed to cool. Transfer sample from crucible to metal container for room temperature cooling.

7) Once sample is removed, turn off temperature scanner but leave water line on for cooling of the furnace overnight.

8) When sample is cooled, take final weight to know weight loss occurring due to oxidation in each sample.
CHAPTER 4
ORE CHARACTERIZATION AND METALLURGICAL TESTWORK RESULTS

The following sections will describe testwork done on the three different stockpiles received for this project. Ore characterization was done in order to get an idea as to how refractory the samples were and to plan for expected results in the subsequent roasting that would take place in the tube furnace. All three stockpiles, depending on feed composition, produced different results that provided different interpretations as to why and how high or low gold recoveries were being achieved.

4.1. Metallurgical Testwork Approach

The approach for this testwork was to identify fundamentals of roasting of each of the three stockpiles, with particular focus on what is occurring in the roast at specific temperatures. On site, each of the three stockpiles, along with a sulfide concentrate created by flotation, are blended prior to entering the roaster. Accurate analyses of individual stockpiles could help to identify where low recoveries are occurring and how to mitigate them by optimizing the roasting process.

To start, each stockpile was submitted for TGA with FTIR evolved gas analysis to identify exothermic and endothermic peaks created by oxidation of sulfidic and carbonaceous components. TGA would also give an indication of percent weight loss in each sample upon heating. From the information gathered from the TGA and FTIR, an experimental procedure was set for running the tube furnace. Initially it was thought that the majority of the roasting work for the experiment could be conducted using only the TGA/FTIR instrument, but because the sample crucibles were so small for the TGA, that philosophy changed. More sample was needed in order to run characterization tests on the roasted samples such as XRD, Carbon/Sulfur tests, and cyanide soluble gold, all of which required more sample than the TGA could provide. Because the tube furnace crucibles could hold more sample (7.5 grams), this was the main instrument used for the fundamental studies.

Once temperatures were decided upon for the procedure with the tube furnace, the instrument was equipped with an oxygen analyzer that was attached to the off-gas line. The oxygen analyzer provides an indication of how quickly reactions in the roast are occurring and also ensure that each sample is roasted to completion. After roasting in the tube furnace at the decided upon temperatures, samples were submitted for XRD, LECO, cyanide soluble gold, and BET in order to characterize what was happening in the roasts for each stockpile. XRD shows the minerals that are forming at each temperature. LECO gives an indication as to how much sulfur and carbon is burning off at each temperature. Cyanide soluble gold provides data as to how amenable to leaching each calcine would be. BET provides information on surface area of the roasted products.
The goal with the tube furnace, and it being a batch roast test, was to take results and try to apply them to parameters needed for a continuous roast. If fundamentals of each stockpile under varying roasting conditions could be established at a batch level, then that data could be used to establish ideal temperatures and retention times for a continuous test.

4.2. Ore Characterization

The first step of this project involved mineralogical and chemical analyses of ~70 grams of split out head samples from each stockpile. The chemical test results are presented in Table 4.1. Mineralogical characterization was done by XRD and presented in Table 4.2, with a key for mineral names to supplement in Table 4.3. These results made it possible to predict what would be formed in the tube furnace roasting process.

The hot stockpile sample could be characterized by having the most sulfide sulfur to burn of the three samples and a relatively low amount of organic carbon. Its head grade of gold was relatively high at 5.208 ppm and had low preg-robbing capacity, which was to be expected with a low amount of organic carbon found by LECO testing. As expected with an un-oxidized ore of this type, the cyanide soluble gold in the feed was low, something that should increase significantly upon roasting. XRD results for the hot stockpile showed sulfides in the form of pyrite and marcasite, along with carbonates in the form of dolomite and calcite at fairly high percentages. Sulfide and carbonate phases identified by XRD were of particular interest due to their tendencies, depending upon temperature of the roast, to take a different form upon high temperature oxidation.

The cold stockpile had the highest gold grade of the three stockpiles and a lower level of sulfide sulfur than the hot stockpile. Its organic carbon was low but it had a reasonable amount of preg-robbing capacity, which is somewhat of a contradiction. The cyanide soluble gold test for this stockpile produced a somewhat significant result, as opposed to less than 0.010 for the other two, but was still very refractory in nature. XRD showed sulfides and carbonates in the same minerals as the hot stockpile, just in lower concentrations. This drop in mineral percentage was due to the cold stockpile having significantly more quartz than the other two stockpiles.

The troublesome stockpile could be summed up by high organic carbon, low sulfide sulfur, and the lowest gold grade of the three stockpiles, making it the most interesting of the three. The XRD results, along with the total carbon number, showed not only that this stockpile was high in organic carbon but also high in carbonate carbon, as seen by the high dolomite and calcite percentages. This stockpile, from looking at the feed data alone, would be expected to have the least gold recovery of the three, as the designation “troublesome” would suggest.
4.3. Fundamental Chemistry

Before proceeding with the experiments, it was important in this project to have a good understanding of the fundamental chemistry involved in the roasting of sulfidic and carbonaceous ore. The high amount of dolomite and calcite in the feed of each sample made the chemistry of these minerals
upon oxidation worth looking at also. Having a good idea of what should be forming upon high temperature oxidation helps to provide a better analysis of the project overall. Key reactions in the TGA and tube furnace roasting processes are shown below (most have been mentioned in Chapter 2):

1) **Oxidation of Pyrite to form Sulfur Dioxide and Magnetite then Hematite**

\[ 3\text{FeS}_2 + 8\text{O}_2(\text{g}) \rightarrow \text{Fe}_3\text{O}_4 + 6\text{SO}_2(\text{g}) \]
\[ 4\text{Fe}_3\text{O}_4 + \text{O}_2(\text{g}) \rightarrow 6\text{Fe}_2\text{O}_3 \]

2) **Oxidation of Organic Carbon to form Carbon Dioxide**

\[ \text{C} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \]

3) **Calcium Sulfate and Carbon Dioxide formation by Calcite Decomposition:**

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2(\text{g}) \]
\[ \text{CaO} + \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaSO}_4 \]

4) **Calcium Sulfate and Carbon Dioxide formation by Dolomite Decomposition:**

\[ \text{CaMg(CO}_3)_2 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2(\text{g}) \]
\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2(\text{g}) \]
\[ \text{CaO} + \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaSO}_4 \]

Magnesium sulfate is another common product of oxidation of dolomite, but one that was not formed in the experiments conducted for this thesis. Based on the results shown below, it can be concluded that conversion of magnesium oxide to magnesium sulfate (\(\text{MgSO}_4\)) is more difficult to do than forming calcium sulfate from calcium oxide in the conditions used for roasting in this experiment.

All of these products form at different temperatures and will be identified by various mineralogical and analytical tests conducted on the calcines. Certain products formed at higher temperatures may tend to occlude gold more and be the reason why a roaster on site is not run that high, and the same for a low temperature. The reactions that occur here at varying temperatures form the basis for why a range of temperatures were run in the tube furnace experiments.

### 4.4. TGA/FTIR Results

TGA/DSC with FTIR evolved gas analysis was crucial in identifying at what temperatures reactions were occurring in the roast. The plan of approach was to use a temperature ramp up from 50-1000°C and identify peaks along the timeline that were endothermic and exothermic. From a literature review, there was a general idea of what was burning off at each temperature, and this was confirmed by FTIR spectra used to evaluate the off-gas of each sample. Three TGA tests were performed: one with a nitrogen atmosphere (shown in black), one with a pure oxygen atmosphere (shown in blue), and one with an air atmosphere (shown in red). The idea here was to compare how weight loss and heat flow was
affected upon high temperature oxidation under each atmosphere. Both plots shown in the TGA figures have temperature and time on the x-axis, with the top half portraying weight of the sample and the bottom half showing heat flow on their respective y-axes. The expected result would be to have more weight loss and heat flow in a pure oxygen atmosphere, but as seen in the results below this was not always the case. Heat flow from the DSC matched up with peak confirmation from FTIR was more of a determining factor in what was being burned off, as opposed to the TGA weight loss plot. Bumps in the DSC plot helped to identify exothermic or endothermic reactions that were occurring during the roasting of sample. Results are shown in Figures 4.1 through 4.6 below.

Figures 4.1 and 4.2 show results for the hot stockpile sample. Peaks generated from the FTIR spectra in Figure 4.2 are matched back to the time it occurred on the DSC plot in Figure 4.1 to identify peaks. FTIR peaks were confirmed by an internal software standard that showed what gas occurs at a certain wavenumber. Absorbance shows the peak intensity and is a way of identifying qualitatively how much of the gas is forming. This sample was characterized by a high amount of sulfide sulfur (shown in section 4.2), so a relatively high amount of SO₂ formation was expected. This is confirmed in the FTIR spectra. Sulfur dioxide formation occurs in the range of 400-470°C, a fairly exothermic reaction of carbon with oxygen, forming carbon dioxide, occurs between 540-610°C, and carbonate decomposition occurs in the range of 680-820°C. These reactions occur due to oxidation of sulfide sulfur, organic carbon, and dolomite/calcite respectively, all of which were identified in the feed. Carbonate decomposition is characterized as an endotherm, which is confirmed here for the most part, but there is a slight bump at 725-750°C that indicates an exothermic reaction occurring. This reaction went unidentified when looking at literature for decomposition of carbonates at high temperatures.

![Figure 4.1. Hot Stockpile TGA/DSC plot](image-url)
Figures 4.3 and 4.4 show results for the cold stockpile sample. FTIR peaks matched back to the DSC plot show a smaller amount of sulfur dioxide formation than the hot sample in the range of 400-470°C. This is an expected result due to the low amount of sulfide sulfur in the feed. This sample also showed a smaller amount of organic carbon oxidation in the range of 540-645°C. Its carbonate decomposition occurred in the same temperature range as the hot sample (680-820°C) but showed no exothermic bumps in that range. Differences in feed composition between the hot and cold sample could be the reason for the contrast in what is reacting in this range.
Figures 4.5 and 4.6 show interesting results for the troublesome stockpile. With little sulfide sulfur in the feed, there was hardly any showing of a sulfur dioxide peak in the DSC plot, the only way it was identified was through a very small peak in the FTIR spectra. The CO$_2$ peak on the other hand, was extremely pronounced in the range of 540-640°C. The high organic carbon in the feed was the reason for the large carbon dioxide peak at this temperature. Dolomite decomposition occurred in the range of 750-890°C according to the FTIR, a higher temperature than was identified for the other 2 samples. It also showed an exothermic bump in the DSC around 750°C, similar to the hot stockpile sample.
Figure 4.6. Troublesome Stockpile FTIR Spectra

Results from Figures 4.1 to 4.6 were the basis for the procedure used in the tube furnace. Seeing what was occurring along a widespread temperature range at a smaller sample size made it possible to identify the key temperatures at which the tube furnace roasts would need to be run in the larger experiment.

4.5. Tube Furnace Roast Results

Using data obtained from the TGA/FTIR runs, an experimental procedure was set up for roasting of larger samples in the tube furnace. Each of the three stockpiles was to have eight roasts, in 50 degree increments from 450-800°C while taking oxygen readings from an off-gas line every three minutes. The goal was to examine temperature and oxygen consumption in the sample bed while comparing that to the furnace temperature and a blank boat run. Each sample was roasted to completion in air, meaning leaving the sample in the furnace until all reactions had taken place and the percent oxygen in the system was back up to 20.8%. A before and after weight would be taken on all samples and the calcines submitted for mineralogical and analytical testing. Analysis of mineral formations during roasting, along with quantifications of sulfide sulfur and carbonaceous carbon burnoff, at each of these temperature increments could help provide fundamental clues as to what is occluding gold in each stockpile. The results will be discussed below.

One graph for each stockpile was chosen for display here and are shown in Figures 4.7 to 4.9. Each was chosen based on showing the most exothermic activity in the run, the other 7 graphs for each stockpile are attached in Appendix A. Comparisons of how oxygen was consumed in each reaction, one
as a function of time and the other as a function of temperature will be discussed in Figures 4.10 to 4.12. These temperatures were chosen for comparison purposes as well and the rest of the oxygen consumption charts are attached in Appendices B and C.

The hot stockpile runs can be summarized by having the most exothermic activity at 550°C and the most oxygen consumption at 750°C. The exothermic portion of the run was determined by the sample temperature rising above the furnace and blank boat temperature between the 8 to 12 minute mark on Figure 4.7. Based on composition of the feed and temperature at which the reaction occurs, this exothermic portion is most likely due to oxidation of sulfides and slight oxidation of carbonaceous carbon. Temperatures of 500, 550, 600, and 650 all saw fairly exothermic reactions occurring during their runs, while at 700, 750, and 800 the sample temperature stayed consistent with the blank boat and furnace temperatures. This can be explained by most sulfide sulfur and carbonaceous carbon burnoff occurring at the lower temperatures, while at the higher temperatures dolomite and calcite decomposition begins to come into play. The furnace runs at the higher temperatures showed not much exothermic activity above the blank run due to the nature of the minerals reacting. In these runs the carbonaceous carbon and sulfide sulfur burnoff (exothermic reaction) would compete with dolomite and calcite decomposition (endothermic reaction), resulting in the energy from both reactions coming out fairly even. Despite this, the higher temperature runs showed what appears to be increased oxygen consumption, leading one to believe an exothermic reaction is occurring. This low reading of oxygen consumption is due, in part, to carbonaceous carbon oxidation (exothermic), and the rest to dilution of the reading by carbon dioxide formation upon dolomite and calcite mineral decomposition. The 450°C run showed no reaction due to it not being hot enough to oxidize sulfides at this temperature.

![Figure 4.7. Hot Stockpile Tube Furnace Run at 550°C and 510 cc/min air](image-url)
The cold stockpile tube furnace runs saw the best exothermic reaction at 550°C and the most oxygen consumption at 800°C. The 500°C run is shown in Figure 4.8. This reaction is still not very exothermic at all due to the low sulfide sulfur composition in the feed, especially when compared to the hot stockpile. Low sulfide in the feed also accounted for only slight exotherms in the 550, 600, and 650 tube furnace runs for this stockpile. Similar to the hot stockpile, the higher temperature runs saw the sample temperature stay even with the blank run throughout the roast, again due to competing exothermic and endothermic reactions. The reaction at 800°C consumed the most oxygen of the eight runs, with a reading of 14.8%, and can be contributed to both carbonaceous carbon oxidation and dilution of the reading by carbon dioxide formation upon dolomite and calcite decomposition.

![Figure 4.8. Cold Stockpile Tube Furnace Run at 500°C and 510 cc/min air](image)

The 550°C troublesome sample run is shown in Figure 4.9 and was the most interesting graph of the 24 total samples that were run. This graph showed a very high exothermic reaction in the range of 11 to 27 minutes in the run. Its oxygen consumption graph was very interesting also in that it had two separate peaks, suggesting that two separate reactions were taking place, one as oxidation of sulfide sulfur and the other as oxidation of organic carbon, the second of which was very high in the feed. The sample temperature rose to 57°C above the blank at maximum consumption on this graph, higher than any of the other runs, suggesting that the oxidation of organic carbon can provide huge amounts of energy to a system when run at the right temperature. Similar to the other two stockpiles, the highest oxygen consumptions for the troublesome sample were at the highest temperatures. The 800°C run saw an oxygen reading as low as 14.1%, for the same reasons mentioned for the other two stockpiles at high.
temperatures. Similar to the other two at the higher temperatures, the sample temperature stayed pretty consistent with the blank run. This was due to competing reactions in the furnace at this temperature.

![Figure 4.9. Troublesome Stockpile Tube Furnace Run at 550°C and 510 cc/min air](image)

Figures 4.10 through 4.12 are used to compare oxygen consumptions of the three stockpiles and should be looked at together to compare and contrast. Figure 4.10 was the original plot and shows oxygen as a function of time. Figure 4.11 takes 4.10 and uses oxygen as a function of temperature in the system and is the most telling for comparison purposes. Figure 4.12 is used to show distinctions between how the consumption plot differs at a higher temperature versus a lower temperature run.

Figure 4.11 is useful in showing where along the temperature range the sulfides or carbon begin to consume oxygen in the system. This figure shows that consumption begins earlier, around 200°C, with the hot stockpile, most likely due to high sulfides in the feed, than the other two. The cold stockpile starts consuming at a higher temperature but has a sharper rate of consumption beginning around 400°C. Both the hot and cold stockpile show maximum consumption at around 500°C, indicating sulfide burnoff. As discussed previously, the troublesome sample shows two peaks of consumption, one close to 500°C, indicating sulfide burnoff, and one close to 600°C, indicating a highly exothermic organic carbon oxidation reaction.
Figure 4.10. Oxygen vs Time Plot for all three stockpiles at 550°C in air

Figure 4.11. Oxygen vs Temperature for all three stockpiles at 550°C in air
4.5.1. Analytical Results

Analytical chemistry results were used to confirm what was burning off during the roasting process and, most importantly, to determine the amount of gold extraction at each temperature. Surface area tests were also a key parameter for indicating what was happening during roasting. Tables 4.4 through 4.6 summarize the results seen at each temperature for the three different stockpiles. The results in each column will be discussed graphically in this section.

Table 4.4. Analytical Results for Hot Feed and Tube Furnace Calcines

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au Extraction %</th>
<th>BET SA (m^2/g)</th>
<th>Organic C %</th>
<th>Sulfide S %</th>
<th>C_TOTAL %</th>
<th>S_TOTAL %</th>
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<tbody>
<tr>
<td>Hot Feed</td>
<td>0.19</td>
<td>0.57</td>
<td>1.90</td>
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<tr>
<td>Hot 450</td>
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<td>Hot 700</td>
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Table 4.5. Analytical Results for Cold Feed and Tube Furnace Calcines

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<th>Sample</th>
<th>Au Extraction</th>
<th>BET SA (m^2/g)</th>
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<th>Sulfide S</th>
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<th>S_TOTAL</th>
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<tr>
<td>Cold Feed</td>
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Table 4.6. Analytical Results for Troublesome Feed and Tube Furnace Calcines

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<th>Sulfide S</th>
<th>C_TOTAL</th>
<th>S_TOTAL</th>
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<td>0.04</td>
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<td>0.60</td>
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Figure 4.13 shows percent gold extraction as a function of temperature. All three stockpiles saw a significant jump in gold extraction from the 450°C to 500°C roasts, with the troublesome stockpile making the biggest leap. All indications from this result are that a roasting operation for any type of gold ore should be run at 500°C at the very least. The hot stockpile did not show much difference at all in percent extraction between 500 and 700°C but dropped off at greater than 700°C. The best recovery was seen in the 700°C roast with a recovery of 72.2%. The cold stockpile hit a maximum at 500°C and 550°C, with almost the exact percent extraction (~70%), and began dropped off at 600°C and greater. The troublesome stockpile in the range of 500°C to 700°C stayed around 70% extraction, similar to the other two stockpiles, and then encountered a drop off at 750°C, followed by a jump at 800°C to its best extraction percentage of 76.5%, the highest overall extraction of any stockpile at any temperature. Lower temperatures for gold extraction in the hot and cold samples could be explained by having more sulfur and less carbon in their respective feeds. The high temperature of 800°C for best extraction in the troublesome stockpile could be explained by the high carbon content in its feed, carbonaceous carbon.
being a component that does not start to burn off until temperatures are greater than 700°C. Sulfur and carbon content as a function of percent gold extraction will be looked at more in depth later in this section. Overall, gold extraction of around 70% tend to be less economical for a gold operation, so investigation into how the last 30% is being occluded in the roast holds particular interest and is worth investigation.

Figures 4.14 and 4.15 show surface area and pore volume data for each calcine produced at the given roasting temperatures. Both figures show results for each stockpile that were unexpected to say the least. Both show data that hits a peak surface area and pore volume number at around 750°C and then there is a slight drop at 800°C. Expected results from a literature review were to see more of an upside down parabola shape of the graph, in which there is a steady rise to maximum results seen around 650°C and then it begins to drop due to pore sintering of particles. There was no indication of that here. A third party lab was consulted to verify BET results as well and they produced the same outcome. Figure 4.14 also shows a higher surface area at the 450°C roast than for 500°C for all three samples, a result that is possibly within the experimental error of the instrument but still very unexpected. Surface area should expand upon high temperature roasting, not decrease.

Figure 4.13. Gold Extraction vs Temperature graph
Figures 4.16 through 4.18 show key chemistry results for the hot stockpile roasts as a function of percent gold extraction. Figure 4.16 plots sulfide sulfur numbers for each roast. This data shows an inversely proportional relationship between sulfide sulfur in the roast and percent extraction, with the majority of oxidation happening in the 450 to 500°C roasts. The best extraction occurs in the range of 500°C to 700°C and this is also where the sulfur numbers are the lowest. Figure 4.17 plots organic carbon in each calcine as a function of percent gold extraction. This graph also shows a significant inverse relationship between organic carbon and percent gold extracted. According to the data,
recoveries increase significantly as soon as the organic carbon in the feed begins to drop out. Similar to sulfide sulfur, this trend begins at around 500°C. The trend may be even more significant than sulfide sulfur, though, in that the lowest organic carbon coordinates exactly to the best percent recovery at 700°C.

Figure 4.18 shows the relationship between gold extraction as it relates to total carbon, total sulfur and surface area of the calcines at each temperature. From the total carbon results, there is a small, steady decline from the percent in the feed to the 600°C roast. At 650°C the carbon really begins to drop and is there is almost none in the final 800°C roast. This data at the higher temperature matches the carbonate decomposition reaction discussed in section 4.3. The total sulfur in each roast shows a steady decline in the feed, 450, and 500°C roasts and then it begins to increase at 550°C and sees a steady increase through to 800°C. At first, this result was confusing due to expectation that all of the sulfide sulfur would be oxidized into sulfur dioxide gas in the roast, but after looking at the fundamental chemistry and seeing that calcium sulfate is a common product of sulfide ore roasting, these results were justified. This increase in total sulfur provides insight into the temperature at which sulfide sulfur that is oxidized begins to convert to sulfate sulfur, which is around 550°C for this stockpile. Sulfate sulfur formation will follow the path of dolomite and calcite breakdown. This is another reaction discussed in section 4.3 and the formation of this product to increase total sulfur in the calcine will be shown and confirmed in the XRD results section. Surface area results were not indicative of gold extraction at all. The peak surface area occurred at 750°C and this is the same temperature when percent gold extraction drops off to 50%, indicating no correlation.

Figure 4.16. Hot Stockpile Sulfide Sulfur comparison with Gold Extraction
Figure 4.17. Hot Stockpile Organic Carbon comparison with Gold Extraction

Figure 4.18. Hot Stockpile BET, Total Carbon, Total Sulfur comparison with Gold Extraction
Figures 4.19 to 4.21 show comparisons for chemistry versus gold extraction for the cold stockpile roasted calcines. Similar to the hot stockpile results, Figure 4.19 shows an expected trend, despite having a low sulfide feed, of recovery going up when the sulfides are oxidized. More than half of the sulfide sulfur is oxidized at 450°C but the recovery does not reach its maximum of 70% until nearly all of the sulfide sulfur is gone at 500°C. Figure 4.20 shows a less convincing trend for organic carbon playing a significant role in recovery for the cold stockpile. The organic carbon goes up in the 450°C roast and so does recovery, possibly a result that is within the experimental error of the LECO test for organic carbon, but still one that does not correlate. There is also a significant amount of lingering carbon in the 500°C roast but the percent gold extraction has reached its maximum, showing that, at least for this stockpile, sulfide sulfur plays a more important role in recovery than organic carbon. Figure 4.21 is very similar to Figure 4.18, just with results that follow a feed with less sulfur and carbon. Total carbon shows a steady decrease with a quicker drop off at the higher temperatures, again indicating carbonate decomposition in the forms of dolomite and calcite. Total sulfur is trending down until the roast temperature gets to 550°C and then it starts to rise, indicating conversion of oxidized sulfur to calcium sulfate in the bed. Surface area also peaks at 750°C here, but it does not match with the temperature at which the maximum percent gold extraction occurs, indicating no correlation between the two in the cold stockpile as well.

![Cold Stockpile Roasts](image.png)

Figure 4.19. Cold Stockpile Sulfide Sulfur comparison with Gold Extraction
Figure 4.20. Cold Stockpile Organic Carbon comparison with Gold Extraction

Figure 4.21. Cold Stockpile BET, Total Carbon, Total Sulfur comparison with Gold Extraction
Figures 4.22 to 4.24 show troublesome stockpile chemistry results in comparison with percent gold extraction. Figure 4.22 shows sulfide sulfur results at each temperature with an original feed composition that is very low in sulfide sulfur to begin with. A majority of sulfide sulfur is gone at 450°C but gold extraction is still very low at this point. The stronger correlation to extraction with this stockpile is shown in Figure 4.23 with organic carbon percent. This graph shows an inverse relationship in that as soon as a majority of the carbon is burned off at 500°C the recovery goes up significantly. The fact that the bulk of the organic carbon content was oxidized by 500°C was a bit of a surprise. The expected temperature for burnoff of carbon was higher (550°C or greater) based on literature review. Figure 4.24 shows trends with total carbon, total sulfur, and surface area. The total carbon in each roast follows the same trend as the other two stockpiles, a steady drop from the feed to 650°C and then a sharp decrease beginning at 700°C. The high dolomite and calcite in the feed, though, accounts for much more carbonate carbon decomposition at these higher temperatures than the previous stockpiles. Total sulfur in this graph shows a small trend going up at 550°C due to calcium sulfate formation, but it does not change much due to the very low sulfur in the feed to begin with. Surface area results are similar to the other two stockpiles in terms of having a weak correlation with gold extraction. The best surface area result occurs at 750°C, where one of the lower gold extraction percentages occurs. Despite this, there is still high surface area at 800°C according to BET results, the same temperature at which the highest gold extraction of 76.5% occurs, indicating a stronger correlation here than either of the other two stockpiles. Overall, though, it is hard to make a claim that surface area had any kind of effect on gold extraction in these experiments.

Figure 4.22. Troublesome Stockpile Sulfide Sulfur comparison with Gold Extraction
Figure 4.23. Troublesome Stockpile Organic Carbon comparison with Gold Extraction

Figure 4.24. Troublesome Stockpile BET, Total Carbon, Total Sulfur comparison with Gold Extraction
4.5.2. Mineralogical Results

X-Ray Diffraction was used to determine mineral content of each calcine product. It is important to reiterate that XRD produces semi-quantitative data and that percentage values are not exact by any means. The results of the analyses are shown in Tables 4.7 to 4.9, with a mineral key for reference in Table 4.10. Quantities were determined using Rietveld refinement and whole pattern fitting. Results greater than two percent were rounded to whole numbers and no internal standard was used to determine amorphous content, resulting in all phases having a sum of 100 percent.

These tables confirm formation of the desired product of hematite, among others, in each stockpile. Formation of hematite was a positive result showing good oxidation of pyrite and marcasite in the tube furnace. Another key mineral formation that was suspected in the previous section, with the total sulfur going up with temperature, is calcium sulfate, identified by XRD as anhydrite. Calcium sulfate is a mineral that can occlude gold in the leaching step. Calcium oxide and magnesium oxide in small amounts indicates formation of intermediate oxidation products in the breakdown of dolomite and calcite at higher temperatures. Calcium hydroxide was an unexpected product identified in fairly large amounts at the higher temperatures for each stockpile, possibly due to water in the gas line that fed air to the furnace. Water's interaction with a calcium oxide in the feed is the possible cause for the formation of this product identified by XRD.

Table 4.7. Hot Stockpile Mineral Phase Formations for Feed and Calcines

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Table 4.8. Cold Stockpile Mineral Phase Formations for Feed and Calcines

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Table 4.9. Troublesome Stockpile Mineral Phase Formations for Feed and Calcines

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Table 4.10. Mineral Key for Tables 4.7 to 4.9

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<td>Py</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Quartz</td>
<td>Qz</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Rutile</td>
<td>Rt</td>
<td>TiO₂</td>
</tr>
</tbody>
</table>

Figures 4.25 and 4.26 show trends for key mineral formations in the hot stockpile experiments from the feed all the way up to the 800°C roast. Figure 4.25 shows that nearly all of the sulfide sulfur in the form of pyrite and marcasite is gone by 500°C. Hematite and calcium sulfate formation begins simultaneously with the oxidation of sulfur as the temperature increases, confirming two of the key fundamental reactions expected with roasting. Hematite shows a significant jump at 650°C and hits its maximum of four percent at 750 and 800°C, but this percentage jump could be due to having less sample as a whole at the higher temperature roasts due to mineral decomposition. The amount of hematite most likely stays the same at the higher temperature roasts as it is at 500 and 550°C. The calcium sulfate, in the form of anhydrite for XRD purposes, steadily rises and hits its maximum at 800°C, showing nine percent. This mineral most likely did form in larger amounts due to the fundamental chemistry involved with mineral decomposition at these higher temperatures. Figure 4.26 shows trends for mineral formation upon the decomposition of dolomite and calcite at high temperatures. Dolomite drops to a third of its feed composition at 700°C and then is completely gone at 750°C. Calcite does not start to decompose until 750°C, with a significant loss, and is gone by 800°C. The production of magnesium oxide and calcium oxides in the roast confirm another fundamental reaction mechanism and, more importantly, confirms that the production of carbon dioxide is occurring in the roast due to dolomite and calcite decomposition. The unexpected product formation of calcium hydroxide is seen at 750 and 800°C in fairly large amounts as well, most likely related to the aforementioned temperature at which calcite decomposes.

![Reactions of Sulfides in "HOT"](image.png)

Figure 4.25. Hot Stockpile Sulfide Formations by XRD
Figures 4.27 and 4.28 show mineral formations for the cold stockpile upon roasting at the various temperatures. Figure 4.27 shows the reactions of sulfide sulfur follow the same trend as the hot stockpile, just with less sulfides to begin with. Like the hot stockpile, all of the pyrite and marcasite is oxidized by 500°C and hematite and anhydrite begin significant formation as a result. Because there is less sulfide to begin with, less anhydrite and hematite form. Similar to what occurred in the hot stockpile results, the hematite percentages increase with roast temperature but this is due to having mass loss as a whole. Most likely no more hematite was formed. The carbonate reactions are seen in Figure 4.28 and follow the hot stockpile trend as well, just with lower feed compositions of dolomite and calcite. The main products of dolomite and calcite decomposition include calcium and magnesium oxide, along with calcium hydroxide. These products begin formation in significant amounts at 750 and 800°C. Dolomite and calcite are completely gone by the 750°C roast.
Figure 4.27. Cold Stockpile Sulfide Formations by XRD

Figure 4.28. Cold Stockpile Carbonate Formations by XRD
Figures 4.29 and 4.30 show the troublesome stockpile mineral formations upon roasting. Figure 4.29 shows the conversion of sulfides to anhydrite and hematite. Due to the very small amount of sulfides in the feed, all of the pyrite is gone by the first roast of 450°C. This graph also shows the significantly smaller amount of anhydrite formed at the higher temperatures of 750 and 800°C in comparison to the other two stockpiles. Hematite formation is also low, in comparison to the hot stockpile, due to less pyrite in the feed. Figure 4.30 shows the reactions of the carbonates upon roasting. These reactions were interesting due to the high percentage of dolomite in the feed. More than half of the dolomite in the original feed is decomposed by 700°C and is completely gone by 750°C. The calcite percentage increased from 10 to 16 percent from the 650°C to 700°C roast, most likely a result of being a product of dolomite decomposition, prior to further breakdown at higher temperatures. The products of decomposition in this stockpile, especially magnesium oxide and calcium hydroxide, show up in higher percentages at 750 and 800°C than the other two stockpiles. These products in high percentages were expected due to the high amount of carbonates, especially dolomite, in the feed composition.

Figure 4.29. Troublesome Stockpile Sulfide Formations by XRD
4.5.3. MLA/SEM and Raman Spectroscopy Results

Some late testwork, in the form of backscattered electron imaging by scanning electron microscope and Raman spectroscopy, was added to this project in order to attempt to explain how and why low gold extraction percentages were occurring in the roasts. Hot stockpile feed and 700°C tube furnace roasted calcine samples were chosen and made into epoxy pucks for first, the MLA, and second for Raman spectroscopy runs.

The objective in looking at the feed under the scanning electron microscope was to try to identify particles pre-oxidation that could potentially produce undesirable products in the roast, or products that could inhibit gold extraction by leaching. Figure 4.31 shows the images produced. Pyrite, the main gold bearing mineral in this ore type, and where it was occurring in the feed was particularly targeted in the images.
The next step was to look at roast products from the 700°C roast and try to identify where any gold encapsulation could be happening, and possibly relate that back to the pyrite occurrences in the feed. This logic involved examining iron oxides and their occurrences in the calcine. Figures 4.32 and 4.33 show examples of iron oxide deportment in the calcine.
Figure 4.32 shows a desired, porous iron oxide, presumably hematite, product from the roast. This is a particle whose gold content would be leached very well into solution and does not contribute to low gold extraction percentages. Figure 4.33 shows two examples of common iron oxides seen in the analysis done by BSE imaging. Both particles contain a porous center with a non-porous outer rim. The outer impervious rim was of much interest, especially with numerous occurrences of particles of this type in the calcine. The outer rim was investigated further with the Raman instrument, with spectra produced of three different locations on the outer impervious rim of the particle on the right in Figure 4.33. These spectra along with maghemite and hematite standard spectra were compared. Results are shown in Figures 4.34 to 4.36.

Figure 4.33. BSE images of two porous center with non-porous outer rim iron oxides in Hot 700°C roast

Figure 4.34. Raman spectra of outer rim of iron oxide particle using the point-and-shoot method
These three figures provide strong indication that the product produced on the outer rim is not hematite, but the intermediate roast product of maghemite. All three spectra of the outer rim points show matching peak location to the maghemite standard used. Being able to show decisively that this outer rim was maghemite, a known gold occluding product of roasting, was a significant finding for an explanation of why the gold extraction percent was so low. From the findings here, the next step was to try to correlate particles in the feed to the maghemite produced in the roast. This was done by using EDS analysis provided by the MLA instrument to look at elemental differences in the maghemite on the outer rim versus the hematite contained on the inside of the particle. Figures 4.37 and 4.38 show these results.
Figures 4.37 and 4.38 show that the outer rim of maghemite contains arsenic, a finding that relates back to the arsenian pyrite rim around pyrite in the feed. This result was a huge breakthrough in terms of making conclusions based on what contributes to the formation of maghemite in the roast, and is discussed in the next chapter.

Another potential reason for low gold extraction was iron oxides encapsulated in silicates. Particles of this type were found in abundance when investigated by BSE imaging and an example is shown in Figure 4.39.
Gold occlusion due to encapsulation in silicates and maghemite formation were both discussed ideas coming into this project based on the nature of this ore and information coming back from the roaster on site. To be able to show that formation of these products was also occurring in a separate lab tube furnace roast was significant to this project. Gold extraction losses due to their formation were more significant in the lab than on site, which is also an interesting finding. The findings by Raman and BSE imaging were important to the overall conclusion of this thesis and for suggestions of ideas on how to nullify the formation of these products with further research. With more time, it would have been interesting to look at calcines from the different temperature runs of each stockpile and try to quantify maghemite formation and iron oxides in silicates to see any differences.

Figure 4.39. Iron oxide encapsulation by silicates in the Hot 700°C roast product
CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

The objective of this research program was to provide fundamental roasting analysis of three different stockpiles containing varying amounts of gold, carbon and sulfur. Providing useful information could help improve roasting techniques on site in order to recover more gold. Many determinations were made with the results produced, along with suggestions for further research into the nature of double refractory ores like the ones seen in this project. The following section will provide conclusions made from results for each stockpile, along with recommendations for changes to operating parameters that could improve roasting efficiency for these ores on site.

Sulfide sulfur and organic carbon burnoff results were very important to this project in being able to show that complete oxidation was achieved in roasting. It could be assumed that complete roasting was achieved based on oxygen consumption not occurring in the roasts anymore, but to be able to confirm this by LECO tests was an important factor in eliminating incomplete oxidation as a possible reason for gold occlusion in the samples. Based on this testwork, along with the presence of hematite formation by XRD, the fundamental chemical reactions of a typical sulfidic and carbonaceous gold ore during high temperature oxidation were confirmed. Low recoveries shown by cyanide soluble gold tests for all three stockpile calcines at the different temperatures, though, raised questions as to how the gold was being occluded in the roast products. This lead to further investigation into these products through backscattered electron imaging produced by a scanning electron microscope.

BSE imaging and Raman spectroscopy of particles contained in the Hot stockpile roast at 700°C, revealed a possible explanation in the form of maghemite as to why gold extraction was so low (<75%) in all three stockpiles roasted at the different temperatures. Evidence for the bulk of the gold occlusion occurring due to maghemite in the tube furnace roasts is shown by the fact that maghemite is an established product for gold occlusion and also by the confirmation of complete carbon burnoff that had the potential to preg-robbing gold in solution in the subsequent leach tests. Another potential reason for low extraction, also confirmed by BSE images, is iron oxide, presumably containing gold, encapsulation in silicates. The images produced showed particles with an oxidized iron center surrounded by silicate mineral. The nature of this hard outer covering around the iron oxide, seemingly keeps cyanide solution from getting to the gold in the iron oxide in the subsequent leach step. This is a common occurrence in ores of this type though, and it is likely that encapsulation in silicates was only responsible for a small percentage of the gold that was occluded overall. The majority of this percentage should be attributed to maghemite formation. Maghemite, in the way that it is formed as an outer impervious layer around the iron oxide in the roasting process, could also explain why surface area and pore volume had no direct correlation to cyanide extractability of the gold into solution. An individual particle overall could have high
surface area and pore volume, in most cases meaning a particle that would be extremely amenable to leaching, but with an impervious maghemite band around the outside, the measurements in the center would be negated in regards to gold extractability into solution. This was confirmed by surface area and pore volume results increasing in the roast calcines for each stockpile from 550°C-700°C, with no real increase at all in percent gold extraction in these ranges.

BSE images for certain particles in the feed of the hot stockpile suggested a theory for how maghemite is forming as an outer rim on particles during the roasting process and inhibiting gold extraction. This theory, also suggested in a paper by Paktunc et al. (14), relates arsenian pyrite rimming around pyrite for numerous particles in the feed to maghemite rimming around certain iron oxides in the roasted product. It suggests that the arsenian pyrite rim somehow inhibits complete oxidation of the particle to hematite and helps to create the impervious maghemite layer around the iron oxide. This notion was further confirmed by energy dispersive x-ray spectroscopy (EDS) that revealed a significant percentage of arsenic was contained in numerous particles that had a maghemite outer layer around the iron oxide.

Another product created in the roast that had potential to occlude gold occurring in pyrite, was the calcium sulfate. As mentioned before, complete oxidation of sulfides did occur in the roasts, but some of that was conversion to a calcium sulfate, with more being formed at higher temperatures due to dolomite and calcite decomposition. Speculation of pyrite occlusion within this product, although never confirmed, was in fact the original reason for moving on to BSE imaging of roast products in order to try to make a conclusion on where gold occlusion was happening during the oxidation process.

Based on the conclusions made above for fundamental analysis of three stockpiles that feed a North American roasting circuit, a few recommendations for improving efficiencies in roasting that lead to better percent gold extraction can be made. The first is to increase retention time for ores inside the roaster. In the site roasting circuit, lingering organic carbon, or carbon that does not oxidize based on the fundamental mechanisms mentioned in this paper, was found in the calcined ore after going through two different stages of high temperature oxidation. Each roast in these experiments was roasted to completion and showed no residual organic carbon that could contribute to gold loss. This suggests that the ore is going through the circuit too fast and does not get a chance to reach complete oxidation. Secondly, grind size of the ore feed to the roaster and if it has any effects on recovery should also be investigated. The gold encapsulation in silicates, a very hard mineral, could possibly be mitigated with a finer grind to liberate sulfides and subsequently iron oxides that contain gold, improving recovery into solution in the leach step. The last recommendation for continuing research based on the results found in this project, is to investigate what role an arsenian pyrite rim around pyrite in the feed ore may play in forming an impervious maghemite layer around iron oxides, and ways to mitigate its formation upon high
temperature oxidation. The possible inhibiting role that arsenic plays in phase transformations to hematite during roasting is especially interesting and its investigation would be worthwhile considering maghemite’s association as a gold occluding product of roasting.
References Cited


22. “Determination of the surface area by the BET method.”
   https://zumbuhillab.unibas.ch/pdf/talks/080425_Tobias_BET.pdf


Figure A-1: Hot Stockpile Tube Furnace Run at 450°C and 510 cc/min air

450 C Hot Stockpile 8/28/15

Minutes

Temperature [°C]

Percent Oxygen

Series1 Series2 Series4 O2
Figure A-2: Hot Stockpile Tube Furnace Run at 500°C and 510 cc/min air

Figure A-3: Hot Stockpile Tube Furnace Run at 600°C and 510 cc/min air
Figure A-4: Hot Stockpile Tube Furnace Run at 650°C and 510 cc/min air

650 C Hot Stockpile 8/12/15

Figure A-5: Hot Stockpile Tube Furnace Run at 700°C and 510 cc/min air

700 C Hot Stockpile 8/13/15
Figure A-6: Hot Stockpile Tube Furnace Run at 750°C and 510 cc/min air

Figure A-7: Hot Stockpile Tube Furnace Run at 800°C and 510 cc/min air
Figure A-8: Cold Stockpile Tube Furnace Run at 450°C and 510 cc/min air

![450 C Cold Stockpile - 7/31/15 Graph](image)

Figure A-9: Cold Stockpile Tube Furnace Run at 550°C and 510 cc/min air

![550 C Cold Stockpile 8/7/15 Graph](image)
Figure A-10: Cold Stockpile Tube Furnace Run at 600°C and 510 cc/min air

![Graph: 600 C Cold Stockpile 8/11/15]

Figure A-11: Cold Stockpile Tube Furnace Run at 650°C and 510 cc/min air

![Graph: 650 C Cold Sample 8/12/15]
Figure A-12: Cold Stockpile Tube Furnace Run at 700°C and 510 cc/min air

700 C Cold Stockpile 8/13/15

Figure A-13: Cold Stockpile Tube Furnace Run at 750°C and 510 cc/min air

750 C Cold Stockpile 8/17/15
Figure A-14: Cold Stockpile Tube Furnace Run at 800°C and 510 cc/min air

800 C Cold Stockpile 8/18/15

Figure A-15: Troublesome Stockpile Tube Furnace Run at 450°C and 510 cc/min air

450 C Troublesome Stockpile 8/3/15
Figure A-16: Troublesome Stockpile Tube Furnace Run at 500°C and 510 cc/min air

Figure A-17: Troublesome Stockpile Tube Furnace Run at 600°C and 510 cc/min air
Figure A-18: Troublesome Stockpile Tube Furnace Run at 650°C and 510 cc/min air

Figure A-19: Troublesome Stockpile Tube Furnace Run at 700°C and 510 cc/min air
Figure A-20: Troublesome Stockpile Tube Furnace Run at 750°C and 510 cc/min air

![750 C Troublesome Stockpile 8/17/15 Graph](image)

Figure A-21: Troublesome Stockpile Tube Furnace Run at 800°C and 510 cc/min air

![800 C Troublesome Stockpile 8/18/15 Graph](image)
Figure B-1: Oxygen vs Time comparison at 450°C for all three stockpiles
Figure B-2: Oxygen vs Time comparison at 500°C for all three stockpiles

Figure B-3: Oxygen vs Time comparison at 600°C for all three stockpiles
Figure B-4: Oxygen vs Time comparison at 650°C for all three stockpiles

Figure B-5: Oxygen vs Time comparison at 700°C for all three stockpiles
Figure B-6: Oxygen vs Time comparison at 750°C for all three stockpiles

Figure B-7: Oxygen vs Time comparison at 800°C for all three stockpiles
Figure C-1: Oxygen vs Temperature comparison at 450°C for all three stockpiles
Figure C-2: Oxygen vs Temperature comparison at 500°C for all three stockpiles

500°C O2 vs Temperature

Figure C-3: Oxygen vs Temperature comparison at 600°C for all three stockpiles

600°C O2 vs Temperature
Figure C-4: Oxygen vs Temperature comparison at 650°C for all three stockpiles

Figure C-5: Oxygen vs Temperature comparison at 700°C for all three stockpiles
Figure C-6: Oxygen vs Temperature comparison at 800°C for all three stockpiles