THE FATES OF VANADIUM AND SULFUR INTRODUCED WITH PETCOKE TO LIME KILNS

By

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Abstract

Petroleum coke (pet coke) has been burned at kraft pulp mills to partially substitute for natural gas and fuel oil used in lime kilns. Due to the high vanadium and sulfur contents in pet coke, there had been concerns over the impact of burning pet coke on kiln and chemical recovery operations. Laboratory studies were performed to examine the fate of vanadium and sulfur in lime kilns and chemical recovery cycle. The results suggest that most of the vanadium in pet coke quickly forms calcium vanadates with lime in the kiln, mostly $3\text{CaO} \cdot \text{V}_2\text{O}_5$. In the causticizers, calcium vanadates react with $\text{Na}_2\text{CO}_3$ in green liquor to form sodium vanadate ($\text{NaVO}_3$). Due to its high solubility, $\text{NaVO}_3$ dissolves in the liquor circulating around the chemical recovery system. V becomes enriched in the liquor, leading to vanadium build-up in the system. The S in pet coke would stay in the reburned lime, lower the lime availability, increase $\text{SO}_2$ emissions from the kiln stack, alter the S balance, increase the liquor sulphidity, and potentially contribute to ring formation in the kiln.
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1 INTRODUCTION

1.1 Background

Kraft pulping is the most dominant process for the production of wood pulp. It can be used for many wood species, and produces high strength pulp. Kraft process uses white liquor, a hot, aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na$_2$S) as active pulping chemicals to digest wood chips. Overall, about 96-98% of the chemicals can be recovered in this process [1]. A schematic diagram of the kraft recovery process is shown in Figure 1 [2].

![Kraft recovery process diagram](image)

**Figure 1** Kraft recovery process [2]

Wood, which consists of fiber and lignin, is cooked with white liquor at about 170°C in a digester to generate kraft pulp from fiber [3]. The chemically dissolved lignin, along with
the spent pulping chemicals and spent water from brownstock washers, forms a liquid stream called weak black liquor. Weak black liquor has a solid content about 15%. It is concentrated through a series of evaporators and concentrators to form heavy black liquor with a solid content of about 65-85%. For every ton of pulp produced, the kraft process produces approximately 1.5 tons of black liquor dry solids that need to be processed in the chemical recovery plant [1]. The heavy black liquor is burned in the recovery boiler to generate steam and power from the combustion heat of dissolved organics, and to recover the inorganic chemicals from molten smelt formed at high temperatures under reducing conditions at the bottom of the boiler. The smelt, which consists mainly of sodium carbonate (Na$_2$CO$_3$) and sodium sulfide (Na$_2$S), is dissolved in water or weak wash$^1$ to form a solution called green liquor. In the causticizing plant, the green liquor reacts with slaked lime (calcium hydroxide, Ca(OH)$_2$) to convert Na$_2$CO$_3$ to sodium hydroxide (NaOH) according to Reaction 1.

\[
\text{Ca(OH)}_2(s) + \text{Na}_2\text{CO}_3(aq) \leftrightarrow 2\text{NaOH}(aq) + \text{CaCO}_3(s) \quad \text{Reaction 1}
\]

The white liquor (mainly NaOH and Na$_2$S) is reused in the pulping process. The precipitated calcium carbonate (CaCO$_3$), known as lime mud, is separated from white liquor by sedimentation or filtration. The mud is washed and dewatered on a precoat filter to increase its solids content to 65% or higher, and then is fed to a rotary kiln where it is calcined to produce lime (Reaction 2).

\[
\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad \text{Reaction 2}
\]

$^1$Weak wash is the water that has been used to wash lime mud in the causticizing plant.
Overall, the kraft recovery process includes two closed cycles: the “sodium cycle” where NaOH and Na₂S are recycled, and the “lime cycle” where calcium is recycled.

The lime kiln, shown in Figure 2, is used to convert lime mud into lime that can be reused in the slaker and in the causticizing process.

![Lime kiln at Mill A](image)

**Figure 2** *Lime kiln at Mill A*

The rotary kiln is slightly inclined from the “feed end” to the “discharge end”. Feed end is defined as the inlet for the lime mud feed, whereas discharge end is the outlet of the burned lime after calcination. A burner is built at the discharge end where fuels are burned with ambient air to provide sufficient heat for calcination. Lime mud is fed countercurrently to the hot gas through the feed end, travelling along the kiln by gravity and rotation. The calcination reaction occurs when the mud temperature reaches 800°C in the calcination zone of the kiln, where CaCO₃ decomposes to CaO and CO₂. The product lime, CaO, is resued in
the causticizing plant after exiting the kiln near the hot end. Flue gases from the kiln are passed through a scrubber and/or an electrostatic precipitator (ESP) to remove any SO$_2$ emissions or fine particulates prior to being sent to the stack.

The lime kiln requires a large amount of energy input, ranging from 7.6 to more than 11.6 MJ/kg lime [3]. In North America, two-thirds of the kilns burn natural gas as the primary fuel sources, while fuel oil accounts for the other one-third. Some kilns also burn byproducts and waste streams from various processes, such as non-condensable gases (NCG) and stripper off-gases (SOG). Traditional fuels, such as natural gas and oil, have high operating costs largely due to huge energy requirements. It is possible to partially lower these costs by replacing a portion of traditional fuels with alternative fuels. Such alternative fuels may include petroleum coke, glycerol, tall oil, wood residues, and producer gas from gasifiers [4]. Due to the high energy cost in recent years, many mills, particularly those in the southern United States, have been substituting their traditional fossil fuels with petroleum coke (petcoke). As a byproduct from the crude oil refining process in the Gulf Coast, petcoke is the most commonly used alternative fuel in lime kilns.

In Canada, the production rate for petroleum coke is over 20,000 MT/day as byproducts from tar sand industries [5]. Petcoke has the advantages of low energy costs, low ash contents, and high heating values. It can substitute up to 90% of the traditional fuels burned in lime kiln to offset the increasing energy cost. Petcoke is pulverized into fine powder before being fed into the lime kiln. The fine grind provides particles with high surface areas
for higher rate of combustion. Petcoke has a relatively high heating value, about 35MJ/kg (15000Btu/lb) [5].

There are presently about twenty lime kilns in the United States burning petcoke. Among these, three have been in operation for more than 20 years [5]. Figure 3 shows a comparison of fuel costs for natural gas, residual fuel oil (RFO), and pulverized petcoke in the past eight years [6]. In 2009, the natural gas price reached its lowest value in years, making petroleum coke less attractive from an economic prospective.

![Figure 3](image)

**Figure 3** *Fuel cost comparison for natural gas, RFO, and pulverized petcoke* [6]

The elements introduced into the kraft recovery process are classified as process elements and non-process elements. Process elements are sodium and sulfur that are essential for the pulping process. Non-process elements are the ones that are not required by the process,
but introduced as contaminants into the system with wood and/or make-up chemicals. Such elements include phosphorus (P), chlorine (Cl), silicon (Si), iron (Fe), magnesium (Mg), manganese (Mn), etc. Excessive amounts of non-process elements introduced into the Kraft recovery process may negatively affect the recovery operation.

Despite the economical benefits of burning petcoke, the high concentrations of sulfur and vanadium from petcoke introduced into the lime kiln is a concern for mills that utilize petcoke. The fate of sulfur introduced with petcoke has been studied extensively. In the lime kiln, sulfur is oxidized to SO$_2$ and SO$_3$ which consequently react with lime to form calcium sulfate (CaSO$_4$) [7]. In the causticizing plant, the resulting CaSO$_4$ reacts with Na$_2$CO$_3$ in the green liquor to form CaCO$_3$ (lime mud) and Na$_2$SO$_4$. This reaction becomes part of the sulfate deadload that circulates in the liquor cycle until Na$_2$SO$_4$ is reduced in the recovery boiler to form Na$_2$S. The high sulfur content in petcoke would lower the lime availability$^2$, increase SO$_2$ emissions from the kiln stack, alter the S balance, increase the liquor sulphidity, and potentially contribute to ring formation in the kiln [7].

Due to the high vanadium (V) content of petcoke, concerns arise around the fate of vanadium after it is burned with petcoke as well as the impact that vanadium compounds may have on kiln and chemical recovery operations. For example, the relative high concentration of vanadium burning in lime kiln may lead to corrosion of the kiln chain, refractory damage, reduction in service life, as well as particulate emissions. Vanadium can also be problematic due to its potential role in high temperature superheater corrosion in recovery boilers. It may

---

$^2$ Lime availability: active CaO weight ratio in the total lime to slaker, assuming the rest as inert in the causticizing reaction.
also lead to corrosion caused by acidic sulfates in the back side of the boiler since V$_2$O$_5$ can act as a catalyst in the sulfuric acid production process. The combustion behaviours of vanadium-containing fuels in other industries are well studied. However, little is known on the fate of vanadium in the chemical recovery operation when burning petcoke in lime kilns, the chemical recovery operation of vanadium following the burning of petcoke in lime kilns is not well characterized. The interaction of V with lime in the kiln or with sodium in the recovery boiler is still unclear.

Despite the fact that petcoke has been fired in mills for over 20 years, the combustion behaviours of petcoke in the lime kiln environment, as well as how it affects lime kiln and chemical recovery operation, are not well understood. In lime kilns where calcium compounds (CaO, CaCO$_3$, CaSO$_4$, etc.) are abundant and the operating temperature is high, it is not unclear what happens to vanadium after it has been burned with petcoke, how quickly it can react with lime and what impact it may have on the kiln and chemical recovery operations.
1.2 **Objective**

The objectives of this study are:

i) To determine the thermal behaviour of petcoke and its ash composition.

ii) To investigate the fate of non-process elements from petcoke after combustion, particularly vanadium and sulfur.

iii) To evaluate the impact of vanadium introduced with petcoke to lime kilns on chemical recovery operations.
1.3 Project overview

This project starts with a literature survey of topics on the use of petroleum coke as a fuel source. However, there are no specific studies focused on the problem caused by non-process elements from petcoke after combustion in the lime kiln.

In order to evaluate the effect of burning petroleum coke in lime kiln operation, laboratory studies are conducted to examine the thermal and combustion behaviours of petcoke inside a rotary kiln with and without the presence of lime. The residual ashes are reacted with Na$_2$CO$_3$ in the causticizing reaction. Liquids and solids are analyzed to identify and quantify the amounts of vanadium and sulfur introduced by petcoke in the lime cycle.

FactSage software, a commercially available thermodynamic calculation tool, are used to simulate a kiln or a recovery boiler operating environment with corresponding mass inputs to help predict the equilibrium composition of ash products and flue gases from burning petroleum coke at high temperature.
2 LITERATURE REVIEW

2.1 Lime kiln

2.1.1 Lime kiln chemistry

In a causticizing plant, lime (CaO) is used to convert sodium carbonate from green liquor into sodium hydroxide (NaOH) in Reactions 3 and 4. The causticizing reaction precipitates calcium carbonate (CaCO₃), known as lime mud.

\[
\text{CaO(s) + H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(s) \quad \text{Reaction 3}
\]

\[
\text{Ca(OH)}_2(s) + \text{Na}_2\text{CO}_3(aq) \rightarrow 2\text{NaOH(aq)} + \text{CaCO}_3(s) \quad \text{Reaction 4}
\]

This lime mud is washed and dewatered through a precoat filter to achieve a solid content of about 65% before entering a lime kiln. The resulting lime mud then goes inside the kiln, where it is dried and calcined to calcium oxide (Reaction 2) [8].

\[
\text{CaCO}_3(s) \rightarrow \text{CaO(s)} + \text{CO}_2(g) \quad \text{Reaction 2}
\]

Lime mud consists of approximately 95% of calcium carbonate, with 5% impurities [8]. A list of major impurities in lime mud is shown in Table 1. These impurities may vary from different mills, and are dependent on the wood sources, efficiencies of other equipments in the causticizing cycle, as well as operating conditions for lime kiln.
### Table 1 Major impurities in lime mud [8]

<table>
<thead>
<tr>
<th>Unit: wt %</th>
<th>Average</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>1.14</td>
<td>0.05</td>
<td>1.6</td>
</tr>
<tr>
<td>MgO</td>
<td>1.04</td>
<td>0.4</td>
<td>1.6</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.91</td>
<td>0.3</td>
<td>2.5</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.86</td>
<td>0.2</td>
<td>1.4</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.29</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.14</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.09</td>
<td>0.04</td>
<td>0.12</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.05</td>
<td>0.01</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The table above is used only for simplicity and illustration. Substances in the table do not represent the actual material that present in the lime mud. For example, sodium oxide represents other sodium compounds, including sodium hydroxide, sodium sulfate, etc. Sodium compounds are the largest impurities in lime mud.

#### 2.1.2 Lime kiln operation

A rotary lime kiln is usually made of exterior steel shell with refractory bricks inside. A schematic sketch of a rotary lime kiln from exterior is shown in Figure 4.
Lime kiln is supported by riding rings. The size of rotary kiln ranges from 2.1m in diameter by 53m in length to 4m in diameter by 122m in length. The thickness of the refractory bricks varies between 15.2cm to 25.4cm [2]. The residence time for lime mud inside a kiln ranges between 1.5 hrs and 4 hrs, with a normal rotating speed of a kiln from 0.5 to 2 rpm [2].

Figure 5 illustrates the interior of a rotary kiln. A series of chains hanging from the kiln shell at the feed end enhance heat transfer from combustion gas to the wet lime mud (about 30% water content). The chains provide a good thermal efficiency and large surface
area for heat to be delivered from hot gases to the mud. The decomposition of CaCO$_3$ into CaO and CO$_2$ occurs when the temperature reaches 800°C in the calcination zone. The rate of reaction greatly depends on temperature and local partial pressure of CO$_2$. The resulting CaO, known as reburned lime, is cooled to 300°C by secondary air and discharged from the kiln near the hot end. A dam can provide a longer residence time for the high temperature lime being discharged near the hot end.

Producing good lime quality is essential to kiln operation. Low residual calcium carbonate, high lime availability and reactivity are preferred [9]. The residual CaCO$_3$ is controlled by front-end temperature of the kiln, ranging from 1.5 to 2.5wt%. Depending on the impurities and residual CaCO$_3$, lime availability may vary from 85% to 95% [9]. Porous lime has a higher reactivity due to its larger surface area, and thus, a higher reaction rate in the slaker or causticizer.

For lime kilns burning liquid and gaseous fuels, the flame length is determined by the fuel/air mixing, which depends on primary air flow and burner geometry [10]. A higher flame temperature can increase production efficiency and capacity. However, excessive flame temperature could result in overburned lime and refractory damage. At temperatures above 1200°C, refractories become soft and lose its structural strength [11]. Conventional fuels, such as natural gas and fuel oil, usually operate at elevated pressure (170kPa and 800kPa, respectively) to ensure high momentum for efficient fuel mixing [10].
There are many operating problems associated with lime kiln, including ring formation, poor reburned lime quality, poor thermal efficiency, dusting, refractory damage, and Total Reduced Sulfur (TRS) / SO$_2$ emissions.

Ring formation occurs at different locations inside the kiln [8]. Mud rings result from wet mud entering the kiln with a higher than normal moisture content but inadequate operating temperature. The formation rate for this type of ring is fast, usually within 1/3 length of the kiln from the feed end. Mid-kiln rings are the most common and important ring formation. This type of ring formation happens during the recarbonation process where large amounts of CaO may react with high concentration CO$_2$ from the combustion gas to form calcium carbonate. Flame temperature fluctuation causes ring to grow faster and become thicker inside the kiln. Front-end rings form near the burner. Fuels with high sulfur content causes sulfation to occur at a high temperature about 900°C to 1200°C. Ring formation can be problematic as it damages the kiln refractory, and increases related maintenance costs for ring removal. In severe cases, lime kilns are required to shut down for maintenance, while fresh lime are purchased to handle short time outages.

Dusting is another potential problem, which is due to small fine particles escaping from the feed end. Dusts can be partially captured by scrubbers and electric precipitators, while the rest may leak around the kiln, causing a dusty environment.
2.1.3 Non-process elements (NPEs) in lime kiln operation and kraft recovery process

Non-process elements (NPEs) are defined as the elements that do not participate in the pulping process, such as phosphorus (P), chloride (Cl), aluminum (Al), magnesium (Mg), calcium (Ca), potassium (K), iron (Fe), copper (Cu), and manganese (Mn) [12]. Sodium (Na) and sulfur (S) are considered process elements. In the kraft recovery process, all solids and liquids are re-circulated until purged. Excessive amounts of non-process elements would affect process operation and product qualities. In order to minimize these effects, it is important to reduce non-process elements build-up in process streams.

For lime kilns that burn traditional fuel oil and natural gas, the majority of non-process elements are introduced into the mill operation with wood chips, make-up chemicals and/or mill process water. These elements stay in the kraft process, affecting the purity of lime mud. There are three main purging points in the kraft recovery process: slaker grits, filter dregs, and kiln dust (from electrostatic precipitator). A typical pulp mill purges 3% of the lime mud to manage impurities level and maintain proper operation. Usually in a lime kiln, nominal lime quality is controlled at 85-90% CaO [13]. The impurities in the lime or lime mud cause additional fuel usage in lime kiln, as well as reduced filtration efficiency and settling rate of the lime mud [14].

With data obtained from two kraft mills, Magnusson et al. discusses non-process elements associated with theoretical chemical equilibrium calculations, modeling and experimental work. They conclude that non-process elements can be classified into two
categories [15]. Some of the non-process elements, including Ca, Mg, P, and Mn, can be removed from the recovery system through three purging points in the liquor clarification systems. Others, including K, Cl, Al, and Si, cannot be removed due to their higher solubility in water. They may therefore build up in the liquor cycle. Inputs of these elements should be constantly monitored to avoid accumulation in the cycle. Specific purging processes are also required to remove these elements when necessary.

A case study has been conducted by McGuffie and Taylor on the non-process elements from Elk Falls mill, British Columbia [16]. The major non-process elements are identified as Al, Si, Fe, and P. The increased dead load from non-process elements has caused additional fuel cost in the lime kiln. The kiln fuel oil introduces P, Fe, and Zn into the system. Aluminum enters the causticizing plant through clarified green liquor. 78% of the aluminum dissolves in white liquor, and 16% re-circulates back to the recaust area, while 5% is removed in slaker dregs and sewer. Dregs carryover into lime mud has been proved to lower solid contents in the mud, which negatively affects the lime kiln thermal efficiency. Aluminum is likely to form pargasite (NaCa$_2$Mg$_3$Fe$^{2+}$Si$_6$Al$_3$O$_{22}$(OH)$_2$) and vermiculite (Mg$_{1.8}$Fe$^{2+}_{0.9}$Al$_{4.3}$SiO$_{10}$(OH)$_2$·4H$_2$O) with magnesium that can be purged in dregs. Adding magnesium in the dissolving tank can decrease the aluminum concentration in the clarified green liquor. Pulp production is the major purge point for silicon. Small amount of silicon (about 9%) is lost in dregs from green liquor clarifier, but not through slaker grits. Magnesium is identified from the silicon-magnesium compound in dreg, indicating adding Mg could also reduce silicon in the process. Iron is introduced into the recaust area as a result of equipment corrosion by clarified green liquor (80%) and surprisingly high concentration from fuel oil (18%), about 100ppm. Green
liquor clarifier can remove up to 92% of the iron present in the raw green liquor. Overall, 42% of the iron dissolves in white liquor, while others are purged in grits (29%) with the remaining in precipitator to sewer (25%). Phosphorus is the major dead load contributor present to the lime kiln for Elk Falls mill. There is more fuel consumption required for the kiln since the dead load lowers lime mud solid content. The majority of phosphorus enters the recaustic area from clarified green liquor (79%) and fuel oil (21%). The major purging points for phosphorus are precipitator (39%), grits (30%) and white liquor (27%). NPE mass balances established for the Elk Falls mill can provide information on process modifications to reduce kiln dead load and increase lime mud solid content [14].
2.2 Petroleum coke

Petroleum coke is a carbonaceous solid residue derived from thermal conversion process in crude oil refinery. Coking process has been the preferred technology for refinery industries since 1930s. This process can improve refinery profitability by converting low-value heavy residue fuel oil into high-value light products, such as gasoline and jet fuel [17]. Figure 6 shows samples of petroleum coke received from DTE Energy and Syncrude Canada.

![Image of petroleum coke samples from DTE Energy and Syncrude Canada](image_url)

Figure 6 Pulverized petroleum coke from DTE Energy Services and Syncrude Canada

In 2008, there was 101 million metric tons of petroleum coke being produced worldwide [17]. Since 1994, the production rate for petcoke has increased rapidly until it was impacted by the recent global recession in 2009. The higher coke production is driven by two factors, decreased purchase cost on heavy crude oil and increased production on synthetic crude oil. By 2012, the global petcoke production is projected to increase by 45% from adding coking capacity in existing coker expansion or from new units under construction [17]. China and India have increasing demands for petcoke and have been the primary importers, while
the United States has been the major supplier. The Gulf Coast is the centre for petcoke production in the United States.

The majority of Canadian petcoke is produced by Oil Sands industries in Alberta. The average production rate of petcoke in Canada is 20,000 metric tons per day, or 7.3 million metric tons annually [5]. According to Jacob Consultancy, the Canadian petcoke production is expected to increase by 60% in 2012 even though current recession has caused lower crude oil price and delayed oil sand projects [17].

Petroleum coke can be transported from the refinery by water, ground or rail. Water is the primary route since it can reach further distance globally, and has cost advantages on transportation. In the United States, refineries near Great Lakes or Mississippi River transport petcoke by vessel to domestic industries or export it internationally. Two cokers in the United States continuously provide fuel-grade cokes to power generation plants by the same unit trains as the plants receive conventional fuels. In 2008, 55% of the petcoke produced in the United States are exported, while petcoke made from other parts of the world (such as Europe, China or India) use it domestically [17]. In Canada, only a small portion of the petcoke produced from Alberta Oil Sands enters the global market due to a long transportation route (1400km) by a combination of rail and truck until it can be shipped around the world [17]. The Canadian National Railroad (CN) is upgrading the rail route to make exporting more feasible.
Raw petcoke, usually with high sulfur and metal contents, was traditionally used as a fuel source in cement and steel industries or in electricity power generation facilities [18]. High quality petcoke is manufactured for the aluminum refining industry by calcination to produce carbon anodes for aluminum smelting [19]. During this process, water and high molecular weight hydrocarbons in volatile matters are removed at high temperatures. Calcination promotes further structural change for the petcoke, as well as lowers impurities in petcoke, including lower sulfur and ash contents [20]. Figure 7 shows the major applications for delayed petcoke [20].

![Figure 7 Applications for delayed petroleum coke](image)

**Figure 7 Applications for delayed petroleum coke**

### 2.2.1 Industrial production process for petroleum coke

There are three types of petcoke production process: delayed, fluid, and flexicoking, where coke from delayed process accounts for more than 95% of the total petcoke production worldwide [21]. Delayed coking process is an endothermic reaction that takes place in a semi-continuous batch reactor. At temperatures from 415°C to 450°C and operating pressure, heavy fuel oil is heated and sprayed into a furnace where cracking and polymerization processes
occur. The resulting liquids are converted into vapour and coke [22, 23]. The term “delayed” describes the long residence time for coke staying in the drum. Figure 8 shows a simplified refinery diagram for the crude oil refining process. The coker is used to produce petroleum coke indicated at the bottom of the diagram [21].

Figure 8 Simplified refinery diagram for crude oil refining process [21]
Fluid coke and flexicoke are made from fluidized bed reactors at temperatures from 480°C to 565°C [23, 24]. Since the particles are withdrawn from size classifiers and the system operates at higher temperature, cokes by fluid and flexicoking have smaller grain sizes and significant less volatile matter contents [25].

Fuel-grade petroleum coke needs to be pulverized into fine powders before entering the burner. The raw petroleum coke from refinery is pneumatically conveyed into grinding mills through a feeding system. Raw petroleum coke can be ground on site and fired directly into the burner by an induced draft (I.D.) fan. Alternatively, it can be ground and stored in a storage bin, and conveyed into the burner indirectly through a feeding system. In the direct grinding and firing system, 30-40% of the primary air is used to blow the petcoke out of the grinder directly into the burner, whereas the indirect grinding and firing system only requires 12-15% of the primary air. In the indirect feeding system, a fabric filter is used to collect the ground petcoke, where hot air is applied to dry the coke. A flow meter is used to measure the feed rate of petcoke leaving the storage area to the burner.

DTE Petcoke uses the indirect grinding and firing system, shown in Figure 9. The central grinding facility receives raw petroleum coke that is shipped to the site directly from oil refinery. It was pneumatically conveyed into a feed silo before entering the pulverizer. A bag house is used to dry and filter the grinded petcoke. Truck or rail cars are ready to pick up the fuel-grade petcoke from a storage silo for delivery purposes.
2.2.2 Physical and chemical properties of petroleum coke

Petcoke is an odorless, fine black-colored powder with average particle size less than 200 mesh. Fuel grade petcoke used for lime kiln is typically in the form of pulverized powder so that it can be burned efficiently and completely. Some of the physical and chemical properties of petroleum coke are summarized in Table 2 [26].

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Black powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Solid</td>
</tr>
<tr>
<td>Bulk density (kg/m$^3$)</td>
<td>689 - 897</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Negligible</td>
</tr>
<tr>
<td>Volatile %</td>
<td>Less than 11%</td>
</tr>
<tr>
<td>Specific Surface Area (BET)</td>
<td>5.6(m$^2$/g)</td>
</tr>
</tbody>
</table>

Table 3 shows a typical composition of petcoke [27]. It contains mainly carbon (C), some sulphur (S) and hydrogen (H) and small amounts of oxygen (O), nitrogen (N) and ash.
The high C, S and H contents of petcoke (> 95wt%) give rise to its relatively high heating value, about 35 MJ/kg (15 KBtu/lb). [28].

Table 3 *Typical composition of petcoke [27]*

<table>
<thead>
<tr>
<th>Ultimate Analysis (wt%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>86</td>
</tr>
<tr>
<td>S</td>
<td>5.5</td>
</tr>
<tr>
<td>H</td>
<td>3.6</td>
</tr>
<tr>
<td>O</td>
<td>1.7</td>
</tr>
<tr>
<td>N</td>
<td>1.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proximate Analysis (wt%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter</td>
<td>11</td>
</tr>
<tr>
<td>Ash</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 4 lists the major impurities in petcoke (>100 ppm), beside sulfur (S). Of these, vanadium (V) is by far the largest impurity, ranging from 350 to 2500 ppm with an average concentration of about 1160 ppm. The DTE petcoke samples used in this project contain 6.5 wt% S and 1500 ppm V.

Table 4 *Major impurities in petcoke [13]*

<table>
<thead>
<tr>
<th>Major Ash Analysis (dry basis)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit: ppm fuel</td>
<td>Average</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>V</td>
<td>1160</td>
<td>330</td>
<td>2500</td>
</tr>
<tr>
<td>Ni</td>
<td>250</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>Si</td>
<td>150</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>Ca</td>
<td>230</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>Fe</td>
<td>90</td>
<td>200</td>
<td>650</td>
</tr>
<tr>
<td>Na</td>
<td>40</td>
<td>100</td>
<td>300</td>
</tr>
</tbody>
</table>
Commandré and Salvador conducted a study on petcoke combustion behaviour in an Entrained Flow Reactor (EFR). Twenty-two petcoke samples from different industrial sites were tested for ultimate and proximate analyses. The results are shown in Table 5 [28]. The compositions are similar for all 22 samples in terms of major species, ash content, and heating values.

**Table 5 Proximate analysis and ultimate analysis for 22 petcoke samples [28]**

<table>
<thead>
<tr>
<th>Coke Sample No.</th>
<th>Ultimate analysis</th>
<th>Proximate analysis</th>
<th>LCV</th>
<th>BET</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C%</td>
<td>H%</td>
<td>O%</td>
<td>S%</td>
</tr>
<tr>
<td>1</td>
<td>81.2</td>
<td>3.3</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>87.8</td>
<td>3.5</td>
<td>1.1</td>
<td>7.4</td>
</tr>
<tr>
<td>3</td>
<td>87.9</td>
<td>3.7</td>
<td>0.9</td>
<td>7.2</td>
</tr>
<tr>
<td>4</td>
<td>87.9</td>
<td>3.5</td>
<td>1.1</td>
<td>7.1</td>
</tr>
<tr>
<td>5</td>
<td>87.1</td>
<td>3.9</td>
<td>2.4</td>
<td>4.1</td>
</tr>
<tr>
<td>6</td>
<td>84</td>
<td>3.6</td>
<td>1.7</td>
<td>7.1</td>
</tr>
<tr>
<td>7</td>
<td>83.4</td>
<td>3.9</td>
<td>3.1</td>
<td>6.6</td>
</tr>
<tr>
<td>8</td>
<td>87.7</td>
<td>4.2</td>
<td>1.5</td>
<td>4.7</td>
</tr>
<tr>
<td>9</td>
<td>86.7</td>
<td>3.7</td>
<td>1.5</td>
<td>4.4</td>
</tr>
<tr>
<td>10</td>
<td>82.2</td>
<td>3.8</td>
<td>2</td>
<td>5.9</td>
</tr>
<tr>
<td>11</td>
<td>86.7</td>
<td>3.5</td>
<td>1.9</td>
<td>6.5</td>
</tr>
<tr>
<td>12</td>
<td>85.5</td>
<td>3.8</td>
<td>0</td>
<td>4.6</td>
</tr>
<tr>
<td>13</td>
<td>89.4</td>
<td>3.6</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>14</td>
<td>88.4</td>
<td>3.7</td>
<td>0</td>
<td>6.2</td>
</tr>
<tr>
<td>15</td>
<td>88.5</td>
<td>1.9</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>16</td>
<td>88.5</td>
<td>3.6</td>
<td>0</td>
<td>5.3</td>
</tr>
<tr>
<td>17</td>
<td>85.8</td>
<td>3.5</td>
<td>0</td>
<td>5.9</td>
</tr>
<tr>
<td>18</td>
<td>87</td>
<td>3.6</td>
<td>0</td>
<td>5.7</td>
</tr>
<tr>
<td>19</td>
<td>86</td>
<td>4.2</td>
<td>0</td>
<td>3.8</td>
</tr>
<tr>
<td>20</td>
<td>87.4</td>
<td>4.2</td>
<td>0</td>
<td>4.9</td>
</tr>
<tr>
<td>21</td>
<td>85.6</td>
<td>3.8</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>22</td>
<td>88.3</td>
<td>3.8</td>
<td>0</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Petcoke contains a low amount of volatile matters (VM), usually less than 11%. A study conducted by Amyotte et al. focuses on the explosion parameters of petroleum coke and its ash received from power generation plants, compared with Powder River Basin coal and Columbian coal. From the results of explosion pressure and rate of pressure increase, petroleum coke is a safer fuel to handle than these coals due to lower volatile matters and reduced dust explosion hazards [29].

2.2.3 Combustion behaviour of petroleum coke

Traditional pulverized coal-fired boiler does not burn petcoke as a fuel source due to the high sulfur composition of petcoke. It is not economically feasible to install desulfurization treatment for the flue gas if switching to petcoke. Petcoke can be blended with coal only if the required sulfur emission standards can be met. However, in a circulating fluidized bed boiler (CFB), sulfur can be captured by sorbent materials to meet environmental regulations. Petcoke becomes an increasingly important fuel source for circulating fluidized bed combustors because of high heating values and low energy costs. In such applications, limestone is commonly used to capture SO$_2$ gas [23, 30]. Limestone also plays an important role in capturing vanadium content in calcium vanadates from ash [31]. The bottom ash from CFB boiler can be re-used as a by-product in building material, road construction, and waste stabilizer.

Extensive studies have been conducted on the petcoke combustion in circulating fluidized bed boilers [23, 30, 31]. Recently a large number of steam generators that have been built worldwide use 100% petcoke or coal/coke blends to produce power [31]. Because of the
high operating temperature, vanadium was found to act as a catalyst in the sulfurization/oxidation reactions, leading to severe corrosion damages to the boiler tube surfaces [23].

Commandré and Salvador’s study on combustion behaviour of petcoke shows the combustion rate does not correlate with any of the chemical or physical properties of petcoke [28]. The combustion gas analysis indicates a strong correlation between the SO$_2$ emission and the initial sulfur content in the petcoke as petcoke being heated to 900°C with an air flow rate of 18L/min. The dotted line in Figure 10 represents 100% theoretical burnout of sulfur into SO$_2$.

![Figure 10](image)

**Figure 10** The release of S from solid fuel is proportional to the particle burnout [28]

In the cement industry, petroleum coke has been used to reduce high energy costs of kiln operation. The sulfur content in the cement clinker was found to increase proportionally with the amount of sulfur introduced with the fuel into the kiln [32]. Part of the sulfur
compounds may be gaseous in the burning zone, re-condensed at the cooler end, and circulate within the kiln. It is important to keep the sulfur from accumulating inside the kiln to avoid potential ring formation. Sulfur entering the kiln through the fuels may form $\text{K}_2\text{SO}_4$ or $\text{Na}_2\text{SO}_4$ with alkalis in the cement clinker, or form calcium alkali complexes with the existence of limestone.
2.3 Physical and chemical properties of vanadium and vanadates

Vanadium (Symbol: V; Atomic Number: 23; Molecular Weight: 50.94) was discovered in the 19th century by A. M. del Rio [33]. It is a soft, silver-grey colour transition metal that is widely distributed and naturally exists in minerals and earth’s crust [34]. The estimated concentration of vanadium in the earth’s crustal rocks is 136ppm, ranking vanadium as the fifth abundant transition metal [33]. Vanadium has been characterized in 60 different types of minerals, primarily as a compound with other elements. Vanadium can also be found in the products from the crude oil industries, particularly in Canada and Venezuela. Vanadium in crude oil can be recovered from the solid residues or flue gas dusts in oil-fired boilers. It is one of the most abundant trace metals existing in petroleum products, ranging from 0.1ppm to 1500ppm [35]. In petcoke or petroleum products, the majority of vanadium compounds exist as vanadyl ion (VO$^{2+}$) in the form of vanadyl porphyrins, with others as unknown non-porphyrins or as the cation in the organic acids [35]. The chemical structures of such vanadyl porphyrins and non-porphyrins are shown in Figure 11.
Pure vanadium metal is produced through the extraction of crushed ores or vanadium residues. In this process, vanadium residue reacts with Na$_2$CO$_3$ or NaCl at 850°C to produce water soluble NaVO$_3$ that can be leached out. Adding sulfuric acid to lower pH values (pH=2-3) can precipitate out a “red cake”, known as polyvanadate. Upon fusing at 700°C, a technical grade vanadium pentoxide can be produced. Pure vanadium metal can be produced from the reduction of vanadium pentoxide with calcium. In general, 80% of the vanadium metal produced is used as an additive to steels since it improves the steel quality by increasing resistance, strength, and temperature stabilities [33]. The additive, ferrovanadium, is produced in this process by mixing vanadium with iron or iron oxides in an electric furnace.
Several analytical methods can be used to identify and quantify vanadium in petroleum coke or petroleum products. These include flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) [35].

Vanadium can exist in various oxidation states from -1 to +5 [36]. In air or oxygen at temperatures above 660°C, vanadium metal can be oxidized to vanadium oxides with four distinct colours. Vanadium monoxide (VO or V₂O₂) is grey; vanadium dioxide (VO₂ or V₂O₄) is blue black; vanadium trioxide (V₂O₃) is black; vanadium pentoxide (V₂O₅) is orange [34]. Besides these oxides, vanadium can also form other intermediate vanadium oxide compounds. Overall, there are thirteen distinctive phases of vanadium oxide compounds being identified between vanadium monoxide and vanadium pentoxide [33].

Vanadium pentoxide is the most common vanadium compound. It is the final product in the oxidation reaction if the pure vanadium metal is heated with excess air; however, it may be contaminated with other vanadium oxides. Vanadium pentoxide is an important compound as it can gain or lose oxygen ion in the reversible reaction at high temperatures. This makes vanadium an excellent catalyst in the oxidation reaction for organic compounds, as well as in the sulfuric acid production process where sulfur dioxide is oxidized to sulfur trioxide with the presence of vanadium pentoxide.
Table 6 summarizes physical and chemical properties for vanadium and some of its compounds.

Table 6 Physical and chemical properties of vanadium and its compounds [37, 38, 39]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight (g/mol)</th>
<th>Melting Temperature (°C)</th>
<th>Specific Gravity (g/cm³)</th>
<th>Solubility in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium (V)</td>
<td>50.9</td>
<td>1890±10</td>
<td>6.11 at 18.7°C</td>
<td>insoluble</td>
</tr>
<tr>
<td>Vanadium dioxide (VO₂ or V₂O₄)</td>
<td>83</td>
<td>&gt;1755</td>
<td>4.399</td>
<td>-</td>
</tr>
<tr>
<td>Vanadium trioxide (V₂O₃)</td>
<td>150</td>
<td>1940</td>
<td>4.87 at 18°C</td>
<td>insoluble</td>
</tr>
<tr>
<td>Vanadium pentoxide (V₂O₅)</td>
<td>182</td>
<td>690</td>
<td>3.36 at 18°C</td>
<td>8g/L</td>
</tr>
<tr>
<td>Sodium metavanadate (Na₂O·V₂O₅)</td>
<td>244</td>
<td>630</td>
<td>-</td>
<td>211g/L at 25°C</td>
</tr>
<tr>
<td>Sodium pyrovanadate (2Na₂O·V₂O₅)</td>
<td>306</td>
<td>640</td>
<td>-</td>
<td>soluble</td>
</tr>
<tr>
<td>Sodium orthovanadate (3Na₂O·V₂O₅)</td>
<td>368</td>
<td>850-866</td>
<td>-</td>
<td>soluble</td>
</tr>
</tbody>
</table>

Both V₂O₄ and V₂O₅ are likely to form solid solutions at high temperatures with metal oxides [40]. Vanadium oxides are destructive to the refractory bricks at high temperature. At temperatures higher than 690°C, the molten V₂O₅ not only reacts with the oxide components from the refractory surface, but also forces the slag to penetrate into the pores of the refractory, resulting lowered surface tension and viscosity of the melts [11]. Vanadium may also act as a catalyst for sulfur in the fuel to form corrosive sulfate that causes severe damage to high temperature alloys used in gas turbine and diesel engines [41].

Vanadium pentoxide is slightly soluble in water, yielding a pale yellow acidic solution. It is an amphoteric compound, which produces yellow dioxovanadium ion VO₂⁺ in acids, and
colourless orthovanadate ion \( \text{VO}_4^{3-} \) in alkaline solutions at high pH. If vanadium pentoxide dissolves in an alkaline NaOH solution and is gradually acidified by an acid, the colourless \( \text{VO}_4^{3+} \) ion first turns into orange-red solution when the solution reaches neutral pH. As more acid is added, the solution colour darkens until pH reaches 2, at which brown hydrated \( \text{V}_2\text{O}_5 \) precipitates out. The solid re-dissolves at lower pH to yield pale yellow dioxovanadium \( \text{VO}_2^+ \) ions [33]. Similar to \( \text{V}_2\text{O}_5 \), \( \text{VO}_2 \) is also amphoteric, which produces bluish oxovanadium (vanadyl) ion \( \text{VO}^{2+} \) in non-oxidizing acids, whereas yellow-brownish hypovanadate ion \( \text{V}_4\text{O}_9^{2-} \) is produced in alkaline solutions. Figure 12 gives one of the most comprehensive illustrations on vanadate species at various pH values and total vanadium concentrations [33].

![Figure 12](image)

**Figure 12** Precipitation diagram for the liquid vanadate species based on pH and concentration [33]

In the kraft recovery operation where most of the liquids are alkaline solutions (pH greater than 9), the most common vanadium ions are likely \( \text{HVO}_4^{2-} \), \( \text{V}_2\text{O}_7^{4-} \) and \( \text{VO}_4^{3-} \). Most of the vanadium reacts with sodium and calcium salts to form low melting point (as low as
565°C) vanadate compounds at elevated temperatures [41, 42]. All sodium vanadates are water soluble, while calcium vanadates are only water soluble with pH ranging from 0.5 to 1.8 [42].

Vanadium-containing oil-fired boilers are the largest source of anthropogenic emissions for vanadium. Bacci et al. shows the results from particulate matters analysis in traditional power plant stack where high vanadium content fuel oil was fired. Vanadium is likely to be enriched and concentrated in small particles [43]. NaVO₃ is the dominant vanadate compound found in the fuel oil fly ash. In the boiler where residue fuel oil is used, vanadyl sulphate (VO·SO₄·xH₂O) is the major vanadium species identified in the particulate matter samples [44].

Vanadium is the second largest impurity in petcoke next to sulfur. High vanadium concentration has raised many concerns over problems related to slagging, fouling, and corrosion in combustion systems. From the analysis of ash obtained from firing petcoke in CFB, Chen and Lu reported that all vanadium from petcoke remains in the ash after operation, equally distributed in either bottom or fly ash [24]. A study by Jia et al. investigates vanadium compounds from ash samples in a CFB boiler where 100% petroleum coke is burned, resulting calcium vanadium oxide (Ca₂V₂O₇) as the major species formed after combustion [31]. In this process, limestone and kaolin are used to capture SO₂ and alkali impurities respectively. The same sample was dissolved in a sodium citrate solution for the waste extraction test (WET). The test indicates that the solubility of calcium vanadium oxide is negligible, which means vanadium is still in the form of calcium vanadates, not dissolving in
the solution. If 34.2g such sample is dissolved in 16L of water, only about 12% of the vanadium is extracted after 7 days. This vanadate ion forms cation in the hydrolysis process with an oxidation state of +5. Since petcoke has high sulfur (about 6%) and vanadium (about 1500ppm) contents, salt-roasting treatment by sodium carbonate can be used to minimize the concentrations of these two elements from extraction [45]. Sulfur and vanadium may form water soluble sodium compounds that can be separated by filtration so that sulfur in petcoke can be minimized, along with vanadium being recovered as a by-product.

In the phase diagram for the CaO-V₂O₅ [46] system shown in Figure 13, three calcium vanadate compounds are identified at elevated temperatures: calcium metavanadate, calcium pyrovanadate and calcium ortovanadate (CaO·V₂O₅, 2CaO·V₂O₅, 3CaO·V₂O₅, respectively).

Figure 13 Phase diagram of CaO-V₂O₅ [46]
A study by Slobodin et al. shows that the initial product from the mixture of calcium oxide and vanadium pentoxide is independent from the stoichiometric ratio of the components at high temperatures [47]. As CaO is added into the system, V_2O_5 first forms a vanadate compound with CaO at molar ratio of V_2O_5:CaO=1:1. When the temperature reaches 618°C, CaO-V_2O_5 complex forms V_2O_5 with a eutectic melting point at 9wt%. The liquid phase increases the contact area between the reactants, and thus, accelerates the reaction rate. As the weight percentage of CaO increases, each successive calcium vanadate compound is formed until the formation of 3CaO·V_2O_5, as shown in the diagram. The final product from this CaO-V_2O_5 complex is dependent on the initial molar ratio of the two components. Another research has discovered other calcium vanadate compounds synthesized at high temperatures, including 7CaO:2V_2O_5 and 4CaO·V_2O_5 at 1250°C, and 5CaO·V_2O_5 at 700-1300°C [47]. From the thermodynamic point of view, calcium metavanadate (CaO·V_2O_5) is the initial product formed due to the lowest thermodynamic stability and highest rate of reaction, while calcium orthovanadate (3CaO·V_2O_5) is the final product because it is the most thermodynamic stable compound among the three. For the system of V_2O_5-CaCO_3, it behaves similar to the CaO-V_2O_5 system. The only difference is that calcium carbonate would first decompose to calcium oxide at the eutectic temperature of 618°C and form calcium vanadate compounds with vanadium pentoxide.

Figure 14 and Figure 15 show the phase diagrams for Na_2SO_4-V_2O_5 and Na-V-O, respectively [48]. It is important to understand the interactions between vanadium and sodium in the kraft recovery process since sodium is the major process element involved.
Figure 14 Phase diagram of Na$_2$SO$_4$-V$_2$O$_5$ [48]

Figure 15 Phase diagram of NaVO$_3$-V$_2$O$_5$ [48]
Na$_2$SO$_4$ may exist as the superheater deposits inside the recovery boiler, along with Na$_2$CO$_3$ and Cl compounds. The mixture usually has a lower eutectic melting temperature so that at high temperatures inside the boiler, the compound can be sticky and easily attach to the superheater tubes. According to Figure 14, the mixture of V$_2$O$_5$ and Na$_2$SO$_4$ forms a lower eutectic melting temperature compound at 630°C with vanadium pentoxide at 11mol% V$_2$O$_5$. Similar case for the Na-V-O system in Figure 15, a lower eutectic temperature occurs at 655°C at 8mol% V$_2$O$_5$. Since vanadium in petroleum coke only contributes a small amount of vanadium pentoxide in the kraft recovery system (usually less than 2mol% of V$_2$O$_5$), the melting temperature for sodium sulfate may be lowered by adding V$_2$O$_5$ into the system. However, in the real recovery boiler, the melting temperature of the deposits also depends on other compounds that may present in the mixture, such as KCl or NaCl. The effect of V on deposit first melting temperature may not be significant.
2.4 Economics of petcoke burning in kraft recovery process

For a typical kraft pulp mill that produces 1000 ton per day (TPD) pulp, 250 ton of lime per day is required. The total lime required includes reburned lime and make-up chemicals. Assuming 5% of the lime comes from make-up, it would require 238 TPD of reburned lime produced from the lime kiln. A modern lime kiln requires large amount of energy inputs, about 7 MJ/kg of lime [13]. In the beginning of 2009, the costs of traditional fuels, including natural gas and #6 fuel oil, were $5.7/GJ delivered, compared with $3.8/GJ for petroleum coke [6]. If the petcoke substitution rate is 75% in the lime kiln, the average saving could be $1.4/GJ compared with burning natural gas or fuel oil alone. Therefore, the annual savings on operating cost (based on 350 operating days/year) by burning petroleum coke would be $0.75 million. However, the problems associated with petcoke burning must be taken into consideration, as they may result in additional operating costs to paper mills.

If natural gas or fuel oil price is $2.8/GJ higher than petcoke, the payback period for installing a complete petcoke firing system is about 2-3 years [49]. The price of petcoke is about $2.8-4.3/GJ, delivered, at the end of the first half in 2009 [6]. It is not economically feasible to use petcoke as an alternative fuel due to low energy cost on natural gas for paper mills.
Potential problems associated with petcoke burning

Petroleum coke is widely used as an economical alternative fuel in lime kilns in the United States. There have been three lime kilns that fired petcoke for more than twenty years prior to 2004. From 2005-2007, there were nine more pulp and paper mills decided to burn petcoke, with additional ten mills pending to proceed or under construction. Despite the potential economic benefits of burning petcoke as mentioned in the previous section, there are operational issues with using petcoke which may negatively impact kiln performance, product quality and the environment.

The two major factors affecting petcoke characteristics are: sulfur content and grindability [49]. Petcoke used in lime kiln usually contains 4-6 wt% of sulfur. Mills burning petcoke with wet scrubbers experience no significant increase in SO$_2$ emissions, compared with traditional fuels [50]. Most of the sulfur from petcoke is absorbed by lime to form calcium sulfate, according to Reaction 5.

$$\text{CaO(s) + } \frac{1}{2} \text{O}_2(\text{g}) + \text{SO}_2(\text{g}) \rightarrow \text{CaSO}_4(\text{s})$$  \hspace{5cm} \text{Reaction 5}

97% of sulfur in petcoke converts to calcium sulfate in lime kilns, while some actual mill tests indicate higher conversion of nearly 100% [49]. On average, the conversion rate for sulfur from petcoke to react with lime to form calcium sulfate is above 90%. Most of the CaSO$_4$ formed remains in the reburned lime or lime dust. Calcium sulfate formed near the burner may lead to rapid hot-end ring formation, hindering the kiln operation. Since lime is consumed to form CaSO$_4$, lime availability would be lowered and therefore the system
requires more lime make-up. For mills that burn non-condensable gases (NCGs) or stipper off-gases (SOG), high petcoke substitution rate leads to high SO$_2$ emission, particularly for kilns without scrubbers. If the sulfur is not completely captured by calcium oxide, the remaining sulfur would follow the combustion gas and travel into the wet scrubber where it reacts with sodium hydroxide to form sodium sulfite (Na$_2$SO$_3$) or sodium bisulfite (NaHSO$_3$). These solutions return to the weak wash storage, end up as inactive chemicals in the green liquor and enter the recovery boiler where they are reduced to Na$_2$S.

The formation of CaSO$_4$ occurs mostly on the surface of reburned lime. Since calcium sulfate has a low solubility in water, it renders the CaO less reactive. The interactions between CaO and water in the slaker or with Na$_2$CO$_3$ in the liquor are hindered. The resulting lime with sulfate ion reduces lime settling rate, making it more difficult to slake or filter. Therefore, CaSO$_4$ is commonly enriched in the lime dust or in the grits, where it can be removed with lime dust disposal or grits. In causticizing plants, reburned lime nodules break up into small particles in the slaking and causticizing reactions, while the released CaSO$_4$ can react with sodium hydroxide in caustic to form sodium sulfate and calcium carbonate according to Reaction 6.

$$\text{CaSO}_4(s) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{CaCO}_3(s) \quad \text{Reaction 6}$$

Reaction 6 is parallel to Reaction 4 where calcium carbonate is reacted with green liquor to regenerate sodium hydroxide in white liquor, while producing calcium carbonate.

$$\text{Ca(OH)}_2(s) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow 2\text{NaOH}(\text{aq}) + \text{CaCO}_3(s) \quad \text{Reaction 4}$$
The precipitated lime mud from Reaction 6 would increase the mud load entering the causticizing cycle. Additional make-up caustic is required for the white liquor production. At the same time, the water-soluble sodium sulfate from the causticizing reaction enters the liquor cycle with white liquor, becoming part of the deadload. This may affect the solid content in the evaporator and the recovery boiler. In the recover boiler, most of the Na$_2$SO$_4$ is reduced to Na$_2$S. As more sulfur entering the liquor cycle, it alters Na/S balance, and leads to increase in sulfidity.

Petcoke needs to be ground into fine particles (more than 70% passing through 200# sieve) before burning in the kiln. Large surface area is required for complete combustion. The burner is designed to ensure petcoke particles being burned completely. For the lime kiln, the indirect grinding and firing system is used to provide a more stable flame shape and temperature, and thus, less thermal NO$_x$ formation. The unburned petcoke particles, if any, should be removed by the grits from the slaker. Some of the unburned petcoke particles may precipitate out with the lime mud and re-enter the lime cycle, where it can be combusted once again in the lime kiln. Overall, any unburned petcoke residues from lime kiln should not be a factor that affects white paper quality.

Petcoke has a low combustion rate due to low volatile matters. Traditional natural gas or fuel oil can sustain the burning flame without any additional fuel. The self-ignition temperature for petcoke is higher than 1000°C, whereas lime kiln usually operates at a lower temperature. It is difficult to mix the solid fuels, such as petcoke, with air during the combustion process inside the kiln. Since these solid coke particles can only be mixed with air
under low pressure, the velocity of the mixture from fuel with air is low, resulting longer flame length than conventional natural gas. According to Manning et al., the heat transfer temperature profile for burning the mixture of 75% petcoke/25% gas is similar to burning 100% #6 Fuel Oil. The heat flux peaks for both are closer to the burner than burning natural gas [50]. Petcoke usually can substitute 75% of the conventional fuel and burn as a primary fuel source. The lime kiln would require an auxiliary fuel to heat up the combustion chamber to operating temperature and sustain combustion. Natural gas or fuel oil is commonly supplemented to maintain flame in the combustion chamber.

Nitrogen may form thermal NO\textsubscript{x} or fuel NO\textsubscript{x} inside a lime kiln at high temperatures. Originally, thermal NO\textsubscript{x} was formed in a lime kiln where natural gas was used as a fuel source since it has higher flame temperature than petcoke, fuel oil or coal. Nitrogen introduced by petcoke (usually 1-5%) increases NO\textsubscript{x} emissions for the kiln. The additional NO\textsubscript{x} emission typically ranges from 150-200ppm to 300-400 ppm (based on 2% exit O\textsubscript{2} gas, dry basis) [10]. This problem can be partially solved by optimizing the multi-fuel burner design to ensure sufficient heat transferred from fuel to lime mud [52]. Scrubbers and electrostatic precipitators (ESP) are often used as post treatment devices to remove pollutants from flue gas stream, such as SO\textsubscript{2} emissions and particulates.

As discussed in Section 2.3, vanadium is the second largest impurity in petcoke besides sulfur. It may form low melting temperature compounds, such as vanadium oxide or vanadate compounds, which could cause corrosion in recovery boiler, or damages to the refractory bricks and chains in the lime kiln. Vanadium introduced by petcoke reacts as an
impurity that may negatively affect lime quality, lower lime availability and reactivity. However, the fate of vanadium introduced by petcoke in the lime kiln and in the kraft recovery operation is still unknown [5, 49].

Other NPEs introduced by petcoke into the lime kiln are not expected to have a significant impact on recovery operation because of their low concentrations. Compared with petcoke burning, these elements, such as Si, Ni, Fe, also enter the recovery process through woods and make-up chemicals. Except vanadium, the original purging system for a paper mill through dregs and slaker grits should be sufficient to sustain normal operation and to control excessive amounts of NPE inputs from petcoke.
3 Experimental Setup

3.1 Material

The petcoke samples used in this study was provided by DTE Energy Services and Syncrude Canada. All samples, as received, were dried and finely pulverized into particle sizes less than 200 mesh. A typical composition of petroleum coke is shown in Table 3 in Section 2.2.2. Additional information about ultimate analysis and ash analysis for this specific petcoke are listed in Appendix A and B.

The lime mud samples were obtained from three kraft pulp and paper mills. The mud samples were dried in an oven at 110°C overnight to eliminate any moisture. Their compositions were analyzed by X-ray fluorescence (XRF) spectroscopy and the results are shown in Table 7.

<table>
<thead>
<tr>
<th>Table 7 Composition of lime mud (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Mud A</td>
</tr>
<tr>
<td>CaCO₃</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>P₂O₅</td>
</tr>
<tr>
<td>Na₂O</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>SO₃</td>
</tr>
<tr>
<td>Others</td>
</tr>
<tr>
<td>TOTAL</td>
</tr>
</tbody>
</table>
All of the lime mud samples contain more than 95wt% calcium carbonate, some magnesium, phosphorous and sodium oxides. The trace metal oxides detected other than Si, Fe and Al are expressed as “others”.

Analytical grade Na$_2$CO$_3$, CaCO$_3$, V$_2$O$_5$, NaCl, KCl and Na$_2$SO$_4$ with a purity of >99.9% on dry basis from Fischer Scientific were also used.


3.2 Experimental setup

3.2.1 Heat treatment

Heat treatment experiments were performed to investigate possible chemical reactions between vanadium (V) in petcoke and lime mud. Mixtures of petcoke and lime mud at different ratios were prepared (i.e. 0 wt%, 5 wt%, 10 wt%, 16.7 wt%, 25 wt%, 30 wt%, 40 wt%, and 50 wt% of petcoke in the mixtures). Petcoke was first mixed with pure calcium carbonate by measuring the weights of petcoke and calcium carbonate separately using an analytical balance. The two materials were placed in a sample bottle and shaken vigorously for uniform mixing. In each experiment, these mixtures were housed in three separate boat-shape crucibles that were placed in a mullite tube mounted horizontally in the center of a Lindberg tubular furnace. These crucibles were made of 99.8% cast alumina, with a dimension of 15mm in height, 23mm in width, and 107mm in length. The net weights of the crucibles, initial weights of the mixture and final weights of the product after heat treatment were measured. Figure 16 shows the experimental setup for burning petcoke and pure calcium carbonate mixture in the horizontal furnace. The same experimental setup and procedure were repeated for the petcoke mixed with lime mud samples from pulp and paper mills.
A compressed air gas cylinder supplied constant air flow into the furnace. The air mixed with fuel for the combustion reaction to occur at high temperatures. A calibrated Aalborg GFC gas flow controller was used to set a constant flow rate at 200mL/min through a ¼ inch pipe connected to the mullite tube (52mm in diameter × 1200mm in length). The furnace was placed above the furnace controller, where the temperature inside the mullite tube was kept constant at 950°C. The experiment was carried out for five hours. Preliminary results showed that five-hour was sufficient for the complete combustion of petcoke inside the tube. Compressed air then passed through the mullite tube from one end to flush out the combustion gas of the petcoke and the CO₂ released from the lime mud. The exhaust gas was bubbled through two caustic scrubbers in series that contain 0.01N NaOH solution to remove gaseous S and V compounds, particulates and condensed matters before vented to atmosphere through a fume hood.
The DTE and Syncrude petcoke samples were individually held in ceramic crucibles, and heated in a muffle furnace to measure the weight loss profile in air. The furnace has an open port so that samples are in contact with the ambient air. Constant temperatures are set (i.e. 450°C, 550°C, 650°C, and 750°C) for the furnace to operate. In every 20-30 minutes, samples were taken out of the furnace to measure any weight loss.

3.2.2 Causticizing reaction

The residue from the above heat treatment experiments was essentially a mixture of ash resulting from the combustion of petcoke and lime from the calcination of lime mud. It was used as a source of lime in the causticizing experiment. Six grams of such residue was mixed with an aqueous solution of 200g/L pure sodium carbonate (\(\text{Na}_2\text{CO}_3\)) in a sealed PFA (perfluoroalkoxy) container. It was placed in a water bath controlled at 90°C to simulate the causticizing reaction (Reaction 1).

\[
\text{Ca(OH)}_2(\text{s}) + \text{Na}_2\text{CO}_3(\text{aq}) \leftrightarrow 2\text{NaOH(}\text{aq}) + \text{CaCO}_3(\text{s}) \quad \text{Reaction 1}
\]

The slurry was constantly agitated for 2 hours. The resulting slurry was filtered to separate the solids from the liquid (solution). The solid was dried at 110°C in oven overnight before being subject to chemical analysis along with the liquid.

Since the amount of V in petcoke was much smaller than that of Ca in lime mud, it was difficult to accurately analyze and identify the possible vanadium compounds formed in the samples during heat treatment and causticizing experiments. To further study the fate of vanadium from petcoke combustion, both heat treatment and causticizing experiments were
also performed. Pure CaCO₃ and two mixtures of analytical grade vanadium pentoxide (V₂O₅) and CaCO₃ containing 10 and 20wt% of V₂O₅ were used to resemble vanadium-containing petcoke ash and lime mud. The large amount, high purity, and high V content of the mixtures made the analysis as well as the identification of reaction products easier and more accurate. In the heat treatment test, the two mixtures were burned at 950°C for five hours in the horizontal tube furnace, under the same condition as the petroleum coke and lime mud mixtures. The solid residues after the heat treatment were used to simulate the causticizing reaction with Na₂CO₃ solution under the same reaction conditions and procedures as described above.
3.3 Analytical methods

3.3.1 Thermogravimetric Analysis/ Differential Scanning Calorimetry (TGA/DSC)

The thermal behaviour of petcoke was studied using a simultaneous Thermogravimetric Analysis/ Differential Scanning Calorimetry (TGA/DSC) apparatus from TA instrument (Model SDT Q600™). Figure 17 shows a picture of the apparatus used in this study. The equipment continuously measures the sample weight and heat flow from/to the sample simultaneously. Detailed explanation of the operating principles behind TGA/DSC apparatus can be found in Appendix D.

Figure 17 Thermogravimetric Analysis/ Differential Scanning Calorimetry (TGA/DSC) apparatus
DTE and Syncrude petcoke samples were individually heated up to 950°C in TGA at a heating rate of 20°C/min with an air inflow of 100mL/min. The sample was held at the final temperature for 10 more minutes to track any additional weight loss. Analytical grade V$_2$O$_5$, CaCO$_3$ and the mixture of the two, as mentioned in the previous section (10wt% V$_2$O$_5$ with 90wt% CaCO$_3$, and 20wt% V$_2$O$_5$ with 80wt% CaCO$_3$), were also analyzed under the same experimental condition. In addition, the solid residues from the mixture of V$_2$O$_5$ and CaCO$_3$ in previous runs were heated up to 950°C in the consecutive cycle in TGA/DSC apparatus in order to measure the thermal stability of the residue compounds. The second cycle used the solid residue after it cooled down to room temperature, and to heat it up to 950°C again.

The mixtures of black liquor synthetic deposits with various amounts of V$_2$O$_5$ were heated up to 700°C to determine the first melting temperature. The heating rate was 20°C/min at 100mL/min air inflow.

### 3.3.2 Inductively Coupled Plasma (ICP) and X-ray Florescence Spectroscope (XRF)

Inductively coupled plasma mass spectrometry (ICP-MS) and X-ray florescence spectroscope are two analytical methods to determine and quantitatively identify metal and non-metal elements that may present in the solid sample. The chemical compositions of the solid residues obtained from the three alumina crucibles after heat treatment and from filtered solids in the causticizing reaction were identified and quantified using these methods. The scrubber solutions after heat treatment and the filtrates from causticizing reaction were
collected and analyzed for Ca, V, Na, K, Ni, Fe, etc., by means of Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).

### 3.3.3 X-Ray Diffraction Analysis (XRD)

X-ray diffraction analysis (XRD) is a method to identify unknown crystallographic structure of a substance by comparing its diffraction patterns with database from International Centre for Diffraction Data. It is still not clear what compounds may form from the mixture of \( \text{V}_2\text{O}_5 \) with CaO after the heat treatment. And thus, X-ray diffraction analysis is used to examine the solid residue structure.

A Philips X-ray diffractometer (Model PW3710) was used in this study to characterize samples. The machine operated at 40kV and 40mA. The XRD pattern was recorded from 15° to 60° at a 20 step interval of 0.02°. The acquisition time was measured at 2.5s per step.
4 RESULTS AND DISCUSSION

4.1 Thermal behaviour of petroleum coke

Figure 18 shows the TGA weight loss profiles for two DTE petcoke samples and one Syncrude petcoke sample in comparison with other fuel sources in literature, i.e. Devco Prince coal and Suncor coke char [53]. The coal and coke char were heat up to 1100°C in a Cahn 1100 pressurized TGA analyzer at atmospheric pressure. The heating rate was kept at 20°C/min with a gas flow of 100mL/min (oxygen concentration in the gas = 10.5%).

![Weight loss comparisons of petcoke with char and coal](image-url)

**Figure 18** Weight loss comparisons of petcoke with char and coal
The weight change profiles indicate similarities in combustion behaviour of these fuels. The two DTE petcoke samples had a similar thermal behaviour. They were stable with no weight change up to 300°C and then showed a slight weight gain of about 2 wt% between 300°C and 400°C. This weight gain was presumably due to the oxidization of sulfur to SO$_2$/SO$_3$ and the subsequent absorption of some of these sulphur gases by other minerals in the petcoke to form sulphates (i.e. NiSO$_4$, CaSO$_4$, FeSO$_4$, etc.). However, this weight gain is not observed from Syncrude petcoke, Devco Prince coal or Suncor coke char. As temperature increases to above 400°C, DTE petcakes start to burn and lose weight rapidly during the combustion process when it reacts with oxygen from air, followed by Suncor coke char, Syncrude petcoke, and Devco Prince coal. At temperatures around 950°C, almost all combustion reactions are completed, and the remaining weight of each sample is essentially the ash content of the petcoke. Both DTE petcoke samples burned at a much higher rate (steeper weight loss curve) and completed the combustion process at a much lower temperature (<650°C) compared to other fuels (>750°C). The higher reaction rate for DTE petcoke may result from smaller particle sizes, and thus, higher reactive surface areas. The DTE petcakes also had a much lower ash content (0.4 wt%) than Syncrude petcoke (7 wt%), Suncor coke char and Devco Prince coal (16 wt%). The results suggest that the petcoke used in this study has low ash content and can burn readily in air.

To compare the combustion behaviours of different types of petcoke at a constant high temperature, DTE petcoke and Syncrude petcoke were placed in two separate crucibles inside a muffle furnace where the temperature was kept constantly at 700°C. Figure 19 compares the weight changes for the two petcoke samples with time while they were burned in ambient air.
The results confirmed that DTE petcoke burns at a somewhat faster rate than Syncrude since DTE petcoke has a finer particle size, and thus, larger surface area for the combustion reaction. The DTE petcoke also produces less ash (about 0.5wt%) than Syncrude petcoke (about 7wt%).

![Weight loss profiles of DTE and Syncrude petcoes with time at 700°C](image)

**Figure 19** Weight loss profiles of DTE and Syncrude petcoes with time at 700°C

In order to investigate the chemical compositions of pet coke ash residues at different constant temperatures, Syncrude Petcoke are burned at constant high temperatures (550°C, 650°C, 750°C and 850°C) in a muffle furnace until no further weight loss for the solid was discovered. Table 8 shows the XRF result obtained from the petcoke ash products at four different temperatures.
The results show that most components in the ash did not change significantly with temperatures varying from 550°C to 850°C. The only appreciable change observed was sulfur (expressed as SO$_3$), which decreased from about 5% at 550°C to 0.14% at 850°C. This implies that if petcoke is burned alone at temperatures above 850°C, most of the sulfur from the petcoke may end up as SO$_2$ in the flue gas.

### Table 8 XRF analysis of Syncrude Petcoke

<table>
<thead>
<tr>
<th>Treatment Temperature</th>
<th>550°C</th>
<th>650°C</th>
<th>750°C</th>
<th>850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>0.86</td>
<td>0.87</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>MgO</td>
<td>1.89</td>
<td>1.81</td>
<td>1.75</td>
<td>2.03</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>21.85</td>
<td>21.80</td>
<td>22.08</td>
<td>22.61</td>
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<tr>
<td>SiO$_2$</td>
<td>37.39</td>
<td>37.30</td>
<td>37.68</td>
<td>38.48</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.71</td>
<td>0.72</td>
<td>0.70</td>
<td>0.72</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>4.82</td>
<td>5.09</td>
<td>4.05</td>
<td>0.14</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.68</td>
<td>1.62</td>
<td>1.63</td>
<td>1.71</td>
</tr>
<tr>
<td>CaO</td>
<td>3.48</td>
<td>3.48</td>
<td>3.35</td>
<td>3.59</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>4.75</td>
<td>4.68</td>
<td>4.77</td>
<td>5.01</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>4.18</td>
<td>4.00</td>
<td>3.97</td>
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</tr>
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<td>Fe$_2$O$_3$</td>
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<td>16.17</td>
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</tr>
<tr>
<td>NiO</td>
<td>1.11</td>
<td>1.30</td>
<td>1.87</td>
<td>2.54</td>
</tr>
<tr>
<td>Others</td>
<td>1.90</td>
<td>1.88</td>
<td>1.83</td>
<td>2.04</td>
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<tr>
<td><strong>Total (wt%)</strong></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
4.2 Fate of vanadium in the lime cycle – effect of adding V with petcoke

4.2.1 Reactions between V in petcoke and lime mud

Vanadium is the second largest impurity (next to sulfur) in petcoke. At high temperatures inside the lime kiln, vanadium from petcoke readily reacts with oxygen to form vanadium pentoxide (V$_2$O$_5$). Due to its low melting point (690°C), V$_2$O$_5$ will melt and vaporize at temperatures prevailing in the kiln.

To study the fate of vanadium from petcoke introduced to the lime kiln, petcoke samples are mixed with three different types of lime mud (Mud A, B and C) at different petcoke to lime mud weight ratios. Figure 20 shows the correlation of vanadium content in the residue after each heat treatment experiment with respect to the petcoke content in the petcoke-mud mixture prior to the experiment. In all cases, the amounts of mud input are fixed, but petroleum coke contents vary. In Figure 20, the theoretical values assume all the original vanadium from petcoke would stay in the lime after burning at 950°C for 5 hours with the air inflow, while the square dots are the actual XRF experimental readings.
V content in residue (wt%)

Mud A

- V - theo (%)
- V - actual (%)

Mud B

- V - theo (%)
- V - actual (%)

Coke % in Coke-Mud mixture
For all three lime mud samples used in this study, the amount of vanadium in the residue increased as the petcoke content in the mixture increases. The actual measurements were virtually the same as theoretical values up to 50wt% of petcoke in the coke-mud mixture. This confirms that vanadium is likely to stay with lime to form calcium vanadates after heat treatment, independent from the impurities in the lime mud. No significant differences between mills were found, particularly for mixtures that contained less than 20 wt% petcoke.

Both Figures 20 and 21 are compared for the vanadium contents in the residues of petcoke mixtures and lime mud from three different mills. Assuming all vanadium compounds in the petcoke stayed in the residue after the heat treatment, the amount of vanadium in the residue can be calculated based on the vanadium content in petcoke, the petcoke content in the petcoke-mud mixture, the amount of the mixture used, and the amount of residue obtained. Figure 21 compares the calculated value to the actual vanadium measurements. The dotted
line represents the case where the actual value is exactly the same as the calculated value. From the experimental results, the measured values fit well with the dotted line except high V content (about 0.3 wt%). It suggests that V may vaporize into gas before reacting with lime in the kiln if significant amounts of V present in the mixture. In a typical pulp mill with 75% of petcoke substitution rate in the lime kiln, the weight percentage of V in the solid residue after heat treatment is usually lower than 0.1 wt%; therefore, these experimental results are applicable for typical mill operations. The actual and calculated vanadium contents in lime products after heat treatment are almost equal, particularly when the vanadium content in the residue is below 0.2 wt%.

![Figure 21](image-url)

**Figure 21** Comparison of theoretical and actual amounts of vanadium left in solid residue after heat treatment – XRF results

After the heat treatment, the scrubber solutions and the filtrates from causticizing reaction were collected and analyzed by ICP-AES. The analysis found negligible amount of V
in the solutions. The result again suggests that vanadium stays in the solid residues after the heat treatment.

4.2.2 FactSage simulation on kiln operation when burning V-containing petcoke

Based on the thermodynamic database and calculation, commercially available software, FactSage, can simulate a kiln operating environment with corresponding temperature and mass inputs to help predict the equilibrium composition of ash products burning at high temperature. The input data for this case study are listed in Appendix E. Calculations are performed based on 100% petcoke burning in the kiln with lime in 4.4% excess oxygen. The flue gas compositions for the lime kiln at different operating temperatures are shown in Figure 22.

![Figure 22 Gas composition from burning 100% petcoke in a typical pulp mill](image)
From the above graph, the main gaseous components are nitrogen from excess air and CO\textsubscript{2} from high carbon content in petcoke. The total V, Ni, Fe and Na gaseous compounds are expressed as V, Ni, Fe, and Na, respectively. As the kiln operating temperature increases to 1400°C or higher, gaseous vanadium starts to appear in the combustion gas. However, this temperature is already above the limit of normal operating temperature for lime kilns. The graph implies that only very small amounts of vanadium can escape in the flue gas with increasing temperature, while the majority of the remaining vanadium compounds stay with the lime product.

Figure 23 shows further investigation on the phase of vanadium compounds that may have formed in a lime kiln based on FactSage calculation. The result suggest that up to 1800°C, most of V from burning petcoke is likely to be contained in lime and forms stable compounds, while gaseous vanadium compound emissions are highly unlikely.

![Graph showing the fate of vanadium in a lime kiln](image)

**Figure 23** FactSage result on fate of vanadium on petcoke combustion in lime kiln
4.2.3 Reactions between $\text{V}_2\text{O}_5$ and $\text{CaCO}_3$

To further study the fate of vanadium from petcoke combustion, analytical grade vanadium pentoxide ($\text{V}_2\text{O}_5$) with calcium carbonate ($\text{CaCO}_3$) were used to resemble vanadium-containing petcoke ash and lime mud, respectively. First, pure $\text{V}_2\text{O}_5$ was heated up to 950°C in air. Figure 24 shows the results from TGA/DSC analyzer.

![Figure 24 Weight loss profile for vanadium pentoxide ($\text{V}_2\text{O}_5$) in air](image)

The sample contained 0.5% moisture and melted at around 670°C. It is clear that $\text{V}_2\text{O}_5$ melts and becomes volatile at above 670°C since a large amount of heat is required for melting; however, the overall weight loss is only 2 wt%. The minor weight loss was presumably due to the loss of moisture content and vaporization of $\text{V}_2\text{O}_5$. The relatively constant weight of the sample at temperatures below 670°C as well as the rapid decrease in weight at temperatures above 670°C suggest that $\text{V}_2\text{O}_5$ is stable at temperatures below its melting temperature but is able to volatilize once molten.
Figure 25 shows the TGA profiles in air for two mixtures of V$_2$O$_5$ and CaCO$_3$ at 10 wt% and 20 wt% V$_2$O$_5$, compared with pure CaCO$_3$ (0wt% V$_2$O$_5$).

![Weight loss profiles for pure CaCO$_3$ containing various amount of V$_2$O$_5$ (0wt%, 10wt% and 20wt%)](image)

Figure 25 Weight loss profiles for pure CaCO$_3$ containing various amount of V$_2$O$_5$ (0wt%, 10wt% and 20wt%)

Pure CaCO$_3$ (0 wt% V$_2$O$_5$) started to decompose in air at about 650°C, eventually losing 44% of its weight as the temperature exceeded 830°C. Mixtures containing 10 and 20 wt% V$_2$O$_5$ abruptly lost 2.5% and 5% of their weight at about 620°C, respectively. As shown in Figure 13 for the phase diagram of the V$_2$O$_5$-CaO system, this temperature is almost the same as the eutectic temperature of V$_2$O$_5$ and CaO·V$_2$O$_5$ [47]. This suggests that in the presence of CaCO$_3$, 1 mole of V$_2$O$_5$ starts to melt at 620°C, causing 1 mole of CaCO$_3$ to decompose to CaO. The weight losses at this temperature were close to their respective theoretical values of 2.42% and 4.84% calculated assuming the reaction product was CaO·V$_2$O$_5$ (calcium vanadate), i.e.:
\[
\text{V}_2\text{O}_5(\text{s}) + \text{CaCO}_3(\text{s}) \rightarrow \text{CaO}\cdot\text{V}_2\text{O}_5(\text{s}) + \text{CO}_2(\text{g})
\]  

Reaction 7

The phase diagram of V\(_2\)O\(_5\)-CaO (Figure 13) also shows that below 778\(^\circ\)C, a mixture of CaO and V\(_2\)O\(_5\) would react to form CaO\cdot V\(_2\)O\(_5\). This, along with the TGA/DSC results, suggests that V\(_2\)O\(_5\) immediately reacts with decomposed CaO to form CaO\cdot V\(_2\)O\(_5\) at its eutectic melting temperature since CaO\cdot V\(_2\)O\(_5\) is a thermally more stable compound. The reaction proceeds further at higher temperatures and in the presence of a large amount of CaO, forming 2CaO\cdot V\(_2\)O\(_5\) and 3CaO\cdot V\(_2\)O\(_5\), according to the following reactions:

\[
\text{CaO}\cdot\text{V}_2\text{O}_5(\text{s}) + \text{CaO}(\text{s}) \rightarrow 2\text{CaO}\cdot\text{V}_2\text{O}_5(\text{s}) \\
2\text{CaO}\cdot\text{V}_2\text{O}_5(\text{s}) + \text{CaO}(\text{s}) \rightarrow 3\text{CaO}\cdot\text{V}_2\text{O}_5(\text{s})
\]

Reactions 8 and 9

The decomposition of remaining CaCO\(_3\) was completed at about 830\(^\circ\)C, which is similar to the decomposition temperature of the pure CaCO\(_3\). In the presence of lime, however, V\(_2\)O\(_5\) reacts quickly with lime at temperatures above 620\(^\circ\)C to form calcium vanadates. No further weight loss was observed at higher temperatures up to 950\(^\circ\)C. The result shows that the calcium vanadate compounds formed are stable and do not vaporize at temperatures up to at least 950\(^\circ\)C.

The CaO/V\(_2\)O\(_5\) molar ratios of the 10 wt% and 20 wt% V\(_2\)O\(_5\)/CaCO\(_3\) mixtures used in the above study are respectively 16.4 and 7.3, respectively. These ratios are significantly greater than 3, indicating that there are much more CaO in the mixtures than needed to form any of the three known calcium vanadates: CaO\cdot V\(_2\)O\(_5\), 2CaO\cdot V\(_2\)O\(_5\) and 3CaO\cdot V\(_2\)O\(_5\). These compounds are thermally more stable than V\(_2\)O\(_5\), explaining the constant weight of the mixtures observed at temperatures above 830\(^\circ\)C. Of these compounds, 3CaO\cdot V\(_2\)O\(_5\) is more
likely to form due to the high CaO-to-V$_2$O$_5$ molar ratio of the mixtures according to the phase diagram, shown in Section 2.3.

The XRD scanning results of the two solid residues (10 wt% and 20 wt% V$_2$O$_5$ with remaining pure CaCO$_3$) from V$_2$O$_5$/CaCO$_3$ mixtures suggests the presence of $3\text{CaO}\cdot\text{V}_2\text{O}_5$, shown in Figure 26 (a) and (b), respectively. In both cases, the mixtures undergo heat treatment separately at 950°C. The remaining solid residues are analyzed by XRD to characterize the complex structure.
Figure 26 XRD Results for solid residues after heat treatment from (a) 10wt% V$_2$O$_5$ with 90wt% CaCO$_3$, and (b) 20wt% V$_2$O$_5$ with 80wt% CaCO$_3$. 

Note: The diagrams show the X-ray powder diffraction patterns for the solid residues after heat treatment. The peaks correspond to different phases present in the samples, with labels indicating specific compounds.
According to the diffraction database, the analysis performed on the residues confirms the presence of $3\text{CaO} \cdot \text{V}_2\text{O}_5$, along with the unreacted CaO and a small amount of Ca(OH)$_2$ which was formed as a result of CaO hydration by moisture in the air. The result suggests that all V$_2$O$_5$ reacts with calcium oxide to form tri-calcium vanadate. Negligible amounts of V$_2$O$_5$, CaO·V$_2$O$_5$ and 2CaO·V$_2$O$_5$ were detected. These results are consistent with those obtained by Slobodin et al. [47] showing that 3CaO·V$_2$O$_5$ is the most stable compound and is the final product from the heat treatment of CaO/V$_2$O$_5$ and CaCO$_3$/V$_2$O$_5$ mixtures with 3:1 molar ratio by using TGA/DTA (Differential Thermal Analysis). Similar result was obtained by Jia et al. in a CFB combustor where 100% petcoke was burned [31]. 2CaO·V$_2$O$_5$·2H$_2$O was the major V-containing product after combustion with limestone and kaolin used for SO$_2$ capture.

To investigate the interaction between vanadium pentoxide and reburned lime, the mixture of V$_2$O$_5$ (10 wt% and 20wt%) and pure CaCO$_3$ were heated up to 950°C twice in TGA. In the second heating process, the residual solid contained calcium vanadate compound with decomposed CaO. The TGA results for the mixtures are shown in Figure 27 (for 10wt% V$_2$O$_5$) and Figure 28 (for 20wt% V$_2$O$_5$). In both figures, (a) and (b) represent the first and second runs in each test, respectively. Comparing the two figures shown below, Figure 27(a) shows the same results as Figure 25 where the eutectic melting point of V$_2$O$_5$-CaO starts at 620°C, and the complete decomposition of CaCO$_3$ finishes at 830°C. During the cooling process (not shown in the figures), the decomposed CaO quickly absorbs some of the moisture from air to form partially Ca(OH)$_2$. The weight difference between the finishing material in Figure 27(a) and the starting material from Figure 27(b) confirms the formation of Ca(OH)$_2$. When heating up the mixture of V$_2$O$_5$ with reburned CaO (partially Ca(OH)$_2$), the first weight
loss due to dehydration occurs at around 380°C [56]. However, there is no more weight change at higher temperature, which indicates that $V_2O_5$ forms thermally stable calcium-vanadium oxide complex at temperatures up to 950°C.

Figure 27 Weight loss profile for $V_2O_5$ in (a) 10wt% $V_2O_5 + 90$wt% $CaCO_3$ and (b) ash residue from previous run
Similar to the experiment set up in Figure 27(a) and (b), Figure 28(a) and (b) show the weight loss profile for the mixture of 20wt% $V_2O_5$ with 80wt% pure CaCO$_3$.

**Figure 28** Weight loss profile for $V_2O_5$ in (a) 20wt% $V_2O_5$ + 80wt% CaCO$_3$ and (b) ash residue from previous run.
The two graphs above have same patterns as previous figures, where eutectic temperature first occurs at 620°C for V$_2$O$_5$-CaO system [46]. Part of CaO becomes hydrated during the cooling process, and no more reaction was observed when heating up the residue solid to 950°C except for the dehydration of Ca(OH)$_2$. From the DSC curve in Figure 28(a), one interesting peak was shown at 780°C. The upward peak indicates an exothermic reaction occurring at this point that may result from the formation of some new compound. One of the possibilities is the formation of 3CaO·V$_2$O$_5$ as CaO·V$_2$O$_5$ reacts with additional CaO and releases heat simultaneously. However, this peak is unnoticeable from the mixture of 10wt% V$_2$O$_5$ with CaO due to smaller amount of V present in the sample.

The result is an indication of what happens inside a lime kiln where petcoke with high vanadium content is burned. When the combustion gases interact with lime mud or decomposed lime near the hot end, vanadium pentoxide will first form calcium vanadate compounds as temperature reaches 620°C. It is a thermally stable compound at temperatures up to 950°C inside the kiln. The results imply that all vanadium would be absorbed by the reburned lime and leave the kiln as calcium vanadate compounds from the discharge end. Vanadium particulate emission in the stack from petcoke combustion should not be a concern since the amount of vanadium in the flue gas is negligible.
4.2.4 Causticizing Na$_2$CO$_3$ solution with V-containing lime

As mentioned in the experimental procedure section, in order to complete the lime cycle, two V-containing lime samples were prepared by heating mixtures of V$_2$O$_5$ (10 wt% and 20 wt%) and CaCO$_3$ in the furnace at 950°C for 5 hours. These samples had a V/Ca molar ratio of 0.122 and 0.275 respectively, and were used to causticize a solution of 200 g/L Na$_2$CO$_3$ (equivalent TTA of 20 g/L Na$_2$O) at 90°C for 2 hours. Figure 29 compares the V/Ca ratio of the lime samples before the causticizing reaction to that of lime mud (the precipitated material after causticizing reaction).

![Figure 29 V/Ca ratios of the lime product before causticizing reaction and the precipitate material after causticizing reaction – XRF results](image)

For both 10 wt% and 20 wt% V$_2$O$_5$ cases, the V/Ca molar ratios of the mud were almost the same at about 0.008, which were much lower than that of the lime before the causticizing reaction. The low V content in mud implies that most of the V$_2$O$_5$ that has formed calcium vanadates with the lime mud must have reacted with Na$_2$CO$_3$ in the solution to form
water-soluble sodium vanadate compounds (NaVO₃), and consequently been transferred to the causticized solution, according to Reactions 10, 11, and 12.

\[
\text{CaO} \cdot \text{V}_2\text{O}_5(s) + \text{Na}_2\text{CO}_3(aq) \rightarrow 2\text{NaVO}_3(aq) + \text{CaCO}_3(s) \quad \text{Reaction 10}
\]

\[
2\text{CaO} \cdot \text{V}_2\text{O}_5(s) + 2\text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightarrow 2\text{NaVO}_3(aq) + 2\text{CaCO}_3(s) + 2\text{NaOH}(aq) \quad \text{Reaction 11}
\]

\[
3\text{CaO} \cdot \text{V}_2\text{O}_5(s) + 2\text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightarrow 2\text{NaVO}_3(aq) + 3\text{CaCO}_3(s) + 2\text{NaOH}(aq) \quad \text{Reaction 12}
\]

In these experiments, the precipitated mud was obtained from vacuum filtering only, without washing the mud in water. It was possible that a small amount of V might still remain in the residual solution in the mud. Additional caustic make-up will be required as NaVO₃ is generated as a byproduct from the reaction of Na₂CO₃ to NaOH. Regardless of the CaO/V₂O₅ molar ratios, vanadium from the reburned lime residual solid forms highly water soluble NaVO₃ in the causticizing reaction. And thus in the causticizing plant, NaVO₃ circulates around the recovery cycle with white liquor. It becomes enriched in the liquor, leading to vanadium build-up in the liquor cycle.
4.3 Fate of vanadium in the alkali cycle – effect of adding V with petcoke

One of the concerns over petcoke combustion in the lime kiln is its potential role in high temperature corrosion in recovery boilers. \( \text{V}_2\text{O}_5 \) has a low melting point of 670°C. It may form even lower eutectic melting temperature with other compounds. Chloride (Cl) and potassium (K) are the most troublesome non-process elements in the recovery boiler since they can form low melting temperature salts that attack superheater boiler tubes. Whether vanadium will interact with these non-process elements in the alkali cycle is not clear.

In order to test the effect of adding vanadium to the first melting point of the deposit, two sets of synthetic superheater deposit samples were prepared. Analytical grades \( \text{Na}_2\text{CO}_3 \), \( \text{Na}_2\text{SO}_4 \), \( \text{NaCl} \) and \( \text{KCl} \) were used as starting materials. The two scenarios considered here are: Cl from \( \text{NaCl} \), and Cl from \( \text{KCl} \), along with appropriate amounts of \( \text{Na}_2\text{CO}_3 \) and \( \text{Na}_2\text{SO}_4 \). The molar ratio of Cl/(Na+K) is kept at 10mol%. The samples were individually weighed and premixed in a small bottle. The mixture was placed in a small platinum crucible and melted in an oven at 800°C. The molten mixture was cooled down to room temperature in order to get a uniform solid. It was further ground to fine powders and used to determine the first melting temperature of this synthetic deposit sample. Various amounts of \( \text{V}_2\text{O}_5 \) (up to 2wt%) were added into the mixture to study the effect of adding \( \text{V}_2\text{O}_5 \) to the first melting temperature. Similar procedures were repeated for the mixture of KCl, \( \text{Na}_2\text{CO}_3 \), and \( \text{Na}_2\text{SO}_4 \), along with \( \text{V}_2\text{O}_5 \). Table 9 shows the compositions of the two synthetic samples.
Table 9 *Compositions of the two synthetic samples*

<table>
<thead>
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<th>synthetic deposit, #1</th>
<th>synthetic deposit, #2</th>
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</thead>
<tbody>
<tr>
<td>Na$_2$CO$_3$, wt%</td>
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<td>39</td>
</tr>
<tr>
<td>Na$_2$SO$_4$, wt%</td>
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<td>49</td>
</tr>
<tr>
<td>NaCl, wt%</td>
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<td>--</td>
</tr>
<tr>
<td>KCl, wt%</td>
<td>--</td>
<td>13</td>
</tr>
<tr>
<td>Cl/(Na+K), mol%</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

FactSage was used to compare the simulation results with experimental work. The inputs of the system are the same as the experiment. FactSage can predict the first melting temperature of the synthetic deposit samples, as well as showing the reaction products at that temperature. Figure 30 shows the results from TGA and FactSage simulation on the effect of adding V$_2$O$_5$ to the first melting point of the synthetic superheater deposits.

![Graph showing the effect of V$_2$O$_5$ on melting temperatures](image)

**Figure 30** Effect of adding V$_2$O$_5$ to the first melting point of black liquor synthetic deposits on superheater tubes

In the graph, there are four experimental data points collected for each synthetic mixture. The predicted first melting points from FactSage are drawn in lines for up to 2 wt%
of V$_2$O$_5$ added into the mixture. The initial experimental melting temperatures occurred at 612°C for the sample with NaCl, and 503°C for the sample with KCl, without the presence of V$_2$O$_5$. The experimental work from TGA suggests that up to 2wt% of V$_2$O$_5$ added into the black liquor synthetic deposit, the first melting point of the mixture would not have any significant change.

FactSage shows almost the same result as the experiment that V$_2$O$_5$ did not play an important role of changing the first melting temperature for the synthetic superheater deposits. The product streams from FactSage indicate all V$_2$O$_5$ added into the mixture quickly forms (Na$_2$O)$_2$V$_2$O$_5$, or also known as Na$_2$O•2NaVO$_3$, with sodium carbonate at high temperature by releasing CO$_2$ gases according to the following reaction:

\[ 2\text{Na}_2\text{CO}_3(s) + \text{V}_2\text{O}_5(s) \rightarrow \text{Na}_2\text{O} \cdot 2\text{NaVO}_3(s) + 2\text{CO}_2(g) \]  

**Reaction 13**

The TGA results also show slight weight losses at the melting temperature when adding V$_2$O$_5$ into all mixtures. The resulting Na$_2$O may have a slight advantage in the causticizing reaction from the slaker where it can be directly dissolving in water to form NaOH. The water soluble NaVO$_3$ still circulates around the recovery cycle with white liquor.
4.4 Implications - Fate of vanadium in the chemical recovery operation from burning petcoke in lime kilns

Vanadium (V) is the second largest impurities in petroleum coke (up to 2500ppm). Despite the economical benefits of burning petcoke, the high concentration of vanadium in petcoke remains as a concern for mills that use petcoke as an alternative fuel. Based on the experimental work and simulation results obtained from this study, the fate of V introduced with petcoke to the lime kiln may be postulated. Shown in Figure 31, as petcoke is burned in the kiln, V is oxidized to V$_2$O$_5$. The majority of such formed V$_2$O$_5$ is retained in the combustion residue (petcoke ash) and becomes well mixed with lime in the kiln bed. It then reacts with lime to form calcium vanadates, mostly 3CaO•V$_2$O$_5$, due to the abundance of lime and the high temperature near the kiln front end. A small amount of V$_2$O$_5$ may not take part in the formation of petcoke ash, remaining as vapour in the kiln gas. Some of this gaseous V$_2$O$_5$ may react with CaO to form calcium vanadates if it is in contact with the kiln bed and/or with suspended lime dust particles; others may condense to form fine V$_2$O$_5$ dust particles as temperature decreases. As a result, lime dust$^3$ is expected to contain calcium vanadates and unreacted V$_2$O$_5$. An electrostatic precipitators (ESP) is used to capture any lime dust from the gas stream using an induced electrostatic charge.

$^3$ Lime Dust: the particulates in the lime kiln exhaust gas. It usually contains alkali metals and sulfur. Lime dust is usually captured by electrostatic precipitators (ESP).
For kilns that recycle dust directly from the electrostatic precipitator, the unreacted V$_2$O$_5$, if any, will be well mixed with the feed mud, form thermally stable calcium vanadates in the kiln and exit the kiln with lime. As a result, no significant accumulation of V in the lime dust is expected. For kilns that use scrubbers to eliminate lime dust before feeding it back to the kiln via a precoat filter, the unreacted V$_2$O$_5$ is expected to be washed off along with other water-soluble compounds and become part of the scrubber solution.

In the slaker and causticizers, calcium vanadates in the lime will react with Na$_2$CO$_3$ in the green liquor to form sodium vanadates (NaVO$_3$) and precipitate lime mud (CaCO$_3$). Since NaVO$_3$ has a high solubility in water, 255 g/L at 50°C [57], it dissolves in the liquor, leading to vanadium build-up in the liquor cycle. Less Na$_2$CO$_3$ is converted into NaOH so that additional caustic make-up will be required. Also, since V follows the liquor, it does not accumulate in the mud if the mud is well washed. The net effect is that V is transferred from petcoke to lime in the kiln and from lime to liquor in the causticizing plant. As petcoke is
continuously burned in the kiln, the concentration of V in the liquor increases. Eventually a steady state concentration is reached when the amount of V introduced with petcoke to the lime kiln is equal to the amount lost from the system through dregs, grits, mud disposal, liquor spills, etc.

The black liquor deposits on the superheater tubes inside the boiler may cause corrosion concerns at high operating temperatures. Adding V$_2$O$_5$ (up to 2 wt%) to the mixture of black liquor synthetic deposits is unlikely to change the first melting point of the deposits. All V$_2$O$_5$ added reacted with Na$_2$CO$_3$ to form Na$_2$O•2NaVO$_3$, releasing CO$_2$ gas at the same time. The vanadium from petcoke is therefore unlikely to play a role on high temperature corrosion in recovery boilers.

In the overall chemical recovery operation, vanadium forms calcium vanadate with lime as petcoke burns in the lime kiln. In the causticizing plant, this calcium vanadate dissolves in the green liquor and forms water soluble sodium vanadate. The sodium vanadate enters the liquor cycle with white liquor, becomes enriched in the liquor, leading to vanadium build-up in the system.
4.5 Fate of sulfur in the chemical recovery operation

Sulfur is one of the process elements that are essential for pulp and paper making process. The high sulfur content, about 6.5wt% from petroleum coke, raises the concern of reducing lime availability, increasing liquor sulfidity, larger ring formation inside the kiln, and impact on sodium and sulfur balance. In the combustion process for petcoke, sulfur first reacts with oxygen from air to form sulfur dioxide, which can be further captured by lime to form calcium sulfate. The major chemical reactions for sulfur occurring in the kiln are expressed as:

\[
S(s) + O_2(g) \rightarrow SO_2(g) \quad \text{Reaction 14}
\]

\[
\text{CaO}(s) + \frac{1}{2} O_2(g) + SO_2(g) \rightarrow \text{CaSO}_4(s) \quad \text{Reaction 5}
\]

If burning petcoke alone, sulfur in petcoke may form \(SO_2\) and escape from the kiln as combustion gas at high temperatures (higher than 850°C for Syncrude petcoke, shown in Table 8). For the lime rich environment, the \(SO_2\) emitted from burning petcoke may be further captured by the reburned lime and form \(\text{CaSO}_4\) before leaving the kiln. The amount of ash left after the heat treatment may be increased by the amount of sulfur introduced by petcoke. Figure 32 shows the experimental amount of ash residue left after heat treatment (in dots) when burning pure \(\text{CaCO}_3\) with different mass fractions of petroleum coke. Two theoretical cases are considered: (1) \(SO_2\) was formed and released as combustion gas; (2) \(\text{CaSO}_4\) was formed and left with the reburned lime.
In Figure 32, the dotted line shows the theoretical amount of ash that should remain if all calcium carbonate was converted into calcium oxide and if the ash content of petcoke was 0.4wt%. The solid line represents the theoretical amount of ash left, assuming all sulfur from petcoke is captured by calcium oxide. This line is not straight since at the wt% of coke over 83%, there is not enough Ca to capture all S from petcoke. The actual experimental data, shown as round dots in the figure, fitted almost perfectly on the theoretical line. This suggests that all the sulfur from the petcoke would stay in the lime as calcium sulfate if petcoke is well mixed with lime mud and burned at 950°C. The lime rich environment in the lime kiln can take up almost all sulfur present in petcoke.

Similar to the analysis for vanadium shown in Figures 19 and 20, Figures 33 and 34 compare the sulfur contents in the residues of petcoke and lime mud mixtures from three different mills after heat treatment.
The graphs above suggest that all the sulfur originally from petcoke stays in the lime product after the heat treatment. Figure 34 summarizes the comparisons between the theoretical and actual sulfur contents (wt%) left in the lime products after burning the mixture of petcoke with three different kinds of mud at 950°C. The dotted line shows the case where the theoretical and actual sulfur weight percentages are the same. The square dots from experimental results almost fit the line.
As S input from petcoke increases, the amount of sulfur in the residue increases. The S reacts with lime to form CaSO$_4$, and thus lowering the lime availability. In the slaker, this CaSO$_4$ will react with Na$_2$CO$_3$ to form Na$_2$SO$_4$ and CaCO$_3$:

$$\text{CaSO}_4(\text{s}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{CaCO}_3(\text{s})$$  \hspace{1cm} \text{Reaction 6}

This means that there will be less Na$_2$CO$_3$ to convert into NaOH so that additional caustic make-up will be required. Na$_2$SO$_4$ is water soluble and thus will end up as “dead load” in the liquor [24]. The impacts of burning high S content petcoke in lime kiln are discussed in Section 2.5.
4.6 Fate of other non-process elements in chemical recovery operation

Nickel and iron are two other important non-process elements present in petcoke. Figure 35 compares the amount of nickel and iron left in solid residue after burning petcoke with lime mud at 950°C, with the amount of nickel and iron left in the lime mud after causticizing reaction, respectively.

![Figure 35: Comparison of amount of nickel and iron left in solid residue after burning petcoke and after causticizing reaction – ICP results](image)

Shown as the theoretical dotted line in the graph, if the two metal elements form water insoluble compounds, the amounts of such compounds would stay constant in the cake after causticizing reaction. The results suggest that nickel and iron are likely to form insoluble compounds when react with sodium carbonate solution, and thus, are less likely to cause problems to the alkali cycle.
5 CONCLUSIONS

Laboratory studies are carried out to investigate the fate of V and S with petcoke in lime kilns. Results obtained from this study show that when mixtures of petcoke and lime mud were heated at 950°C, vanadium and sulfur in the petcoke would be completely absorbed by lime to form calcium vanadates, mostly 3CaO·V_2O_5 and CaSO_4, respectively. Vanadium and sulfur will not accumulate in the lime mud if the mud is well washed and dewatered. In the causticizing plant, these compounds react with Na_2CO_3 in the green liquor to form soluble NaVO_3 and Na_2SO_4 which stay in the liquor cycle. Adding vanadium (up to 2wt%) to the black liquor smelt will not change its first melting temperature. High vanadium concentration from petcoke should be a factor causing superheater corrosion in the recovery boiler. Similar to other water-soluble chloride (Cl) and potassium (K) compounds, V accumulates and reaches a steady state concentration in the liquor that is linearly proportional to the amount of its input with petcoke and the amount of the mill soda loss. Most of the other non-process elements, including Ni and Fe, stay as oxides in the mud solids. Since oxides of these elements are either insoluble or slightly soluble in an alkaline solution, they are more likely to be removed from the system through grit/dreg disposal.
6 REFERENCES


APPENDICES
### Appendix A – Typical Ultimate Analysis for Pulverized Fuel Grade Petroleum Coke [58]

<table>
<thead>
<tr>
<th>% by weight</th>
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</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>
### Appendix B – Typical Ash Analysis for Pulverized Fuel Grade Petroleum Coke [58]

<table>
<thead>
<tr>
<th>Element</th>
<th>PPM Fuel, dry basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>1160</td>
</tr>
<tr>
<td>Nickel</td>
<td>250</td>
</tr>
<tr>
<td>Calcium</td>
<td>230</td>
</tr>
<tr>
<td>Silica</td>
<td>150</td>
</tr>
<tr>
<td>Iron</td>
<td>90</td>
</tr>
<tr>
<td>Sodium</td>
<td>40</td>
</tr>
<tr>
<td>Magnesium</td>
<td>30</td>
</tr>
<tr>
<td>Aluminum</td>
<td>20</td>
</tr>
<tr>
<td>Fluorine</td>
<td>11.0</td>
</tr>
<tr>
<td>Copper</td>
<td>3.5</td>
</tr>
<tr>
<td>Manganese</td>
<td>2.4</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1.5</td>
</tr>
<tr>
<td>Lead</td>
<td>0.6</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.3</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt; 1 ppb(^4)</td>
</tr>
</tbody>
</table>

\(^4\) Below detectable limits
### Appendix C – Characteristics of Raw Petroleum Coke [49]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Typical Range</th>
<th>Specification for Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardgrove Grindability</td>
<td>20 – 90 HGI</td>
<td>35 – 55 HGI</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.5 – 7 wt%</td>
<td>As low as possible</td>
</tr>
<tr>
<td>Moisture</td>
<td>3.5 – 12 wt%</td>
<td>Less than 6%</td>
</tr>
<tr>
<td>Ash</td>
<td>0.5 – 1.5 wt%</td>
<td>As low as possible</td>
</tr>
<tr>
<td>Metals (V, Ni, Fe, etc.)</td>
<td>100 – 5000 ppm</td>
<td>Not a constraint</td>
</tr>
<tr>
<td>Particle Size (as received)</td>
<td>3 – 200 mm</td>
<td>Less than 50 mm</td>
</tr>
<tr>
<td>Heating value</td>
<td>32.5 – 33.5 MJ/kg</td>
<td>32.5MJ/kg</td>
</tr>
</tbody>
</table>
Appendix D – Thermogravimetric Analysis / Differential Scanning Calorimetry in TA instruments SDT Q600™.

Thermal analysis is a technique to monitor the physical and chemical changes of a substance as a function of time or temperature. The conventional techniques include thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) [59].

SDT Q600™ can simultaneously generate TGA and DSC data for each sample. TGA measures changes in mass associated with heating, cooling, or a given temperature to determine composition and thermal stability of a material [60]. Weight is plotted as a function of temperature at constant heating/cooling rate, or as a function of time at isothermal condition [61]. Under the inert of nitrogen, a substance may dehydrate or decompose at elevated temperatures. When input air or oxygen, TGA can track any oxidation reaction if occurred during the process.

DSC is a method to measure the amount of energy absorbed / released to produce a zero temperature difference between a sample and a reference, as a function of temperature or time [60]. It requires both the sample and the reference operate under the same experimental condition. The independent thermocouples (platinum/platinum-rhodium) under each sample holder provide heat separately. First, the sample and the reference are heated or cooled at a constant rate. If there is any temperature difference, the power input for the reference will be adjusted to eliminate the difference. This continuous and automatic power adjustment is directly proportional to the amount of heat required during the process by the sample and reference [62]. An exothermic process corresponds to increase in heat flow, which is indicated
as a positive peak, while an endothermic process has a decrease in heat flow, shown in the downward direction.

Figure 36 gives an example of TGA/DSC results for pure calcium carbonate being heated up to 950°C in air at 20°C/min. The initial heat flow occurs at 100°C due to dehydration of moisture from the chemical. A large amount of weight loss starts from 700°C, and finishes around 830°C due to the decomposition of calcium carbonate to calcium oxide [63], while producing carbon dioxide gas. The heat associated with the decomposition is clearly shown where heat is absorbed during this process, i.e. endothermic reaction. Calcium carbonate is not reactive under oxygen or air since weight loss is only associated with the decomposition.

Figure 36 Weight loss profile for pure calcium carbonate in air
Appendix E – Data input of FactSage Calculation

Basis: 1,250 metric tons/d kraft mill. Lime kiln with precipitator and no lime mud dryer (LMD).

<table>
<thead>
<tr>
<th><strong>Pulp Production</strong></th>
<th>1250 t/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mud mass flow, dry basis</td>
<td>573.48 t/d</td>
</tr>
<tr>
<td>Residual CaCO3</td>
<td>4.2 %</td>
</tr>
<tr>
<td>Lime availability</td>
<td>87.5 %</td>
</tr>
<tr>
<td>Inerts in lime</td>
<td>8.3 %</td>
</tr>
<tr>
<td>Lime production rate</td>
<td>281.01 t CaO/d</td>
</tr>
<tr>
<td>Lime production rate</td>
<td>321.15 t lime/d</td>
</tr>
</tbody>
</table>

**Petroleum Coke**

100 % of fuel

**FUEL DATA**

<table>
<thead>
<tr>
<th>Type</th>
<th>100% Petcoke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Value</td>
<td>32,936 KJ/Kg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition</th>
<th>C</th>
<th>86.7 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Fuel flow rate

| Total heat required per day | 2,422 GJ/d |
| Petroleum Coke | 73,539 Kg/d |

**KILN OPERATING DATA**

| Mud solids | 75 % |
| Dust loss (recycle) | 15 % |
| Fuel heating rate | 8,619 MJ/ton CaO |
| Excess O2 (mass basis) | 3.3 % |
| Excess O2 (vol basis) | 3.0 % |

| Wet mud flow (total) | 764,640 kg |
| Total air mass flow | 1,062,494.46 kg |