

Improved Process Safety of Petroleum Coke Calcination by Improved Knowledge and Control Measures

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<https://doi.org/10.71659/icsoba2024-el003>

Abstract

The petroleum coke rotary kiln calcination process has not changed considerably in recent decades. The only exception is improvements in instrumentation with technological advancements. Calcination is a mature process which is well understood, and operation is reasonably well controlled. Nevertheless, in 2020, a combustion blast occurred after a restart following a short stop of the rotary kiln at a Rio Tinto calcination site. This highlighted a risk that had not been previously identified through the Process Hazard Analysis used by Rio Tinto.

The investigation identified the presence of residual volatiles in the coke bed between the feed end and the air injection nozzles as the cause for the incident. Thermogravimetric analysis indicated the presence of residual volatiles in the coke bed when the kiln rotation was restarted after 12 minutes. This study allowed Rio Tinto's calcination plants to improve the robustness of their operations through procedures adapted to the risk.

Keywords: Calcination, Petroleum coke, Volatiles, Process safety.

1. Calcination of Green Coke

Calcined petroleum coke (CPC) has been used since about 90 years in the manufacture of carbon anodes for the Hall-Héroult aluminium electrolysis process [1]. CPC is obtained by heating (calcining) green petroleum coke (GPC) at temperatures above 1200 °C [1, 2]. Rio Tinto calcines GPC in four rotary kilns in Canada. GPC is fed at the upper end to the inclined kiln, as shown in Figure 1. The coke travels downwards due to the kiln rotation. Upon heating, water vapour and volatiles in the form of hydrogen, methane, and hydrocarbons are released from the coke [3].

By controlled injection of so-called “third air”, a portion of the volatiles is burned, producing the process heat [4, 5]. At the third air injectors, the maximum temperature of some 1 300 °C is reached in the so-called calcination zone. The combustion gases travel towards the upper end of the kiln, where they transfer to an incinerator or a boiler. Further downstream of the incinerator/boiler are cyclones for dust collection, a SO₂ scrubber and, finally, a stack. The gas flow in the kiln is controlled by the pressure at the gas outlet at the upper end. It depends on the draft at the stack, which is controlled by a fan.

Downhill of the third air injectors, the coke slowly cools down. Nevertheless, it typically remains above 1000 °C. In this zone, the graphitic character of the coke increases. A natural gas-fired burner, located at lower end of the kiln, is required for kiln start-up and shutdown. Rio Tinto does not rely on this burner in routine operation. However, it is used under certain circumstances. These include processing of certain “hard-to-calcine” GPCs requiring additional heat to reach the desired calcination level, as defined by the X-ray diffraction (XRD) parameter L_c [6]. Finally, at

the lower end of the kiln, the CPC is transferred to a cooler. Gases and entrained coke fines from the cooler are cleaned in a wet scrubber.

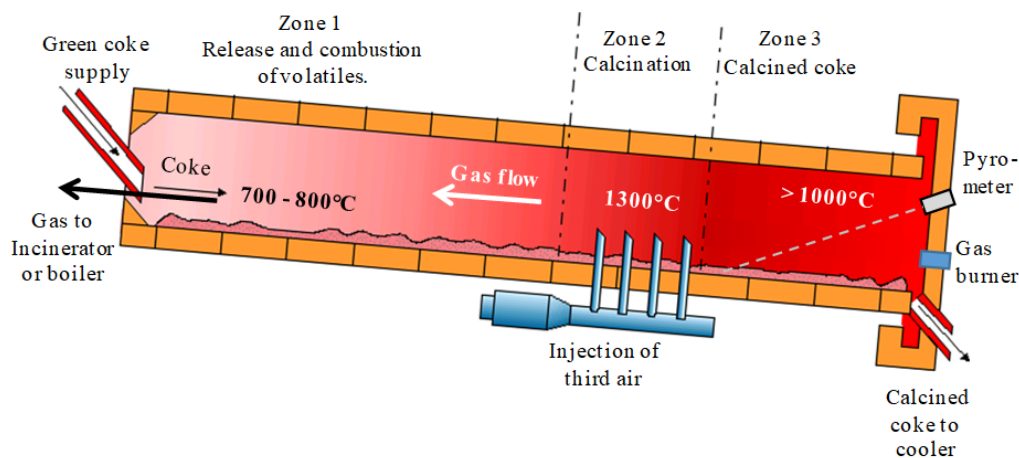


Figure 1. Schematic diagram of a rotary coke calcination kiln.

2. Key Aspects and Process Safety Risks of Petroleum Coke Calcination

2.1 Routine Operation

2.1.1 Process Control

The coke calcination level (Lc value) increases with increasing temperature and increasing soaking time. The coke residence time in the kiln, and therefore the coke soaking time, depends on the kiln rotation speed. With increasing speed, the velocity at which the coke travels downstream increases. In addition to a shorter soaking time, the coke bed becomes thinner. In practice, the soaking time is not significantly varied. This is because it should be as short as possible in order to maximise production while still allowing to reach the desired calcination level. Heat generation, and therefore the calcination temperature, is usually controlled by the quantity of injected third air. The air quantity is under stoichiometric. Increased air injection therefore results in increased volatiles combustions, associated with increased heat generation, and increased temperatures. Furthermore, coke fines entrainment also increases with increasing air injection and the associated gas velocity [7].

Finally, the coke feed rate can be changed. However, kilns are usually operated at or close to the maximum allowed rate in order to maximise production.

2.1.2 Calciner Feed Variations

The energy required for coke heat-up fluctuates. For example, at Rio Tinto's calciners, GPC is stored in the open. Thus, its humidity content varies depending on the weather, storing conditions, and from where in a pile the GPC was recovered. Obviously, the energy requirement to heat GPC increases with its humidity.

Furthermore, blends of GPCs with different granulometries are usually fed to the kiln. The blend recipe is typically changed every week or so. The corresponding coke granulometry changes influence the heat transfer in the coke bed. Fluctuating heat demands and heat transfers result in changes in the temperature profile in the kiln, including movement of the calcination zone.

2.1.3 Temperature Measurements

Temperature measurements in coke calcination kilns are not straightforward. The conditions in coke calcination kilns are very harsh, due to high temperatures, the presence of oxidising and corrosive gases (O_2 , and SO_2), and the movement of abrasive coke particles. Thermocouples are therefore not used by Rio Tinto for routine measurements. Instead, the temperature of the coke bed is measured using pyrometers. This approach is not suitable for sections of the coke bed obstructed by flames in the calcination zone. Thus, the pyrometer reads the temperature at a fixed location just downhill of the air injectors (Figure 1 in section 1). As the calcination zone moves, the measured temperature is not always in (close to) the calcination zone.

It can be summarised that, due to changing GPC feed properties and limited information on the changing temperature profile, it is very challenging to control coke calcination in a rotary kiln.

2.2 Kiln Start-up

During start-up, the kiln is first preheated using the gas-fired burner at its lower end. Then, feeding with GPC is started at a low rate, which is gradually increased up to the desired rate. In parallel, increasing quantities of third air are injected. It is important that (a portion of) the liberated volatiles react with the injected air. For this, the gas temperature has to be high enough for self-ignition of the volatiles. Furthermore, there must be enough air available to burn the desired portion of the volatiles. If volatiles combustion stops, unburned volatiles start to accumulate in the kiln and/or in the boiler. Re-ignition might result in uncontrolled, sudden volatiles combustion, including explosions. Therefore, it is very important to avoid uncontrolled stops of volatiles combustion. Combustion can stop for several reasons, including:

- Too rapid an increase of the GPC feed rate,
 - the energy provided by the gas-fired burner and/or by burning volatiles is not sufficient to heat the increased coke mass flow,
 - the temperature is no longer sufficiently high for volatiles self-ignition,
- An intermittent GPC feed rate,
 - as above, insufficient energy to always heat the coke feed to the temperature required for volatiles self-ignition,
- The gas-fired burner is stopped too early,
 - again, insufficient energy to heat the coke feed, and
- A significant reduction of the kiln rotation rate,
 - increased coke bed height, most probably resulting in poorer heat transfer, therefore slower volatiles release, combustion, and associated heat generation.

2.3 Other Risks

There are also other risks:

- An insufficient draft in the kiln,
 - resulting in overpressure due to build-up of volatiles,
- A gas leak at the gas burner,
 - caused by failure of the gas burner management system,
 - resulting in gas accumulation and potentially in uncontrolled combustion,
- Blockages at the CPC cooler, caused by
 - blocked CPC outlet, loss of cooler fan, or complete closure of the wet scrubber venturi damper,
 - possibly resulting in emissions of sulphur dioxide (SO_2) and hot steam.

All the risks mentioned above are well known and taken into account by Rio Tinto. Nevertheless, previously unknown risks may result in serious events. One of these is discussed below.

3. Combustion Blast Inside the Rotary Kiln

3.1 Kiln Rotation

The blast occurred after the kiln rotation had stopped. Thus, stoppages are briefly discussed. As long as the kiln is hot and filled with coke, a certain minimum rotation should always be maintained. Otherwise, gravity exerts a continuous mechanical pressure on the same lengthwise section of the kiln. This may result in deformation of the kiln, especially at elevated temperatures when the steel hull has a lower mechanical strength. Rotation might stop due to a power failure. In this case, an auxiliary drive ensures a minimum kiln rotation.

Obviously, maintenance cannot be performed on rotating kilns. Preferably, it is performed during a full shutdown (cold kiln). However, short duration maintenance is also possible during a partial shutdown. Here, the kiln burner keeps the kiln hot. However, the coke was removed from the kiln prior to maintenance.

Finally, a reduction of the kiln rotation may be required for different reasons, such as a physical blockage at the kiln discharge, inside the cooler, or at the cooler discharge.

3.2 Blast Incident

In November 2020, the rotation of a kiln was completely stopped. Prior to the stoppage, the kiln operated at a GPC feed rate of 23 t/h and a rotation speed of 2.5 rotations per minute (rpm). The reason for stopping the kiln rotation was a maintenance intervention. Nearly the entire rotary kiln was still filled with coke. As mentioned before (section 3.1), such a practice is not recommended. Nevertheless, it was sometimes used for short interventions. Performing interventions on a hot kiln, still filled with coke, reduces the time required for stoppage and restart. However, on that day, upon restart of the kiln rotation, a combustion blast occurred inside the kiln.

3.2.1 Incident Sequence

The event sequence can be summarised as follows:

- Stoppage of the GPC feed,
- Stoppage of the kiln rotation,
 - gradual decrease, complete stoppage after 3 minutes,
- Performance of maintenance,
 - injection of third air and kiln draft were maintained at the same level as during routine operation,
- Kiln rotation was restarted 12 minutes after it was stopped,
 - rotation was rapidly increased from 0 to 2.6 rpm in less than one minute,
 - all other parameters were kept constant,
 - the GPC feed rate was maintained at zero,
- An uncontrolled combustion blast occurred inside the kiln,
 - within 30 seconds following the restart of the kiln rotation,
 - observed by a camera monitoring the kiln interior (Figure 2),
- The consequences of the blast include:
 - fortunately, no injuries and equipment breakage occurred,
 - the pressure target at the GPC feed inlet could not be reached, and
 - access doors to the boiler were open.

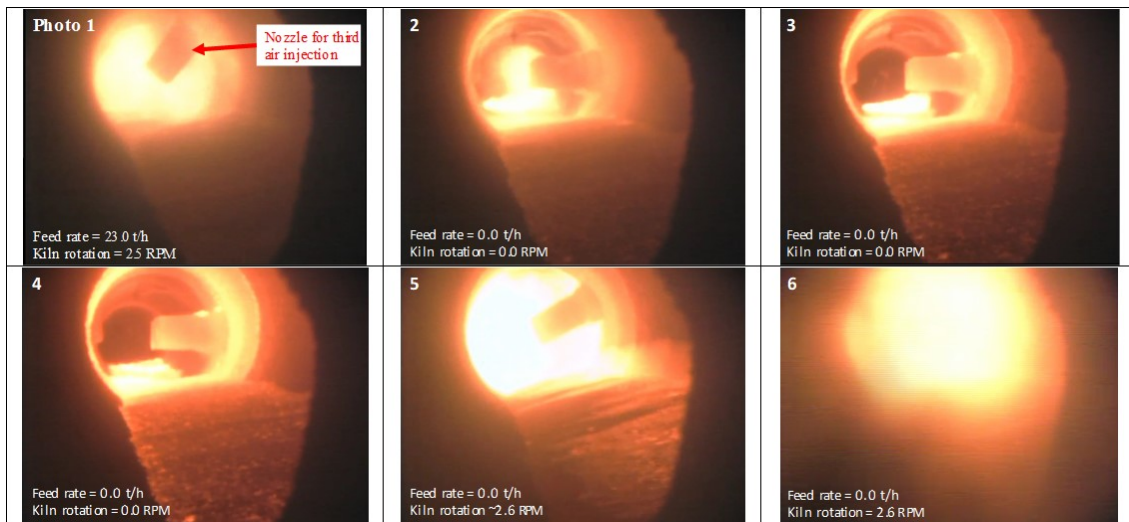


Figure 2. Photos of the kiln interior, taken from the lower end of the kiln, before and during the combustion blast.

3.3 Investigation of the Blast

The investigation was based on the photos of the kiln interior taken before and during the blast, as well as on process data that are routinely recorded (Figure 3 and Table 1). These are discussed below.

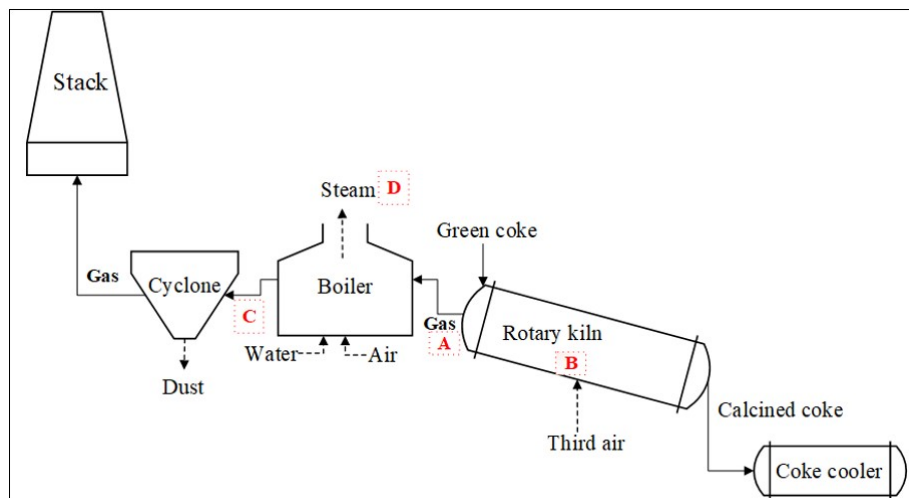


Figure 3. Locations of data measuring points.

Table 1. Process variable variations before and during the combustion blast.

Parameter, measuring point (Figure 3)	Difference to standard operation ^a					
	1	2	3	4	5	6
Photo in Figure 2	1	2	3	4	5	6
Time (min)	-	5	11	15	16	17
Gas temperature, kiln upper end (°C)	A	-5	-37	-98	-115	-124
Coke temperature, centre of kiln (°C)	B	-65	-163	-257	-274	-230
O ₂ concentration at boiler outlet (%)	C	2	11	11	13	10
Boiler steam production (t/h)	D	-10	-30	-29	-26	-19

^a Relative to some 5 min. before kiln rotation was reduced

3.3.1 Kiln Data

Photo 1 in Figure 2 was taken 5 minutes before the kiln rotation was reduced. It is typical for routine operation. The view is from the lower end of the kiln. It shows the most downhill nozzle for third air injection and an intensive flame beginning at the nozzle and extending uphill. The flame indicates combustion of volatiles supported by the injected air.

After kiln rotation was stopped, the intensity of the flame decreased (Photo 2) and finally disappeared close to the nozzle (Photo 3). Instead, there appears to be a flame above the coke bed, further uphill in the kiln. Later, this flame faded. Photo 4 only shows glowing coke in the same kiln section. As the flames died down, temperatures in the kiln dropped (Points A and B in Figure 3).

About 30 seconds after restart of the kiln rotation, corresponding to a complete rotation of the kiln, the combustion blast occurred. It was indicated by intense flames (Photos 5 and 6). Comparing these two photos, it appears that the origin of the blast was upstream of the most downhill nozzle.

The results can be explained as follows. After GPC feed and kiln rotation were stopped, the release of volatiles was significantly reduced. Despite the availability of oxygen through continued third air injection and temperatures high enough for volatiles ignition, combustion could no longer be sustained. However, when kiln rotation started again, volatiles were again released, and combustion restarted.

3.3.2 Boiler Data

In the kiln, roughly half of the released volatiles are burned. The remainder is swept to a boiler where volatiles and entrained coke fines are burned for energy recovery. Air is injected into the boiler to support the combustion. The O₂ concentration is measured at the boiler outlet to allow monitoring of the quantity of excess air (Point C in Figure 3). During kiln rotation stoppage, the air quantity was not modified. Thus, the O₂ concentration is an indirect measure of the fuel quantity burned in the boiler. After stoppage of the kiln rotation, the O₂ concentration strongly increased (Table 1). This indicates that much less volatiles and coke fines were swept from the kiln to the boiler and burned there. The decreased steam production in the boiler (Point D in Figure 3) also indicates a lower transfer of volatiles and coke fines from the kiln to the boiler.

After restart of the kiln rotation, the O₂ concentration slightly decreased, whereas the steam production increased. This suggests that, again, volatiles reached the boiler from the kiln.

3.4 Retention of Volatiles in the Coke Bed During Stoppage of Kiln Rotation

The results from the previous sections (3.3.1 and 3.3.2) clearly indicate that, upon restart of the kiln rotation, volatiles were released. As the GPC feed was still stopped, the volatiles must have originated from the coke that remained in the kiln during the rotation stoppage. This implies retention of some volatiles in the coke bed during the rotation stoppage. Despite some cooling (Table 1), the temperature at the kiln centre remained above 1000 °C. It is therefore surprising that volatiles in the coke bed were not released and swept out the kiln by the continued third air flow. Thus, differences between volatiles release in a rotating and a non-rotating kiln are briefly discussed below.

3.4.1 Volatiles Release in Rotating and Non-rotating Kilns

Green coke at ambient temperature is fed at the upper end of the kiln. Due to the kiln rotation, the coke bed travels downhill. The surfaces of the coke bed are heated by heat transfer from the gas phase (upper surface) and from the inner kiln shell (bottom surface) [5]. Inside the coke bed, heat transfer mainly occurs by movement of the coke particles. In the most uphill section of the kiln, the rotation introduces a circular movement of the coke bed perpendicular to the kiln's length axis (Figure 4). This movement effectively mixes the coke particles in the coke bed, especially since mixing is enhanced by lifters [8]. In the kiln centre (calcination zone), mixing of the coke particles is even more effective. In this region, volatiles are burned. The corresponding heat heats up the coke bed. Large quantities of volatiles are released, which fluidise the coke bed. Quick coke particle movement results in fast heat transfer. Furthermore, the movement of the coke particles facilitates the escape of volatiles from the coke bed and their transfer to the gas phase.

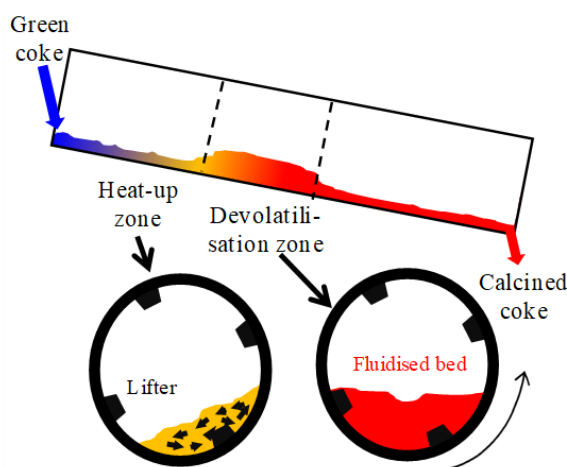


Figure 4. Coke bed in rotating kiln.

As compared to a rotating kiln, heat transfer to and in the coke bed is much slower in a non-rotating kiln. First, in a rotating kiln, an important portion of the heat transfer to the coke bed surface occurs by radiation from the flame [9]. As the flames extinguished after the kiln stoppage (section 3.3.1), this heating mode disappeared. Furthermore, the particles movement in the coke bed ceased. In the most uphill section of the kiln, without kiln rotation, there was no circular movement of the coke bed. In the calcination zone, the coke bed was no longer fluidised (Photos 2 to 4 in Figure 2). Within the stagnant coke bed, heat transfer relied on particle-to-particle transfer, which is much less effective than heat transfer by moving particles. It is therefore reasonable to assume that significant temperature gradients developed in the coke bed. For example, coke particles in contact with the hot inner kiln shell were certainly much hotter than particles in the centre of the coke bed.

Coke volatiles are released over a large temperature range. For example, at a heating rate of some 40 °C/h, volatiles are emitted from ~500 °C to ~1200 °C [10]. When the kiln rotation was stopped, a large portion of the coke remaining in the kiln had not yet reached temperatures above 1200 °C and therefore still contained volatiles. Even at lower temperatures, volatiles are released, albeit at a lower rate. More specifically, the time without kiln rotation (12 minutes) was not long enough to remove all the volatiles remaining in the coke that reached 500 °C (section 3.4.3).

In addition, volatiles released from coke particles might have been trapped in the coke bed. The GPC feed contains up to some 20 % fines, here defined as -0.425 mm material. A large portion of these fines is entrained by the kiln gases [11]. Nevertheless, in uphill sections of the kiln, the coke bed still contains significant concentrations of coke fines. Fines are known to reduce the

permeability of particle beds [12]. This might have resulted in the retention of released volatiles in the coke bed during rotation stoppage.

3.4.2 Volatiles Release upon Restart of Kiln Rotation

Based on the discussion in the previous section, it can be concluded that, just before the restart of the kiln rotation, a portion of the coke in the kiln still contained not-yet-released volatiles. In addition, gaseous volatiles were probably trapped in the coke bed. Finally, there were important temperature gradients within the coke bed. When kiln rotation restarted, the coke bed was again effectively mixed, as shown in the sketch at the bottom of Figure 4 (section 3.4.1). This resulted in intermediate liberation of gaseous volatiles trapped in the bed. Furthermore, mixing of hot and cold coke suddenly increased the temperature of initially cold particles. This was associated with a release of volatiles.

It is reasonable to assume that most volatiles were released from coke which still contained large quantities of not-yet-released volatiles in the coke particles and/or contained trapped gaseous volatiles in the bed. These conditions are met in the uphill portion of the kiln. Furthermore, due to the continued third air injection, there was sufficient air available for the volatiles to react. Photos 5 and 6 in Figure 2 indicate indeed that the blast originated in this region.

Finally, GPC contains coke fines, a large portion of which is entrained by the gas stream in the kiln [11]. The transfer of the fines to the gas phase is favoured by the kiln rotation. Thus, upon restart of the rotation, the contribution of reactive coke fines in the kiln most likely increased, which may have contributed to the blast.

3.4.3 Coke Volatiles Release

In order to measure the residence time of volatiles in coke at elevated temperatures, thermogravimetric analysis (TGA) tests were performed. The objective was to simulate the devolatilisation behaviour of the coke remaining in the in kiln during stoppage of rotation. As discussed in the previous section (3.4.2), the blast apparently occurred in the uphill portion of the kiln. In this zone, the coke is heated from ambient temperature to the maximum temperature of about 1300 °C. Thus, TGA experiments were conducted at an intermediate temperature of 500 °C.

3.4.3.1 Experimental Details

Rio Tinto calcines various GPCs. Representing the property range of these GPCs, in the present study, eight GPCs were studied. All these GPCs are used in the calciner blend. The samples were ground in a coffee grinder to particle sizes smaller than 0.85 mm (20 mesh). The small particle sizes favoured volatiles release and therefore represented the worst-case scenario as compared to coarser GPC particles normally fed into the calciner. For reference, a CPC sample was included in the study as a reference for mass loss that was not related to volatiles release. The samples were placed in crucibles closed with non-gas-tight lids.

The TGA tests were performed using TGA model 701 from Leco (St. Joseph, MI, USA). Some 3 g of the eight GPC samples were heated under a nitrogen atmosphere (10 L/min) as follows:

- Ramp-up (15 °C/min) to 25 °C and keeping this temperature for 25 minutes,
 - replacement of oxygen by nitrogen in the TGA instrument,
- Heat-up at 15 °C/min to 500 °C; keeping the temperature for 6 hours (360 minutes),
 - fast heat-up to a temperature typical for the uphill portion of the kiln,
 - simulating coke devolatilisation,
- Heat-up at 15 °C/min to 1000 °C; keeping the temperature for 60 minutes,

- desorption of residual volatiles from the cokes,
- simulating desorption upon restart of kiln rotation.

The mass loss of the CPC was subtracted from the losses of the CPC samples. This accounted for losses not related to volatiles release, such as oxidation due to air leaks.

3.4.3.2 Results

Upon heating to 500 °C, the GPC samples lost about 1 % of their initial mass (Figure 5). Most of this mass loss can be attributed to the removal of humidity. As GPC is produced at temperatures close to 500 °C [2], it is reasonable to assume that only a small portion of volatiles was lost at temperatures below 500 °C.

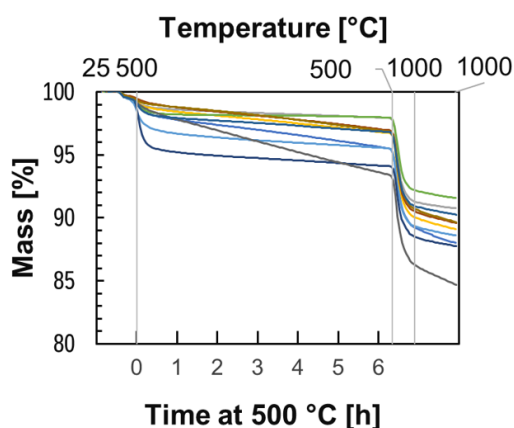


Figure 5. Mass of coke samples upon heating under nitrogen atmosphere.

During the plateau at 500 °C, the samples continued to lose mass. The mass loss rates stabilised after some 20 minutes and then remained, for a given coke, fairly constant. Furthermore, the mass loss rates differed considerably between the different samples. The mass loss at 500 °C is attributed to desorption of volatiles. In another TGA study [13], important differences between volatiles desorption of different cokes were observed, suggesting differences in their chemical nature. Apparently, this was also the case for the coke samples in the present study.

Finally, upon heating from 500 °C to 1000 °C, the cokes still lost considerable quantities of volatiles. This mass loss was especially pronounced in the initial stages of this heating step.

In section 3.4.1, two potential sources were discussed for the volatiles responsible for the blast incident: gaseous volatiles trapped in the coke bed and/or not-yet desorbed volatiles, liberated upon restart of the kiln. The TGA data is consistent with both possibilities. After 12 minutes at 500 °C, on average, some 0.4 % of volatiles were lost (Figure 6). A portion of these gaseous volatiles may have remained trapped in the coke bed. In gaseous state, a concentration of 0.4 % of volatiles in the coke bed remaining in the kiln during the stoppage corresponds to about 25 % of the kiln volume. This is well within the explosion limits.

Upon further soaking at 500 °C, followed by heating to 1000 °C, still on average, some additional 9 % volatiles were lost (Figure 7). A portion of these volatiles might have been suddenly released when the coke at 500 °C was quickly heated. Figures 6 and 7 show the distribution of volatiles losses during different stages of the heating program.

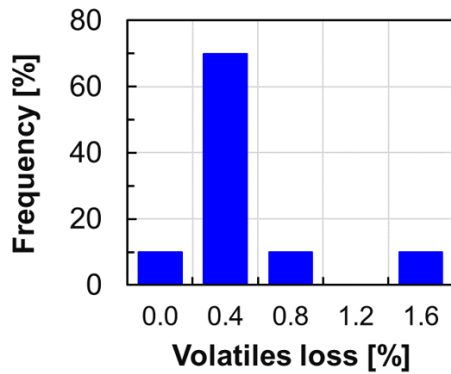


Figure 6. During the first 12 min. at 500 °C.

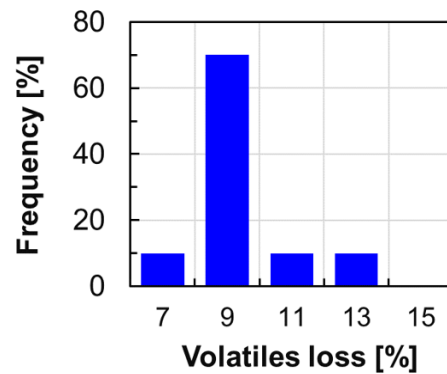


Figure 7. Between after 12 min. at 500 °C and the end of the TGA experiment.

3.4.4 Similar Intervention without Incident

About one week prior to the blast incident, another maintenance intervention was performed. The procedure was similar to that of the intervention that resulted in a blast (section 3.2.1). However, there were also some differences in third air injection and resumption of kiln rotation after maintenance (Table 2).

Table 2. Differences in operation for a maintenance stop without and with a blast.

Parameter	Without blast	With blast
Injection of third air	<ul style="list-style-type: none"> • Stopped before kiln rotation was stopped • Zero during maintenance • Restarted after kiln rotation was resumed 	<ul style="list-style-type: none"> • Maintained at the same level as during routine operation
Resumption of kiln rotation after the maintenance	<ul style="list-style-type: none"> • Moderate <ul style="list-style-type: none"> ○ From 0 to 2.3 rpm in about 6 minutes 	<ul style="list-style-type: none"> • Fast <ul style="list-style-type: none"> ○ From 0 to 2.6 rpm in less than one minute

It is reasonable to assume that, due to these differences, no blast occurred at that time. A reduced pressure was maintained in the kiln during maintenance. Even if no third air was injected, due to the reduced pressure, air may have leaked into the kiln, for example from the hood at the lower end. Upon moderate resumption of the rotation, volatiles were released. However, as compared to the day when the blast event occurred, resumption of the kiln rotation was much slower. Thus, volatiles were also released at a much slower rate. Consequently, their reaction and the associated pressure increase were much less pronounced.

4. Improvements to Operational Procedures

Based on the investigation of the blast event, changes to operational procedures have been made. At the site where the combustion occurred, rotation stoppage of a kiln still filled with coke (full-load stoppage) is no longer permitted. The only exception is an emergency that prevents the kiln from being emptied. For this situation, a new procedure has been defined for a safe restart of operations.

4.1 Injection of Third Air

During a full-load stoppage, the quantity of third air is maintained at the same level as before the stoppage. The intention is to burn off the volatiles which are still released during stoppage. A reduction in air flow was considered to reduce the oxidising atmosphere inside the kiln. However, given the complexity of defining the limits for all the stoppage conditions, this strategy was not adopted.

4.2 Kiln Rotation

Two new elements were integrated into the procedure. First, automated programming now ensures a 90° rotation of the kiln every 5 minutes at a very slow speed of 0.3 rpm. As outlined in section 3.1, this avoids deformation of the kiln. Furthermore, periodic kiln rotation promotes some mixing of the coke bed and reduces temperature gradients in the coke bed. These gradients are believed to have contributed to the sudden volatiles release and, finally, to the blast upon resumption of the kiln rotation.

Secondly, for the resumption of the kiln rotation, only a moderate increase in the rotation rate is now allowed. This progressive start-up ensures that volatiles release, and its associated oxidation, only slowly increases. Ramp-up of the rotation rate takes some 3 minutes. This corresponds to a minimum of 4 rotations from 0.3 to 2.0 rpm. After that, the conditions in the kiln are considered the same as for standard operation.

4.3 Information Exchange with Other Calcination Sites

Information about the incident was shared with other Rio Tinto calcination sites. The newly identified risk has been integrated into their Process Hazard Analysis (PHA). Unlike the production site where the blast occurred, the other sites encounter safety issues due to the presence of slag deposits on the kiln refractories. Complete removal of coke from the kiln results in rapid cooling of the kiln. This favours detachment of slag pieces and blocking by them of the kiln discharge chute. Such blockage occurs require manual interventions that represent an important safety risk for the operators. Comparing the risks of removing and not removing the coke during kiln stoppages, it was decided to allow short stoppages of few minutes at the other calcination sites. The blast risk is addressed by a slow resumption of kiln rotation after the stoppage. Furthermore, operators were made aware of the blast risk.

5. Summary and Conclusions

At a Rio Tinto calciner, a blast occurred after the rotation of a kiln filled with coke was restarted following a stoppage. The investigation identified a previously unknown safety risk. During stoppage of kiln rotation:

- The coke remaining in the kiln still contained volatiles,
 - not-yet-released volatiles in the coke particles and/or
 - gaseous volatiles trapped in the coke bed,
- Their concentration slowly decreased,
 - prior to the restart, the coke bed still contained significant quantities of volatiles,
- The heat transfer inside the coke bed during stoppage was much less effective than with rotation,
 - important temperature gradients developed in the coke bed.

Upon resumption of kiln rotation:

- Cold portions of the coke bed were quickly heated,

- significant quantities of volatiles were released by desorption,
- Movement of the coke bed liberated gaseous volatiles trapped in the bed,
- Likely, coke fines were transferred to the gas phase,
- Fast combustion of the released volatiles and coke fines resulted in the blast.

In order to address this newly identified risk, changes to operation procedures were made:

- At the site where the blast occurred,
 - rotation stoppage of a kiln still filled with coke (full load stoppage) is no longer permitted,
 - if a full-load stoppage cannot be avoided,
 - only a moderate increase of the rotation rate is now allowed,
- At the other sites,
 - Full-load stoppages are still required,
 - only a moderate increase of the rotation rate is allowed, and
 - operators have been made aware of the risks.

6. References

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