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

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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 SO_2 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 Lc [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.
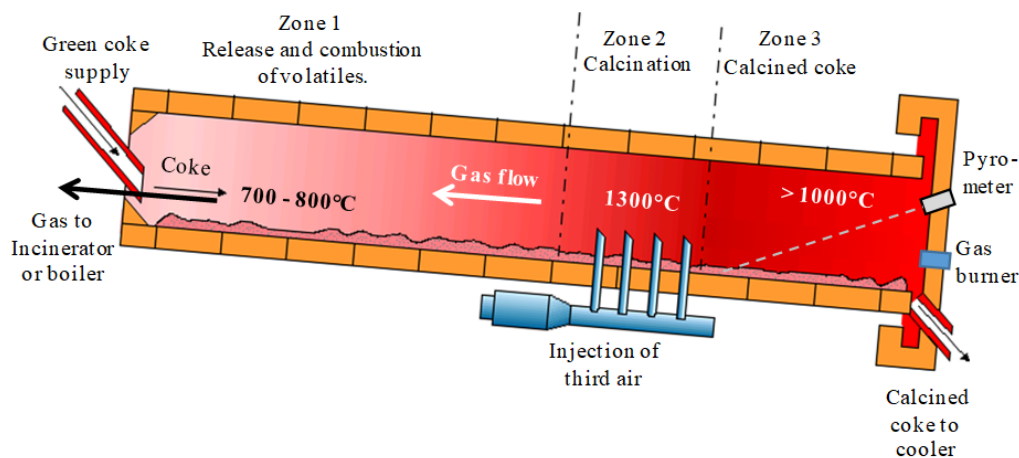

Figure 1. Schematic diagram of a rotary coke calcination kiln.

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.

      o 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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