A Case Study for Emissions Free CPC

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Abstract

For aluminium smelters operating with emissions free power like hydroelectric, nuclear and renewables, the carbon raw materials supply chain accounts for around 15 % of the total smelter CO² footprint. The calcined petroleum coke supply accounts for 85 % with the balance from coal tar pitch. Work aimed at reducing CPC related emissions can have a meaningful impact on the smelter $CO₂$ footprint and this paper provides a review of calciner $CO₂$ emissions including a carbon capture solution.

The two primary contributors to CPC emissions are green petroleum coke (GPC) production (40 %) and calcination (60 %). Rain Carbon (RC) has done a substantial amount of work to quantify calciner process emissions. A key enabler was the development of a method which utilizes online $CO₂$ concentration and flowrate analyzers to quantify emissions in real time. Reducing GPC fines carryover during calcination is a key means of reducing $CO₂$ emissions. The calciner technology, operating conditions and GPC quality also play a key role.

 $CO₂$ capture and storage can be used as a final reduction method. RC has undertaken a detailed capital and operating cost analysis to add a $CO₂$ capture system to its Lake Charles Calciner. The plant is located less than 20 km from a qualified $CO₂$ sequestration site in Louisiana and would qualify for US CO_2 sequestration tax credits. Relative to a smelter, CO_2 can be captured more efficiently at a calciner due to higher $CO₂$ concentrations. The technology exists today to execute a project like this, but the primary challenge is achieving a satisfactory return on investment. Without a price premium for low- $CO₂$ CPC, the investment return remains a major hurdle.

Keywords: Carbon, Anode, CO₂ Capture, Petroleum coke, Decarbonization.

1. Introduction

The amount of work being done around the world to decarbonize the primary aluminium production is growing rapidly. In its 2021 report [1], the International Aluminium Institute makes estimates of the emissions reductions needed by the aluminium industry to help the world achieve a 1.5 °C global warming limit by 2050. Collectively, the industry will need to reduce scope 1-3 emissions from 1.1 billion tonnes in 2020 to 53 million tonnes in 2050 representing a 95 % reduction. Decarbonizing the power supply represents the biggest opportunity but improvements will be required across the entire supply chain. Production of aluminium from recycled scrap will also need to grow to 81 million tonnes to support the 1.5 degree warming limit.

The contributors to scope 1-3 emissions for primary aluminium production have been well documented [2, 3, 4]. In a 2022 study [5], a detailed breakdown was provided for the Alouette primary aluminium smelter which operates with 100 % hydroelectric power. The total scope 1-3 emissions per tonne of aluminium were estimated at 3914 kg CO₂. Smelter direct emissions from anode consumption, fluoride emissions, anode baking and casting represented 47 % of the total and the alumina supply chain contributed 35 %. The next largest contributor was scope 3 emissions related to production of carbon raw materials used for anode production – calcined petroleum coke (CPC) and coal tar pitch (CTP). The paper provided a further breakdown that showed ~85 % of the carbon raw material emissions were due to CPC and GPC (green petroleum coke) production.

The purpose of this paper is to provide a more detailed review of the contributors to $CO₂$ emissions for CPC production. As more researchers undertake detailed $CO₂$ footprint studies, the need for reliable data on scope 3 emissions is increasing. Aluminium smelters making estimates of their scope 1-3 emissions are now turning to raw material suppliers to help provide this data. A recent paper [6] provided the first detailed product carbon footprint analysis of graphitized cathode blocks and this is a good example of the sort of data needed by aluminium smelters.

Rain Carbon (RC) operates six calcining plants in the US and two in India and has studied CO₂ emissions in detail to look for reduction opportunities. In 2022, RC started to investigate online measurement of $CO₂$ emissions for comparison against emissions calculated using a mass balance approach. The results of some of these studies will be presented in this paper. Carbon capture remains the only way to substantially reduce ($> 90\%$) calciner CO₂ emissions and the technology is available today, albeit at high capital and operating costs.

2. Review of Calciner Emissions

An overview of the calcining process and GPC production is provided in a 2015 review paper [7]. The primary goal of calcination is to remove volatile matter (VM) from GPC which is typically at levels of 9–13 %. At normal calcining temperatures (1250–1350 °C), the VM level is reduced to < 0.2 % in CPC. The VM level and composition varies by coke type, but all GPC contains carbon, hydrogen, nitrogen, oxygen, sulphur, and trace metals like vanadium and nickel. Table 1 shows some typical ranges for C, H, N, and S in GPC and CPC. Oxygen levels are not measured directly but calculated by subtracting the sum of C, H, N, S and ash levels from 100 %. The table also shows the average change in C, H, N, and S levels from GPC to CPC for a wide range of samples.

			% Change
	$GPC\%$	$CPC\%$	GPC to CPC
Carbon	86–92	$92 - 97$	$+6.5$
Hydrogen	$3.4 - 4.4$	${}_{0.2}$	- 98
Nitrogen	$1.3 - 2.5$	$0.8 - 1.5$	- 38
Sulfur	$0.3 - 6.5$	$0.3 - 5.7$	-10

Table 1. Typical ranges for GPC and CPC

A detailed description of the chemical species generated during VM loss has been described previously [8] but the condensable tars, methane and hydrogen evolved are eventually combusted to form $CO₂$ and $H₂O$ in the kiln and pyroscrubber. As shown in Table 1, nearly all the hydrogen in GPC is lost during calcination. Some sulphur is also lost [9] and the amount varies as a function of the GPC S level and temperature and is typically 7–8 % for low S cokes and up to \sim 15 % for high S cokes ($> 5\%$ S). The loss of nitrogen and oxygen varies by coke type but is significantly lower than the loss of H.

Most calciners operate with strict emission limits for $SO₂$ and many also have NOx emission limits. At RC, five of eight calcining plants use SO_2 scrubbers to reduce SO_2 to permitted levels. The extent of SO_2 removal varies by plant and depends on the permit limit and the sulphur level required to achieve target real densities. This will be eliminated once rates exceed \sim 85 % of the design level.

Calciners that operate with a higher yield of CPC per tonne of GPC have lower $CO₂$ emissions and changes that reduce GPC fines carryover have a positive benefit on reducing $CO₂$ and $SO₂$ emissions. WHR in combination with $SO₂$ scrubbing has a significant benefit for society in reducing SO_2 emissions and net CO_2 emissions. Calciners that operate with these systems offer a more sustainable solution for production of CPC.

Carbon capture technology offers the potential to substantially eliminate calciner $CO₂$ emissions and is both proven and available today. The paper presents a case study for a carbon capture option at the Lake Charles calciner which could be fully powered by the WHR system. The technology comes with a high capital and operating cost however and would not be feasible without a significant price premium for a low $CO₂$ CPC product.

The other long-term option which would eliminate CPC emissions and all smelter related anode emissions is inert anode technology. It is not clear if this will ever be successfully developed and implemented however, and the broader industry must continue to work on all options to reduce supply chain emissions.

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8. References

- 1. Aluminium sector greenhouse gas pathways to 2050, International Aluminium Institute, September 2021, https://international-aluminium.org/resource/aluminium-sectorgreenhouse-gas-pathways-to-2050-2021/
- 2. Angxing Shen and Jihong Zhang, Technologies for CO_2 emission reduction and low-carbon development in primary aluminum industry in China, *Renewable and Sustainable Energy Reviews,* 189, 2024, 1-17.
- 3. Halvor Kvande, Gudrun Saevarsdottir and Barry Welch, Decarbonizing the aluminium industry – opportunities and challenges, *Light Metal Age*, February 2023, 38-45.
- 4. Gudrun Saevarsdottir, Thordur Magnusson, and Halvor Kvande, Reducing the carbon footprint: primary production of aluminum and silicon with changing energy systems, *Journal of Sustainable Metallurgy*, Vol 7, August 31 2021, 848-857 DOI: https://link.springer.com/article/10.1007/s40831-021-00429-0
- 5. Les Edwards et al., Quantifying the carbon footprint of the Alouette primary aluminum smelter, *Journal of Metals*, Vol 74, 27 September 2022, 4909-4919 DOI: https://link.springer.com/article/10.1007/s11837-022-05501-y
- 6. T. Carrère, B. Allard and T. Reek, Cradle-to-gate carbon footprint assessment of graphite cathode used for aluminium electrolysis pots, *Light Metals* 2024, 671-678.
- 7. Les Edwards, The history and future challenges of calcined petroleum coke production and use in aluminum smelting, *Journal of Metals*, Vol 67, 20 December 2014, 308-321 DOI: 10.1007/s11837-014-1248-9
- 8. Duygu Kocaefe, André Charette, and Lise Castonguay, Green coke pyrolysis: investigation of simultaneous changes in gas and solid phases, *Fuel*, Vol 74, No. 6, 1995, 791-799.
- 9. Les Charles Edwards, Keith J Neyrey, Lorentz Petter Lossius, A review of coke and anode desulfurization, *Light Metals* 2007, 881-886.
- 10. Les Edwards, Quality and process performance of rotary kiln and shaft calciners, *Light Metals*, 2011, 895–900.
- 11. Qian Yao et al., Investigation of NOx Emission under different burner structures with the optimized combustion model, *Neurocomputing*, Vol 482, 14 April 2022, 224 – 235.
- 12. Hans Darmstadt et al., Estimation of the coke calcination yield by granulometry analysis, *Light Metals*, 2024, 822-827.
- 13. Lei Zhao and Ting Wang, Simulation of char dust combustion inside a pyroscrubber downstream of a petroleum coke calcining plant, *Journal of Thermal Science and Engineering Applications*, March 2012, Vol. 4.
- 14. Les Edwards et al., Sustainable CPC production at the Vizag calciner, *Proceedings of the 38th International ICSOBA Conference*, 16-18 November, 2020, Paper CB05, *TRAVAUX* 49, 525-535.
- 15. Entergy renewable energy projects in service or in development as of April 2024, https://www.entergy.com/renewable-energy/
- 16. Sewa Bhawan and R.K. Puram, CO₂ baseline data for the Indian power sector, December 2022, Government of India, Ministry of Power, Central Electricity Authority
- 17. Emission Factors for Greenhouse Gas Inventories, EPA Center for Corporate Climate Leadership, June 2024 https://www.epa.gov/climateleadership/ghg-emission-factors-hub
- 18. Yutaka Tanaka et al., Tomakomai CCS demonstration project of Japan, CO2 injection in process, *Energy Procedia,* 114, 2017, 583-5846.