Carbon Monoxide Emissions from Electrolysis Process in EGA Smelters

Mohammad Al Jawi[1], Eiman Al Obaidli[2], Ramanathan Natesan[3], Shane Pollé[4], Mohamed Mahmoud[5], Kindle Williams[6], Alexis Fenton[6] and Albert Wu[6]

1. Senior Manager – Environment & Waste Management
2. General Superintendent - Environment
3. Supervisor Environment & Waste Management
4. Manager – Cell Lining and Environment Control
5. Manager – Centre of Excellence

Emirates Global Aluminium (EGA), Abu Dhabi, United Arab Emirates

6. Students, David H. Koch School of Chemical Engineering Practice, MIT

Corresponding author: maljawi@ega.ae

Abstract

Carbon monoxide (CO) is generated in the aluminium reduction process mainly by back reaction, leading to current efficiency loss. CO is also generated by the Boudouard reaction or so-called CO_2 burn of the anodes. These two reactions occur under the anode cover and crust. It has been most often assumed that the CO burns in the air nearly completely as soon as it emerges from below the crust and that the CO emissions from the potrooms and the gas treatment centres (GTCs) are negligible. However, measurements in EGA, which were set up to follow UAE Environment regulations, show that the CO emissions from the GTCs are typically from 800 to 1200 mg/Nm^3 (approximately 53 to 76 kg/t Al), which are well above the UAE Environment limit of 500 mg/Nm^3. This limit was set up on the basis of combustion processes, which can effectively control CO emissions; however, the ability for aluminium electrolysis processes to control CO emissions is much less understood. A three-part kinetic model was developed which accounts for chemistry in the bath, anode pores, and gas above bath, to better understand the reactions at hand. It is shown in the paper that the measured CO emissions can be understood from theory and cannot be decreased without significant changes to the current configuration of the smelting process. The CO measurement technique and equipment are also described.

Keywords: CO generation in aluminium electrolysis, CO emissions, back reaction, current efficiency loss, Boudouard reaction.

1. Introduction

Aluminium is produced through the Hall-Héroult process, in which aluminium is electrochemically reduced from alumina in a cryolite bath. Within this bath, the alumina is dissolved and aluminium ions migrate to the cathode, where they are reduced to molten aluminium metal. Oxygen (O_2) from alumina reacts with the consumable carbon anodes to form carbon dioxide (CO_2). In parallel, back reaction occurs according to Equation (1) in Section 2.1, to form carbon monoxide (CO). Various other reactions produce gaseous side products such as CO, hydrofluoric acid (HF), perfluorocarbons (PFCs), and sulphur dioxide (SO_2).

CO_2, CO (indirectly), and PFCs are contributors to climate change as greenhouse gases. Among these, CO is also toxic to humans, but this is of no concern in open areas such as smelters because its concentration is very low for the amounts emitted by the stack. CO is generated both by back reaction of aluminium with CO_2 occurring in the bath and by the Boudouard reaction occurring under the anode cover and crust. It has usually been assumed that whatever CO is generated under the anode cover completely combusts in the air under the hood and, consequently, that the CO emissions from the Hall-Héroult process are negligible. However, measurements made by EGA, required by UAE Environment regulations, show that CO emissions range typically from 800 to 1200 mg/Nm^3, starkly disagreeing with conventional understanding of CO emissions from aluminium smelting. EGA CO measurements are shown in Figure 1. Given this large discrepancy between experimental values and conventional understanding, we set out to gain better understanding of CO emissions generated in aluminium smelting and emitted to the atmosphere. After employing a third-party assessment of CO emissions in the aluminium industry, it was found that no other aluminium smelter worldwide has attempted to manage their CO emissions, nor has any other governmental agency instituted CO regulations for smelters. Given this, we set out to fundamentally understand the factors that contribute to CO emissions and the theoretical and realistic level of CO emissions from aluminium smelting.

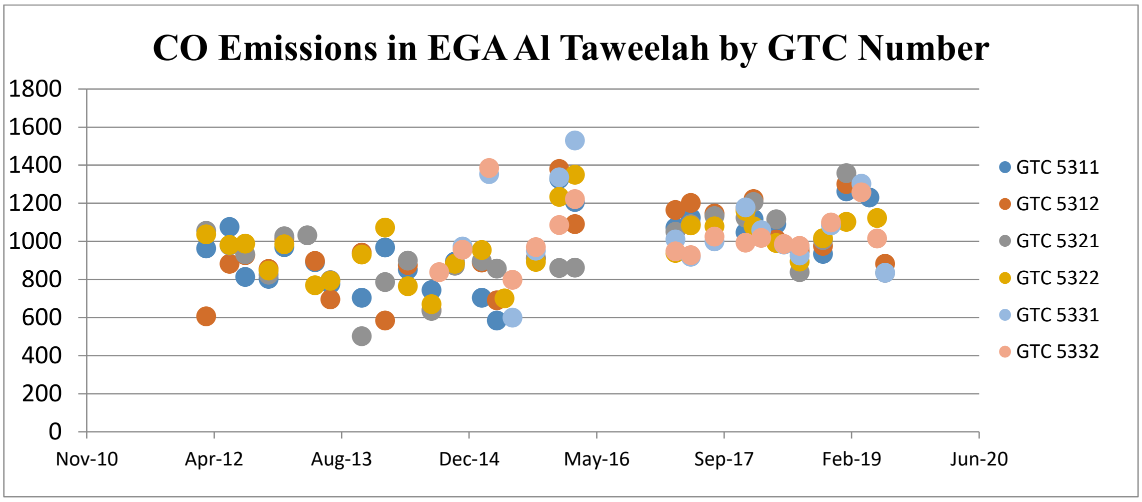

Figure 1. CO emissions measurements in EGA Al Taweelah

Our efforts resulted in a three-part kinetic model that fundamentally explains the generation of CO in the bath and the anode pores, as well as its consumption in the gas space above the bath. The results of this model are in agreement with measured values, providing insight into the nature of CO emissions and demonstrating that, unfortunately, these emissions cannot be decreased without significant changes to the current configuration of the smelting process. As such, we believe that this model is a first step towards better understanding of CO emissions in aluminium smelters.

This work is the result of collaboration between EGA and Massachusetts Institute of Technology (MIT), David H. Koch School of Chemical Engineering Practice wherein a team of three MIT students spent one month at EGA to work on the project of CO emissions.

2. Methodology

The kinetic model, constructed in MATLAB, was divided into three modules: the electrolyte bath, the porous anode, and the "above-bath" space. These divisions capture the regimes where the physics are most distinct from one another. In a first-pass approach to the model, many simplifying assumptions were made within each of these modules, which were relaxed when possible. The priority when developing the model was to estimate the minimum CO emissions that might reasonably be expected of an aluminium cell. As such, the simplifying assumptions made in the development of the model were each selected so that the exiting CO concentration was underestimated.

be expected and can be explained by the major reactions occurring within the model smelting pots.

5. Conclusions

A kinetic model accounting for reactions in an aluminium electrolysis cell was developed, with particular attention to the emission of CO from the process. The three-part model accounts for reactions in the electrolyte bath, inside the pores of the anodes, and in the gas above the bath. Many assumptions went into the generation of this model; these are partially documented in this report. It was determined that a range of ambient air conditions (e.g., 40 - 80 % relative humidity and 20-40 °C) corresponded to the measured emissions of 800 – 1200 mg CO/Nm^3. Therefore, the primary recommendation is process validation of the amount of water available to react with CO, along with further model refinement as the kinetics of reactions involving water inside the hood are investigated. Through a sensitivity analysis of model parameters, it was found that the model was most sensitive to bath temperature and composition, current, and the relative humidity and temperature of ambient air. The smelting operation parameters are optimised for best pot performance and cannot be manipulated for reducing CO emissions, while the relative humidity and temperature of the ambient air around most smelters cannot be controlled. With additional model validation and further refinement, it is likely that the cell model developed herein will be a useful tool for understanding the CO emissions from aluminium smelters.

6. Acknowledgements

We would like to thank the teams at EGA and MIT for taking the time to provide all necessary information. In particular, we would like to thank Vinko Potocnik for very helpful and informative discussions and the EGA modelling team, Alexander Arkhipov, Ievgen Necheporenko, and Alexander Mukhanov, for providing CFD model set up, parameters, and results for our validation. We would also like to thank Dr. Mohamed Mahmoud, Muhammad Aqeel, Omar AlMheiri, and Satish Ranjalkar for the large amount of work done to coordinate the station of MIT students at EGA and ensure the necessary resources to pursue this project were provided. Lastly, we would like to thank the external professionals contacted, Asbjørn Solheim, Prof. Donald Sadoway, and Dr. Alton Tabereaux, for their insight into the current state of the smelting literature.

The group would also like to thank the station director, Dr. Brian Stutts, for his mentorship, as well as everyone on the MIT Practice School team for their support and encouragement.

7. References

1. http://www.aluminum-production.com/current_efficiency.html, retrieved on 19 July 2019.
2. Ruth A. Roberts and Phillip J. Ramsey, Evaluation of fluorocarbon emissions from the aluminum smelting process, *Light Metals* 1994, 1007-1014.
3. Barry Welch, Controlling laws – part 2: Mass and energy balance, *The University of Auckland - Postgraduate Certificate in Light Metals Reduction*, 2016.
4. Richard S. Brokaw, Ignition kinetics of carbon monoxide-oxygen reaction, *NASA Technical Note*, Washington, D.C., 1966.
5. Ievgen Necheporenko, EGA internal communication - CFD results of aluminium electrolysis pots, Dubai, UAE, 2017.
6. Asbjørn Solheim, personal correspondence, 2017.
7. Donald Sadoway, personal correspondence, 2017.

8. Asbjørn Solheim et al., Current efficiency in laboratory aluminium cells, *Proceedings of 33rd International ICSOBA Conference*, 29 November – 1 December 2015, Dubai, UAE, Paper AL14, *Travaux* 44, 625-634.
9. Warren E. Haupin, Electrochemistry of the Hall-Heroult process for aluminum smelting, Journal of Chemical Education, Vol. 60, No. 4, (1983), 279-282.
10. Karthish Manthiram, personal communication, 2017.
11. Alton Tabereaux, personal correspondence, 2017.
12. Mark M. R. Dorreen et al., Influence of heat transfer on anode reactions when electrowinning metal from its oxides dissolved in molten fluorides, *Journal of the Electrochemical Society*, Vol. 164, No. 8, (2017), H5108-H5118.
13. Geir Martin Haarberg, Effects of electrolyte impurities on the current efficiency during aluminium electrolysis, *Proceedings of 33rd International ICSOBA Conference*, 29 November – 1 December 2015, Dubai, UAE, Paper AL27, *Travaux* 44, 761-767.
14. Per A. Solli et al., A laboratory study of current efficiency in cryolitic melts, *Light Metals* 1994, 195-203.
15. Shiva Prasad, Studies on the Hall-Heroult aluminum electrowinning process, *Journal of the Brazilian Chemical Society*, Vol. 11, No. 3, (2000), 245-251.
16. Barry Welch, Martin Iffert and M. Skyllas-Kazacos, Applying fundamental data to reduce the carbon dioxide footprint of aluminum smelters, *JOM*, Vol. 60, No. 11, 2008, 17-24.
17. Troy Lee Hudson, Growth, diffusion, and loss of subsurface ice on Mars: experiments and models, *CalTech Thesis*, (2008), 16-28.
18. Barry A. Sadler and S. H. Algie, A porosimetric study of sub-surface carboxy oxidation in anodes, *Light Metals*, (1991), 594-605.
19. Stein Rørvik and Lorentz Petter Lossius, Measurement of tortuosity of anode porosity by 3D micro x-ray computed tomography, *Proceedings of 35th International ICSOBA Conference*, Hamburg, Germany, 2017, Paper CB13, *Travaux* 46, 757-766.
20. Khalil Khaji and Mohammed Al Qassimi, The role of anode manufacturing processes in net carbon consumption, *Metals*, Vol. 6, No. 128, (2016).
21. Uthaiporn Suriyapraphadilok et al., Anode butt cores: physical characterization and reactivity measurements, *JOM*, Vol. 57, No. 35, (2005), 35-41.
22. F. Chevarin et al., Characterization of carbon anode constituents under CO_2 gasification: a try to understand the dusting phenomenon, *Fuel*, Vol. 156, (2015), 198-210.
23. Alexander Arkhipov, EGA internal data, 2017.
24. Chao'en Li and Trevor C. Brown, Carbon oxidation kinetics from evolved carbon oxide analysis during temperature-programmed oxidation, *Carbon*, Vol. 39, (2001), 725-732.
25. NIST, *NIST-JANAF thermochemical tables*, Available at: http://kinetics.nist.gov/janaf/.
26. Juan Li et al., A comprehensive kinetic mechanism for CO, CH2O, and CH3OH combustion, *International Journal of Chemical Kinetics*, Vol. 39, No. 3, (2007), 109-136.
27. R. A. Yetter, F. L. Dryer and H. Rabitz, A comprehensive reaction mechanism for carbon monoxide/hydrogen/oxygen kinetics, *Combustion Science and Technology*, Vol. 79, (1991), 97-128.