Peertechz

Annals of Environmental Science and Toxicology

submitpaper@peertechz.com

LIFE SCIENCES GROUP

ISSN: 2641-2969 DOI: https://dx.doi.org/10.17352/aest

Short Communication

Thermodynamic Analysis of Ca-Mg-Al-based Refractory Resistance to Na_2CO_3 Corrosion

Zheng Quanjun[1], Zhang Qiushi[2], Dong Changqing[2]*, Hu Xiaoying[2] and WU Huiyu[2]

[1]Beijing Aerospace Petrochemical EC and EP Technology Co. Ltd., Beijing 100176, China

[2]North China Electric Power University, Beijing 102206, China

Received: 28 May, 2025
Accepted: 04 June, 2025
Published: 05 June, 2025

***Corresponding author:** Dong Changqing, North China Electric Power University, Beijing 102206, China, E-mail: cqdong1@163.com

Keywords: Refractory materials; Na_2CO_3; Corrosion; FactSage

Abstract

Papermaking black liquor contains Na_2CO_3, which can corrode refractory materials and cause economic losses. It is considered to introduce CaO and MgO alkaline oxides into Al_2O_3 to prepare calcium magnesium aluminum composite oxides as a substitute for Al_2O_3 as corrosion shell materials. Using the FactSage material balance module, the optimal ratio of CaO-MgO-Al_2O_3 was calculated, and it was found that the Gibbs free energy of $C_2M_2A_{14}$ reacting with Na_2CO_3 at 800-1200 ℃ was positive. $C_2M_2A_{14}$ was selected as the optimal ratio of calcium-magnesium aluminum composite oxide to resist Na_2CO_3.

The alkali recovery method for treating papermaking black liquor can recycle Na_2CO_3, realizing the reuse of resources [1-4]. When burning in the furnace, sodium salts will adhere to the surface of the refractory materials, and undergo cladding and penetration, causing corrosion and spalling of the refractory materials [5-7]. Al_2O_3 has stable performance and has high hardness and strength. SiO_2 has strong resistance to molten slag erosion, and MgO has the characteristic of resistance to alkali molten slag erosion [8-10]. FactSage can be used for the simulation and calculation of corrosion reactions of refractory materials and molten salts [11,12]. This paper focuses on the research of the corrosion resistance of Ca-Mg-Al-based materials against Na_2CO_3.

The corrosion and penetration mechanism of Na_2CO_3

The vapor of Na_2CO_3 in the alkali recovery furnace at 1200 °C penetrates the pores of the refractory material, resulting in the loss and thinning. The vapor of Na_2CO_3 reacts with the refractory material to form new products, and the thermal expansion and contraction properties of these new products are different from those of the original refractory material. This leads to changes in the internal stress, causing cracks to appear [13,14], as shown in Figure 1.

Thermodynamic Simulation of the Reaction between Na_2CO_3 and Al_2O_3/SiO_2/ MgO/CaO

As shown in Figure 2, the Gibbs free energy of the reactions between Al_2O_3, SiO_2, and Na_2CO_3 is negative. In contrast, the Gibbs free energy of the reactions between

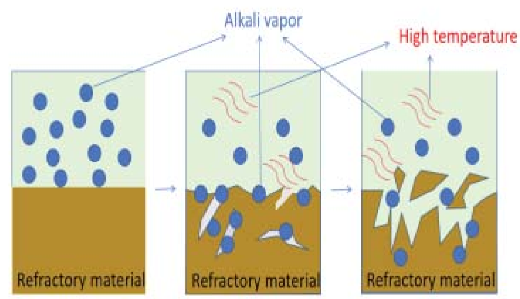

Figure 1: Schematic diagram of the corrosion principle of refractory materials.

Citation: Quanjun Z, Qiushi Z, Changqing D, Xiaoying H, Huiyu WU. Thermodynamic Analysis of Ca-Mg-Al-based Refractory Resistance to Na_2CO_3 Corrosion. Ann Environ Sci Toxicol. 2025;9(1):027-029. Available from: https://dx.doi.org/10.17352/aest.000087

MgO, CaO, and Na_2CO_3 is positive. Use the FactSage 7.3 software, select the databases of Fact PS, FToxid, and FTsalt, and perform the calculation assuming a pressure of one atmosphere, it is found that for the reaction between Al_2O_3 and Na_2CO_3, the reaction intensifies as the temperature rises. At 800 °C, approximately 99.9% of Al_2O_3 is converted into $NaAlO_2$. At 1200 °C, there is a tendency for approximately 98.6% of $NaAlO_2$ to transform into $Na_2Al_{12}O_{19}$. Under the same reaction conditions, approximately 99.9% of the SiO_2 is converted into Na_2SiO_3.

Simulation of calcium-magnesium-aluminum composite oxide

Simulation and screening of composite oxides: In Figure 3, the substances generated by different ratios of $MgO/Al_2O_3/CaO$ at different temperatures are $Ca_3MgAl_4O_{10}$, $CaMg_2Al_{16}O_{27}$, and $Ca_2Mg_2Al_{28}O_{46}$, all of which are derived from the magnetoplumbite crystal structure of $CaAl_{12}O_{19}$ [14]. $Ca_2Mg_2Al_{28}O_{46}$ is a high-melting-point compound in the sub-solid phase of the Al_2O_3-rich part of the Al_2O_3-MgO-CaO ternary system. The solid solution effect of Mg^{2+} promotes the growth of the crystal along the c-axis direction, and the crystals exhibit hexagonal plate-like and hexagonal prismatic morphologies respectively. Its reaction products with Na_2CO_3 under air and water vapor conditions are mainly CO_2, $Na_2Al_{12}O_{19}$(s), $Na_2Ca_3Al_{16}O_{28}$(s), $NaAlO_2$(s) and NaOH(g).

The influence of oxide additives on the properties of refractory materials: As shown in Figure 4, at a temperature range of 800-1200 °C, when $Ca_2Mg_2Al_{28}O_{46}$ is added with CuO and reacts with Na_2CO_3, the Gibbs free energy is positive. This is because after the addition of CuO, the Gibbs free energy required for the reaction between $Ca_2Mg_2Al_{28}O_{46}$ and Na_2CO_3 to form other products increases. When $Ca_2Mg_2Al_{28}O_{46}$ is added with Fe_2O_3, MnO_2, TiO_2 and reacts with Na_2CO_3, the Gibbs free energy is negative. Therefore, when choosing additives for $Ca_2Mg_2Al_{28}O_{46}$, CuO can be selected.

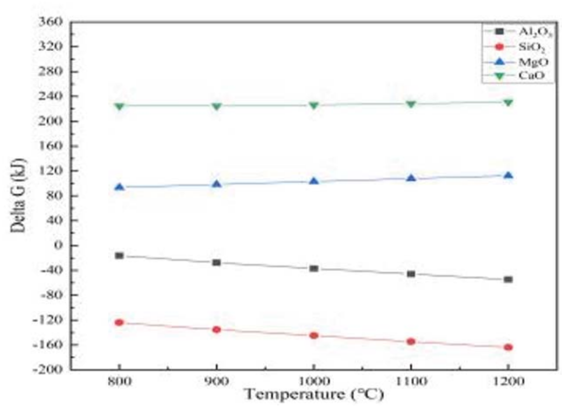

Figure 2: Gibbs free energy of the reaction between Na_2CO_3 and four kinds of refractory materials.

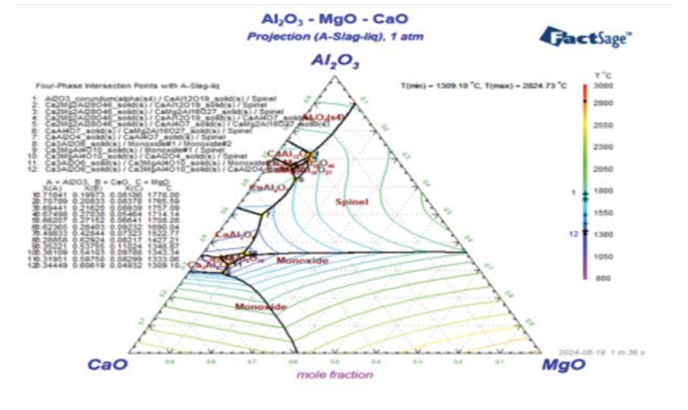

Figure 3: High-temperature Ternary Phase Diagram of MgO-Al_2O_3-CaO.

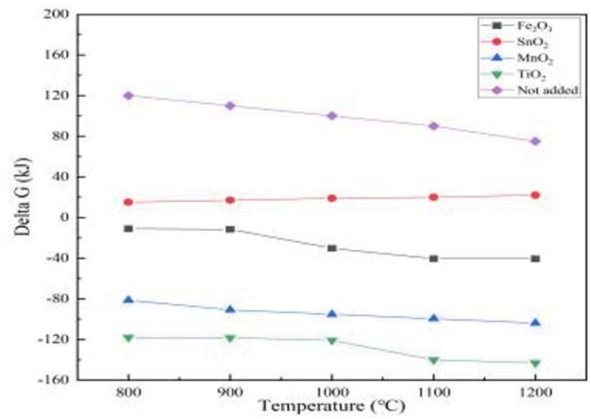

Figure 4: Effect of Additives on the Gibbs free energy of the Reaction between $Ca_2Mg_2Al_{28}O_{46}$ and Na_2CO_3.

Conclusion

According to the simulation calculation, the calcium-magnesium-aluminum composite oxide $Ca_2Mg_2Al_{28}O_{46}$ has the best resistance effect against Na_2CO_3. When the additive CuO is added, the Gibbs free energy of the reaction with Na_2CO_3 is positive. Therefore, CuO can be selected as the additive for $Ca_2Mg_2Al_{28}O_{46}$ to enhance the performance of the material.

References

1. China paper newsletters. 2023 Annual Report of China's Paper Industry. China Pap Newslett. 2024;14(05):6-11.
2. Mo HT, Zhang XY, Xiao CU. A clean and high value utilisation method for the preparation of xanthic acid and fertiliser from black liquor of papermaking [patent]. China patent CN102532204A. 2012 Jul 4.
3. Liu XM, Zhang JY, Zhang B. Study on the Composition and Evaporation Characteristics of Pulping Black Liquor. Trans China Pulp Pap. 2018;33(2):35-39.
4. Sun SJ. Emphasis on the use of biomass energy in pulp and paper production. China Pap Newslett. 2010;(12):11-12.
5. Liu DQ, Li HM, Li H. Effect of SiO_2 in modified pulp black liquor on high temperature stability of refractories. J Xinyang Norm Univ Nat Sci Ed. 2000;13(6):442-445.

Citation: Quanjun Z, Qiushi Z, Changqing D, Xiaoying H, Huiyu WU. Thermodynamic Analysis of Ca-Mg-Al-based Refractory Resistance to Na_2CO_3 Corrosion. Ann Environ Sci Toxicol. 2025;9(1):027-029. Available from: https://dx.doi.org/10.17352/aest.000087

6. Enestam S, Bankiewicz D, Tuiremo J, Mäkelä K, Hupa M. Are NaCl and KCl equally corrosive on superheater materials of steam boilers. Fuel. 2013;104:294-306. Available from: https://doi.org/10.1016/j.fuel.2012.07.020

7. Wang S, Guo OH, Yan G, Liao S, Bao L, Yu G. Corrosion in high alumina refractory serviced in a bench-scale entrained flow gasifier. Ceram Int. 2021;47:2214-2221. Available from: http://dx.doi.org/10.1016/j.ceramint.2020.09.061

8. Fu LP, Gu HZ, Huang A. Enhanced corrosion resistance through the introduction of fine pores: Role of nano-sized intracrystalline pores. Corros Sci. 2019;161:108-182.

9. Zhang YK, Sun L, Yun L, Ma W, Li Z. Corrosion behavior of carbon, Al_2O_3, and MgO refractories during the preparation of a Ti-Si-Al alloy via the aluminothermic reduction of a Ti-bearing blast-furnace slag. Ceram Int. 2021;47(13):18044-18052. Available from: https://doi.org/10.1016/j.ceramint.2021.03.120

10. Zhang WX, Huang A, Zou YS, Gu H, Fu L, Li G. Corrosion modeling of magnesia aggregates in contact with CaO-MgO-SiO_2 slags. J Am Ceram Soc. 2020;103:2128-2136. Available from: http://dx.doi.org/10.1111/jace.16841

11. Ohmk MK, Park JH. Effect of fluorspar on the interfacial reaction between electric arc furnace slag and magnesia refractory: Competitive corrosion-protection mechanism of layer. Ceram Int. 2021;47(14):20387-20398. Available from: http://dx.doi.org/10.1016/j.ceramint.2021.04.047

12. Jung IH, Decterov SA, Pelton AD. Critical thermodynamic evaluation and optimization of the MgO-Al_2O_3, CaO-MgO-Al_2O_3, and MgO-Al_2O_3-SiO_2 systems. J Phase Equilib Diffus. 2005;25(4):313-333.

13. Zhou L, Zhao HF, Jiang H. Refractory Erosion by High Aluminum Silicate Glass. J Mater Sci Eng. 2016;34(4):634-637. Available from: https://doi.org/10.14136/j.cnki.issn1673-2812.2016.04.025

14. Domínguez C, Chevalier J, Torrecillas R, Fantozzi G. Microstructure development in calcium hexaluminate. J Eur Ceram Soc. 2001;21(3):381-387. Available from: https://doi.org/10.1016/S0955-2219(00)00143-6

Citation: Quanjun Z, Qiushi Z, Changqing D, Xiaoying H, Huiyu WU. Thermodynamic Analysis of Ca-Mg-Al-based Refractory Resistance to Na_2CO_3 Corrosion. Ann Environ Sci Toxicol. 2025;9(1):027-029. Available from: https://dx.doi.org/10.17352/aest.000087