

Ultra-Net Emission and Solid Waste Transfer of Air Pollutants in Steel, Power and Cement Industries

—The Idea of Construction and Key Technology of Denitration Engineering Transformation and By-Product Formation

Weiling Chu¹, Linling Wu¹, Jing Yuan^{2,3*}, Qianfeng Zhang^{1*}

¹Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, China

²Department of Civil Engineering, Tongling University, Tongling, China

³Department of Civil Engineering, Manitoba University, Winnipeg, Canada

Email: 3293711510@qq.com, 1427736536@qq.com, *154427@tlu.edu.cn, *zhangqf@ahut.edu.cn

How to cite this paper: Chu, W.L., Wu, L.L., Yuan, J. and Zhang, Q.F. (2024) Ultra-Net Emission and Solid Waste Transfer of Air Pollutants in Steel, Power and Cement Industries. *Journal of Environmental Protection*, 15, 995-1005.

<https://doi.org/10.4236/jep.2024.1511058>

Received: October 9, 2024

Accepted: November 8, 2024

Published: November 11, 2024

Copyright © 2024 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

In this paper, an integrated desulfurization and denitrification technology is proposed for ultra-low emissions of SO₂ and NO_x in the steel, power and cement industries. A cost-effective and operationally efficient control strategy is realized through a forced oxidation-absorption-reduction process, which reduces equipment investment and operating costs. The technology was adapted to continuous and intermittent denitrification in different temperature zones, promoting the recycling of desulfurization and denitrification products. The study also explored the use of a highly active absorbent obtained by the hydration reaction of coal ash and lime from a power company for the desulfurization and denitrification of sintered flue gases in iron and steel mills, which produces by-products that can be used as retarding agents in the cement industry, resulting in a circular economy. The article emphasizes the importance of improving the lime digestion process and developing new denitrification agents for environmentally safe and cost-effective flue gas treatment.

Keywords

Air Pollution, Denitration Engineering, Ultra-Net Emissions, Solid Waste Transfer

1. Introduction

In today's wave of social development, the problem of air pollution is becoming

more and more serious, and the main sources of these air pollutants outdoor are from the iron and steel, power and cement industries [1]. With the rapid development of China's economy, SO₂ and NO_x emissions are also growing, and SO₂ and NO_x is the main reason for the formation of acid rain and other pollution. China's annual losses caused by acid rain pollution is about a billion dollars, for this reason, the research and application of integrated desulfurization and denitrification technology has become one of the key points of the future comprehensive flue gas treatment technology [2] [3]. China's desulfurization process is now more complete and mature development, but denitrification engineering and technology has been a controversial issue. China's annual NO_x emissions are second only to the United States, and it is predicted that China's total NO_x emissions will reach 40 million tons by 2030.

China's pollution treatment industry market demand is huge. From the point of view of subsectors, the revenue and net profit growth in the field of water treatment, solid waste and monitoring are the most significant, and the profit and revenue growth are basically consistent [3]. Among them, the production volume of hazardous waste has been rising year by year, from 34.312 million tons in 2011 to 39.761 million tons in 2015, with a compound growth rate of about 3%. In the long term, with the gradual implementation of China's industrial transformation and upgrading, the actual production of hazardous waste will not increase, will gradually reflect the source of reduction and tend to intensive growth [4] [5]. In recent years, due to policy encouragement, it has a broad market development space and potential, in the future gradually developed into environmental protection industry marketization, expansion and scale.

Today's domestic and foreign commonly used flue gas desulfurization (FGD) and denitrification integration technology is mainly wet FGD and SCR or SNCR technology denitrification combination [6]. SCR denitrification reaction temperature of 250°C - 450°C, denitrification efficiency of up to 70% - 90%, the technology is mature and reliable, especially in the developed countries are widely used, but there is a result of the catalyst is easy to poison inactivation, easy to damage equipment, investment costs and operating costs are higher shortcomings [7]-[9]; SNCR reduction temperature region at 870°C - 1200°C, denitrification efficiency is less than 50%, its temperature requirements are strict, easy to cause secondary pollution, easy to damage equipment, denitrification efficiency is lower.

This study proposes a new process for desulphurization and denitrification, the forced oxidation-absorption reduction (FOAR) technology. This technology realizes a low-cost and high-efficiency control strategy through cross-referencing with the environmental protection technologies of Energy Saving and Environmental Protection Technology Limited, Power Company Limited and Cement Company Limited, as well as the recycling of solid wastes. By using coal ash from the power company and lime hydrated at a certain ratio to obtain a highly active absorbent, which is applied to the desulphurization and denitrification process of sintered flue gas in iron and steel mills, desulphurization and denitrification by-products

of certain added value can be obtained. Then the desulfurization ash is applied to cement industry as a retarder, and other high temperature denitrification to form a circular economy and utilization, thus forming a benign industrial cycle, which not only saves the high cost of fly ash and desulfurization ash treatment costs and avoids harm to the environment, but also produces better economic benefits.

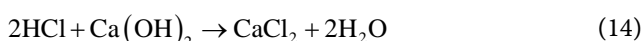
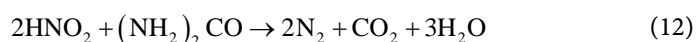
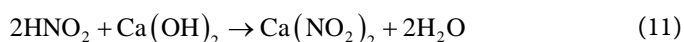
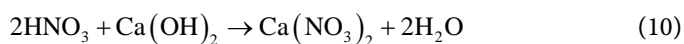
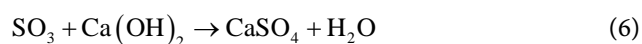
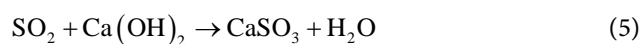
2. Principle of Forced Oxidative Denitrification

The denitrification method is mainly through forced oxidation → reduction and absorption to complete the denitrification process. The principle of forced oxidation is that the oxidizing catalyst reacts with NO through free radicals to produce a mixture of NO_x. The principle of reduction and absorption is a mixture of NO_x in the role of complex reducing agent to generate N₂ [10], or with alkali, calcium-based solution, magnesium-based solution reaction to generate NO₃⁻ and a small amount of NO₂⁻.

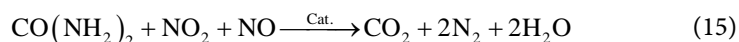
First, the NO and SO₂ in the flue gas are oxidized, as described by the following simplified reactions:



Next, some of the formed oxidation products diffuse from the gas phase to the bulk of the atomized liquid phase across the two-phase interface through molecular diffusion. The specific absorption reactions are represented by the following reaction equations:



The overall redox reactions are described by the following equations:



The denitrification method adopts CaSO₄, Al₂(SiO₄)₃·CaSO₄, Ca₃Al₂(SO₄)₃ as

raw materials to manufacture sulfoaluminate system cement, gypsum slag cement [11]-[13], gypsum bauxite expanded cement and so on. At the same time, it can also be used as sulfate exciter: it can stimulate the activity of fly ash and improve the strength of fly ash cement; as a mineralizing agent: it can reduce the calcination temperature and save coal; as a cement retarder: it can play the effect of retardation, make the setting time comply with the requirements, and improve the shrinkage and corrosion-resistant function of cement; it also has the function of regulating the sulfur-alkali ratio in clinker: it can reduce the possibility of crusting and clogging, and improve the compatibility with concrete [14] [15]. This denitrification method realizes the green environmental protection industry chain of circular economy and comprehensive utilization of iron and steel plants, power plants and cement plants, and its use of fly ash reacts with the by-products of desulfurization and denitrification to achieve the effect of partial denitrification and as a cement retarder [16] [17]. The solid dosage is small, only 0.35 - 0.45 of NO_x , the raw material is easy to obtain, there is no secondary pollution, play the role of the top and bottom, combined with low nitrogen graded combustion, and strive to achieve the source management, greatly improve the efficiency of denitrification embodies the necessity of this method, and realize the high-temperature and high-efficiency reduction of the composite polymer [18]-[20].

3. Forced Oxidative Denitrification Applications

Specifically applied to (1) circulating sulfurized bed boiler (CFB), as shown in **Figure 1**, with CFB as the main body, calcium-based absorber activity is low,

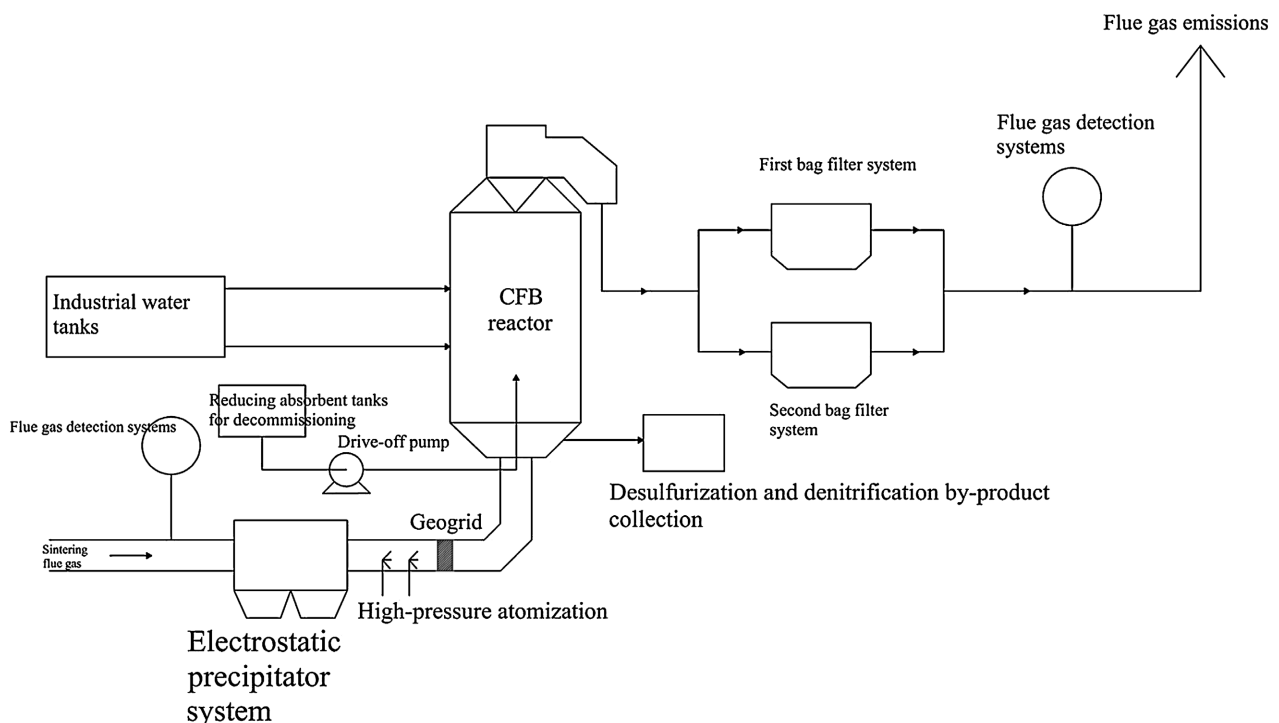


Figure 1. Schematic diagram of the structure of the process unit of circulating fluidized bed denitrification technology modification.

reducing the use of lime CaO or lime emulsion Ca(OH)₂, cheap fly ash can replace part of the CaO or Ca(OH)₂, reducing its actual use, which can reduce the operating costs, this denitrification process is easy to control, and the use of measures that can be doubly controlled can achieve the sintering or pelletizing flue gas. The denitrification process is easy to control and can achieve ultra-low emission of sintering or pelletizing flue gas by adopting double control measures, and it can realize denitrification function at the same time of desulfurization without the need to add more new equipment, so it has a broad market application prospect.

Based on the desulfurization process in the steel plant, we use denitrification transformation on the original basis. Different from the traditional transformation method, the forced oxidation-absorption-reduction process is to complete the denitrification process of the flue gas by using three parts: oxidation, absorption and reduction. Taking a steel company as an example, the comparison of data before and after the transformation is shown in **Tables 1-4**. After the forced oxidation of the flue gas, it needs to be absorbed and reduced in time, because there is a dynamic equilibrium between NO and high-valent nitrogen oxides, therefore, if the high-valent NO_x is not reduced and absorbed in time, it will cause the phenomenon of “yellow smoke”. In order to make nitrate desulfurization of calcium-based absorption completely and a large amount of calcium sulfite can be comprehensively utilized, we need to activate and modify the calcium-based absorbent, not only to improve the utilization rate of calcium absorbent, but also to reduce the cost of calcium-based desulfurization lime in bulk. The use of coal-fired fly ash and Ca(OH)₂/CaO hydration reaction to improve the calcium-based absorber activity, the Ca(OH)₂ and fly ash hydration, tempered with oxidizing agent to obtain a highly active absorber, which can be effective in removing SO₂ and NO_x from flue gas.

Based on SDA desulfurization project, establish a demonstration project and achieve ultra-low emission after forced oxidation and absorption reduction, the formed desulfurization ash by-products can be docked with the cement plant,

Table 1. Average of flue gas monitoring data before retrofit of CFB.

Flue gas quantity (mg/Nm ³)		98,800
Inlet	SO ₂ concentration (mg/Nm ³)	927.29
	NO ₂ concentration (mg/Nm ³)	224.32
	Soot concentration (mg/Nm ³)	57.98
Exits	SO ₂ concentration (mg/Nm ³)	13.69
	NO ₂ concentration (mg/Nm ³)	42.97
	Soot concentration (mg/Nm ³)	9.97
Effect	Desulfurization efficiency (%)	98.52
	Denitrification efficiency (%)	80.84
	Dust removal efficiency (%)	82.80

Table 2. Average of flue gas monitoring data after modification of CFB.

Flue gas quantity (mg/Nm ³)		100,000
Inlet	SO ₂ concentration (mg/Nm ³)	932.04
	NO ₂ concentration (mg/Nm ³)	221.59
	Soot concentration (mg/Nm ³)	27.23
Exits	SO ₂ concentration (mg/Nm ³)	9.80
	NO ₂ concentration (mg/Nm ³)	22.07
	Soot concentration (mg/Nm ³)	3.06
Effect	Desulfurization efficiency (%)	98.95
	Denitrification efficiency (%)	90.04
	Dust removal efficiency (%)	88.76

Table 3. Average of flue gas monitoring data after modification of SDA.

Flue gas quantity (mg/Nm ³)		800,000
Inlet	SO ₂ concentration (mg/Nm ³)	694.49
	NO ₂ concentration (mg/Nm ³)	293.88
	Soot concentration (mg/Nm ³)	67.50
Exits	SO ₂ concentration (mg/Nm ³)	18.81
	NO ₂ concentration (mg/Nm ³)	274.29
	Soot concentration (mg/Nm ³)	12.02
Effect	Desulfurization efficiency (%)	93.70
	Denitrification efficiency (%)	6.64
	Dust removal efficiency (%)	82.29

Table 4. Average of flue gas monitoring data after modification of SDA.

Flue gas quantity (mg/Nm ³)		800,000
Inlet	SO ₂ concentration (mg/Nm ³)	706.38
	NO ₂ concentration (mg/Nm ³)	294.92
	Soot concentration (mg/Nm ³)	68.22
Exits	SO ₂ concentration (mg/Nm ³)	15.74
	NO ₂ concentration (mg/Nm ³)	58.01
	Soot concentration (mg/Nm ³)	6.67
Effect	Desulfurization efficiency (%)	97.78
	Denitrification efficiency (%)	80.32
	Dust removal efficiency (%)	90.26

while the fly ash of the power plant can be applied in the modification of the absorber, and then achieve the comprehensive utilization of the fly ash solid waste.

Due to the increasing tension of mineral resources, one of the CaO and CaCO₃ used in desulfurization and denitrification absorbent has unstable quality of active ingredients, incomplete absorption of calcium-based in nitrate sulfur removal, and a large amount of calcium sulfite has been characterized as hazardous waste, which is difficult to be comprehensively utilized. For this reason, it is necessary to activate and modify the calcium-based absorbent, on the one hand, to improve the utilization rate of calcium absorbent, on the other hand, to reduce the cost of calcium-based desulfurization lime in batches.

Power plant coal fly ash and lime hydration in a certain proportion to obtain a highly active absorbent, applied in the steel plant sintering flue gas desulfurization and denitrification process, you can get a certain value-added desulfurization and denitrification by-products, and then desulfurization ash applied to cement as a retardant, and high temperature denitration such as cement to form a cycle of economic and utilization. As such a virtuous cycle, not only to save fly ash and desulfurization ash high disposal costs also avoid harm to the environment, but also can produce better economic benefits. The three parts of the intersection of each other, each other to form a certain benign industrial circular economy.

Since the lime digestion process is an important part of air pollution control, it affects the efficiency and operating costs of the entire process. And the digestion of lime is greatly affected by the stirring rate, lime particle size, digestion temperature, water (H₂O)/calcium oxide (CaO) ratio and various impurities, sometimes about nearly one-quarter of the CaO cannot be fully reacted and waste of resources, for this reason, it is necessary to improve the lime to become an active calcium-based absorbent. In addition, the forced oxidizing agent, as well as the absorbing and reducing agents are complex additives with different ratios for different conditions. Due to the existence of the above influencing factors, and the optimal use ratio and range of each factor, the preparation of denitrification composites and the modification program on different equipment are our research content. And it is also important to provide an environmentally safe, low-cost and efficient denitrification reductant instead of ammonia and liquid ammonia, which is one of the key research projects of forced oxidation-absorption reduction technology.

The original SNCR process technology, the excessive use of liquid ammonia, ammonia, and denitrifying agents such as urea, can cause a large amount of ammonia escape, thus forming organic aerosols, which can contribute to the elevation of PM_{2.5}, one of the main causes of haze. Our new denitrifier components after compounding, compared with the SCR process, its investment and operating costs are low; compared with the ammonia SNCR process, not only the denitrification efficiency is high (can be increased to 40% - 50%), but also can solve the problem of ammonia escape and equipment corrosion. On the one hand, the original equipment is utilized to reduce the cost of equipment modification, and on the other hand, the application of new denitrifying agent components after

compounding reduces the denitrification operation cost, so that synergistic control of green denitrification project can be realized.

Make full use of the principle of gas-liquid phase chemical reaction, rapid oxidation and combined with absorption and reduction of NO_x into N_2 to achieve denitrification of ultra-clean emissions, and with wet electrostatic precipitator program, which can effectively reduce the emission of $\text{PM}_{2.5}$ particles; NO_x concentration of exhaust gas to adapt to a strong, high processing and purification rate, which can completely solve the “yellow smoke” phenomenon! At the same time, it can achieve the effect of “whitening” of the flue gas; it can achieve low investment cost and low operation cost, which can be suitable for the timely adjustment of continuous denitrification process and can be adapted to intermittent denitrification process; it can achieve the systematization of process flow from the principle of the idea, process steps, key construction and ultra-clean emission to achieve the effect of “whitening” on the flue gas of cement kiln and garbage incinerator, the flue gas of sintered flue gas, coal-fired boiler flue gas and other denitrification of the end of the perfect governance effect.

4. Conclusion

The long-term strategy for flue gas denitrification involves promoting a comprehensive technical scheme that adapts to both high-temperature continuous and low-temperature intermittent flue gas treatments across various industries, such as cement kilns, waste incinerators, sintering processes, and coal-fired boilers. This approach includes the timely adjustment of composite polymer reductants, new compound denitrifying agents for SNCR in high-temperature areas, and catalyst concentrations in low-temperature areas, ensuring the universality of the process. The strategy integrates desulfurization and denitrification without altering the existing desulfurization process, streamlining operations for simplicity, efficiency, and lower costs. It maintains high efficiency in desulfurization and denitrification through adjustable slurry components, ensures a continuous supply of reagents, and minimizes equipment corrosion, ultimately facilitating the recycling and comprehensive utilization of solid by-products in cement plants.

Data Availability

The data used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Acknowledgements

The paper was partially supported by Anhui University Excellent Research and Innovation Project (No. 2022AH010094). Authors appreciate the reviewers for their invaluable comments which have led to significant improvement in the paper.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Li, Q., Hou, Y., Han, X., Wang, J., Liu, Y., Xiang, N., *et al.* (2020) Promotional Effect of Cyclic Desulfurization and Regeneration for Selective Catalytic Reduction of NO by NH₃ over Activated Carbon. *Journal of Cleaner Production*, **249**, Article ID: 119392. <https://doi.org/10.1016/j.jclepro.2019.119392>
- [2] Chen, K., Huang, Y., Wang, S., Zhu, Z., Cheng, H. and Yuan, Q. (2023) Integrated Technology for Dust Removal and Denitration of High-Temperature Flue Gas in Coal-Fired Power Plants. *Fuel*, **342**, Article ID: 127687. <https://doi.org/10.1016/j.fuel.2023.127687>
- [3] Song, J., Sun, X., Zhang, G., Cheng, S., Xu, Y. and Jiang, Y. (2024) Recent Advances in Improving SO₂ Resistance of Ce-Based Catalysts for NH₃-SCR: Mechanisms and Strategies. *Molecular Catalysis*, **564**, Article ID: 114347. <https://doi.org/10.1016/j.mcat.2024.114347>
- [4] Jiang, D., Wang, Y., Zhou, Y., Li, Z., Li, S., Zhang, S., *et al.* (2023) Performance of Sintering Dust-Modified Metal Oxides Catalyst in SCR-NH₃ Technique. *Research on Chemical Intermediates*, **49**, 2299-2319. <https://doi.org/10.1007/s11164-023-04995-8>
- [5] Wang, D., Huang, B., Shi, Z., Long, H., Li, L., Yang, Z., *et al.* (2021) Influence of Cerium Doping on Cu-Ni/activated Carbon Low-Temperature CO-SCR Denitration Catalysts. *RSC Advances*, **11**, 18458-18467. <https://doi.org/10.1039/d1ra02352g>
- [6] Li, Y., Lin, Y., Wang, B., Ding, S., Qi, F. and Zhu, T. (2019) Carbon Consumption of Activated Coke in the Thermal Regeneration Process for Flue Gas Desulfurization and Denitrification. *Journal of Cleaner Production*, **228**, 1391-1400. <https://doi.org/10.1016/j.jclepro.2019.04.225>
- [7] Liu, F., Lei, Y., Shi, J., Zhou, L., Wu, Z., Dong, Y., *et al.* (2020) Effect of Microbial Nutrients Supply on Coal Bio-Desulfurization. *Journal of Hazardous Materials*, **384**, 121324-12333. <https://doi.org/10.1016/j.jhazmat.2019.121324>
- [8] Wang, H., Huang, B., Yu, C., Lu, M., Huang, H. and Zhou, Y. (2019) Research Progress, Challenges and Perspectives on the Sulfur and Water Resistance of Catalysts for Low Temperature Selective Catalytic Reduction of NO_x by NH₃. *Applied Catalysis A: General*, **588**, Article ID: 117207. <https://doi.org/10.1016/j.apcata.2019.117207>
- [9] Zhou, Y., Wang, J., Wei, X., Ren, S., Yang, X., Beiyuan, J., *et al.* (2021) Escalating Health Risk of Thallium and Arsenic from Farmland Contamination Fueled by Cement-Making Activities: A Hidden but Significant Source. *Science of the Total Environment*, **782**, Article ID: 146603. <https://doi.org/10.1016/j.scitotenv.2021.146603>
- [10] Lahaye, D., Abbassi, M.e., Vuik, K., Talice, M. and Juretić, F. (2020) Mitigating Thermal NO_x by Changing the Secondary Air Injection Channel: A Case Study in the Cement Industry. *Fluids*, **5**, 220-233. <https://doi.org/10.3390/fluids5040220>
- [11] Benhelal, E., Shamsaei, E. and Rashid, M.I. (2021) Challenges against CO₂ Abatement Strategies in Cement Industry: A Review. *Journal of Environmental Sciences*, **104**, 84-101. <https://doi.org/10.1016/j.jes.2020.11.020>
- [12] Yang, Y., Zhang, Y., Li, S., Liu, R. and Duan, E. (2020) Numerical Simulation of Low Nitrogen Oxides Emissions through Cement Precalciner Structure and Parameter Optimization. *Chemosphere*, **258**, Article ID: 127420. <https://doi.org/10.1016/j.chemosphere.2020.127420>
- [13] Liu, B., Peng, D., Chiang, P. and Chu, C. (2023) Performance Evaluation of NO_x Absorption by Different Denitration Absorbents in Wet Flue Gas Denitration. *Journal of the Taiwan Institute of Chemical Engineers*, **145**, Article ID: 104840. <https://doi.org/10.1016/j.jtice.2023.104840>

- [14] Peruski, K.M., Parker, C.J. and Cary, S.K. (2023) Analysis of Neptunium Oxides Produced through Modified Direct Denitration. *Journal of Nuclear Materials*, **587**, Article ID: 154704. <https://doi.org/10.1016/j.jnucmat.2023.154704>
- [15] Huang, B., Shi, Z., Yang, Z., Dai, M., Wen, Z., Li, W., *et al.* (2022) Mechanism of CO Selective Catalytic Reduction Denitration on Fe-Mn/Ac Catalysts at Medium and Low Temperatures under Oxygen Atmosphere. *Chemical Engineering Journal*, **446**, Article ID: 137412. <https://doi.org/10.1016/j.cej.2022.137412>
- [16] Wu, X., Yu, X., Xu, R., Cao, M. and Sun, K. (2022) Nonlinear Dynamic Soft-Sensing Modeling of Nox Emission of a Selective Catalytic Reduction Denitration System. *IEEE Transactions on Instrumentation and Measurement*, **71**, Article ID: 2504911. <https://doi.org/10.1109/tim.2022.3141154>
- [17] Wang, Y., Zhang, J., Qian, G. and Zhang, T. (2023) Data-Driven Discovery of Low Temperature Denitration Catalysts with Strong Anti-Sulfur and Anti-Water Property. *Materials Letters*, **342**, Article ID: 134315. <https://doi.org/10.1016/j.matlet.2023.134315>
- [18] Wang, B., Song, K., Li, Z., Li, K. and Shi, J. (2022) One-Pot Synthesis of Rare Earth Modified Cu/Sapo-34 for Enhanced Selective Catalytic Reduction Denitration Performance. *Separation and Purification Technology*, **303**, Article ID: 122281. <https://doi.org/10.1016/j.seppur.2022.122281>
- [19] Zhang, Y., Wang, Z., He, Y., Zhu, Y. and Liu, J. (2023) Experimental Study on Three Additives Used for the Removal of Nitrite, a Byproduct of Ozone Oxidation Denitration Technology. *Environmental Technology & Innovation*, **32**, Article ID: 103236. <https://doi.org/10.1016/j.eti.2023.103236>
- [20] Chen, Y., He, H., Wu, S., Ning, X., Chen, F., Lv, Y., *et al.* (2020) Mn/Ce Oxides Decorated Polyphenylene Sulfide Needle-Punching Fibrous Felts for Dust Removal and Denitration Application. *Polymers*, **12**, 168-180. <https://doi.org/10.3390/polym12010168>