Recent Advances in Simultaneous Desulfurization & Denitrification

A summary of recent technical advances in simultaneous desulfurization and denitrification techniques, with an emphasis on wet scrubbing.

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Smog problems in China have been repeatedly hitting the global media headlines during the past few years.\textsuperscript{1, 2} Figure 1 shows a building in Beijing in regular and smog atmosphere. Sulfur dioxide (SO\textsubscript{2}) and nitrogen oxides (NO\textsubscript{X}) are two major contributors to the formation of smog, and they are primarily associated with energy production and consumption.

China and the United States are the two largest energy producers and consumers in the world; both utilized approximately 100 quadrillion Btu of energy in 2011.\textsuperscript{3, 5} As a result, in 2011, 21.179 and 24.042 Mt of SO\textsubscript{2} and NO\textsubscript{X}, respectively, were emitted to the atmosphere in China,\textsuperscript{5} whereas 6.539 and 15.517 Mt, respectively, were emitted to the atmosphere in the United States.\textsuperscript{6} SO\textsubscript{2} and NO\textsubscript{X} emissions in China were 3.24 and 1.55 times higher than those in the United States, due to China’s great dependence on coal as an energy resource and less stringent air emission limits (China did not adopt world-class pollutant standards until 2012). In 2011, coal consistently provided approximately 20\%\textsuperscript{3} and 67\%\textsuperscript{5} of total energy consumption in the United States and China, respectively.

Stringent environmental laws and regulations have driven recent advances in air emission control technologies. The U.S. Environmental Protection Agency (EPA), for example, established the Acid Rain Program (ARP) and Cross-State Air Pollution Rule (CSAPR) to curb SO\textsubscript{2} and NO\textsubscript{X} emissions from thermal power plants.\textsuperscript{7} China’s newest national air emission standards, which were even stricter than those in European Union (EU) and the United States, became effective in January 2012.\textsuperscript{8} Flue gas desulfurization (FGD) and selective catalytic reduction (SCR) are deployed for the
abatement of SO₂ and NOₓ emissions, respectively.⁹,¹⁰ As of 2011, 61% of coal-fired power generating capacity in the United States has FGD, and nearly 66% in China.¹¹ Comparatively, the installation of SCR remains lower: in 2012, 43% of total coal-fired utility power generation capacity had SCR installed in the United States,¹¹ with fewer than 18% in China.⁹ In addition, separate control of SO₂ and NOₓ led to great capital and operational costs, large footprint, and reduced flexibility of optimal control economics.¹²

Recently, researchers have placed immense efforts in seeking cost-effective alternatives for multiple air cleaning processes. From a system design and cost perspective, it is desirable to integrate air pollution control system for SO₂ and NOₓ into a single operational unit. One example is the SOₓ–NOₓ–Rox Box (SNRB) technology. The SNRB method incorporates dry sorbent injection for SOₓ removal and zeolite SCR for NOₓ reduction.¹²

Electron beam purification is another early approach for multicomponent pollutant control.¹³ With the advances in SCR technology, SO₂, which acts as a contaminant, could be simultaneously treated with certain specific additives, such as copper and vanadium oxides.¹⁴ Furthermore, wet scrubbers using strong oxidants⁹ and transitional metal complexes¹⁵–¹⁷ have also been proposed for simultaneous desulfurization and denitrification. In addition, hybrid processes are under development.¹⁸

**Wet scrubbing**

The motivation behind simultaneous wet scrubbing of NOₓ and SO₂ is to take advantage of existing FGD scrubber system, thereby lowering capital and operational costs, along with smaller plant footprint. The absorbents using for NOₓ/SO₂ wet scrubbing can be categorized as strong oxidants and transitional metal chelates. The strong oxidants can convert NO and SO₂ into soluble NO₂ and SO₃, respectively, followed by the absorption of SO₂ and NO₃ to form sulfuric and nitric acids and/or sulphates and nitrates. In addition, some metal complexes can quickly coordinate with NO to form nitrosyls, followed by liquid treatment. Related aqueous absorbents are tabulated in Table 1.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Working Conditions</th>
<th>Performances</th>
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<tbody>
<tr>
<td>Fe²⁺EDTA²⁰</td>
<td>Fe²⁺EDTA = 100 mM, T = 323 K, SO₂ = 2360 mg·m⁻³, NO = 400 mg·m⁻³, O₂ = 5%</td>
<td>Desulfurization = 98%; Denitrification = 99%</td>
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<tr>
<td>Ferrate⁶ solution²¹</td>
<td>Ferrate (VI) solution = 0.25 mM, T = 320 K, SO₂ = 2000 mg·m⁻³, NO = 700 mg·m⁻³</td>
<td>Desulfurization = 100%; Denitrification = 64.8%</td>
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<td>H₂O₂ with Fe-based ammonia¹⁶,²²</td>
<td>H₂O₂ = 30 wt%, Preheat temp. = 403 K, SO₂ = 17000 ppm, NO = 550 ppm, Ammonia = 1wt%, Washing temperature = 293 K</td>
<td>Desulfurization ~ 100%; Denitrification ~ 80%</td>
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<tr>
<td>UV/H₂O₂²³,²⁴</td>
<td>H₂O₂ = 0.75 mol·L⁻¹, Ca(OH)₂ = 20 mmol·L⁻¹, T = 293K, SO₂ = 1000 ppm, NO = 400 ppm, O₂ = 6.0%, UV energy density per unit solution = 0.015 W·mL⁻¹</td>
<td>Desulfurization = 100%; Denitrification = 81.8%</td>
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<td>Fenton reagent⁹</td>
<td>H₂O₂ = 11 wt%, Fe²⁺ = 2.8 mmol·L⁻¹, T = 328K, SO₂ = 2400 mg·m⁻³, NO = 420 mg·m⁻³</td>
<td>Desulfurization = 100%; Denitrification &gt; 90%</td>
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<tr>
<td>Urea/KMnO₄²⁵</td>
<td>Urea = 5 wt%, KMnO₄ = 7 mmol·L⁻¹, T = 328K; SO₂ = 2900 mg·m⁻³, NO = 650 mg·m⁻³</td>
<td>Desulfurization &gt; 98%; Denitrification = 43–52%</td>
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<tr>
<td>Pyrolusite slurry/ozone²⁶</td>
<td>Pyrolusite = 40 g·L⁻¹; T = 298 K, SO₂ = 2000 ppm; NO = 750 ppm, O₂ = 4%, O₃ injection = 900 ppm</td>
<td>Desulfurization ~100%; Denitrification ~ 75%</td>
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<tr>
<td>Sodium persulfate²⁷</td>
<td>Na₂S₂O₈ = 0.1 mol·L⁻¹, T = 343 K, SO₂ = 1550 ppm, NO = 1000 ppm</td>
<td>Desulfurization ~100%; Denitrification = 77–83%</td>
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Table 1. Summary of selected wet scrubbing for simultaneous desulfurization and denitrification.
The pilot-scale De-NO\textsubscript{X} project using wet scrubbing was reported several years ago. The U.S. Department of Energy supported the pilot tests of simultaneous removal of SO\textsubscript{2} and NO\textsubscript{X} using Fe\textsuperscript{II}EDTA in 1992.\textsuperscript{19} Although excellent desulfurization and denitri-

cation efficiencies were reported, expensive regeneration of absorbent hindered its commercialization. An electrochemical treatment of liquid product reported recently may reduce the cost for waste stream treatment, but more evaluation is needed.\textsuperscript{20}

Recently, Guo et al. studied the absorption of SO\textsubscript{2} and NO\textsubscript{X} into a Fe\textsuperscript{II}EDTA spray in a horizontal reactor. This reactor was equipped with two sets of corrugated impellers at pH = 8.0.\textsuperscript{20}

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Figure 2. System for simultaneous removal of NO\textsubscript{X} and SO\textsubscript{2}.

Notes: (1) mass flow meter, (2) N\textsubscript{2} cylinder, (3) NO cylinder, (4) SO\textsubscript{2} cylinder, (5) compared air cylinder: (A) anode, (C) cathode, and (M) proton exchange membrane (Adapted from Guo et al.\textsuperscript{20}).
The produced liquid was processed in an electrochemical cell with activated carbon as a catalyst. In this approach, NOX and SO2 were converted into N2 and Na2SO4. The sodium sulphate was recovered as a byproduct by low-temperature crystallization. Such progress in liquid treatment would promote the application of wet scrubbing.

Figure 2 shows the process for simultaneous desulfurization and denitrification. The experiments were conducted using a FeIIEDTA concentration of 100 mM, a liquid-to-gas ratio of 4 L m−1, a rotating rate of 156 rpm, the voltage of absorbent regeneration of 1 V, activated carbon of 25 g and temperature of 323 K. Simulated flue gas containing 326 parts per million (ppm) of NO, 900 ppm of SO2, and 5% of O2 was treated continuously. The NO and SO2 removal efficiencies remained at 99% and 98%, respectively, in the 10 hours of operation. Highly pure Na2SO4 was crystallized at 278 K. There was a negligible change in Fe2+ concentration in the FeIIEDTA solution before and after crystallization. The catalytic electrochemical liquid treatment would greatly reduce costs, thereby making wet scrubbing using FeIIEDTA a promising solution to multicomponent gas cleanup.

**Conclusion**

Heavy reliance on fossil fuels in the developing world are increasing SO2 and NOX emissions, which pose severe threats to human health and the environment. More stringent environmental laws and regulations drive the development of cost-effective technologies for simultaneous control of SO2 and NOX. Wet scrubbing using FeIIEDTA is an excellent candidate for this purpose.

**References**

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23. Liu, Y.X.; Pan, J.F.; Wang, Q. Removal of Hg0 from containing-SO2/NO flue gas by ultraviolet/H2O2 process in a novel photochemical reactor; Aiche J. 2014, 60 (6), 2275-2285.