



# Recent Advances in Simultaneous *Desulfurization* & *Denitrification*

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



Figure 1. A construction in Beijing in regular (upper photo) and smog (lower photo) atmosphere.

Smog problems in China have been repeatedly hitting the global media headlines during the past few years.<sup>1,2</sup> Figure 1 shows a building in Beijing in regular and smog atmosphere. Sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) 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.<sup>3-5</sup> As a result, in 2011, 21.179 and 24.042 Mt of SO<sub>2</sub> and NO<sub>x</sub>, respectively, were emitted to the atmosphere in China,<sup>5</sup> whereas 6.539 and 15.517 Mt, respectively, were emitted to the atmosphere in the United States.<sup>6</sup> SO<sub>2</sub> and NO<sub>x</sub> 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%<sup>3</sup> and 67%<sup>5</sup> 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<sub>2</sub> and NO<sub>x</sub> emissions from thermal power plants.<sup>7</sup> 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.<sup>8</sup> Flue gas desulfurization (FGD) and selective catalytic reduction (SCR) are deployed for the

Technology	Working Conditions	Performances
Fe <sup>II</sup> EDTA <sup>20</sup>	Fe <sup>II</sup> EDTA = 100 mM, T = 323 K, SO <sub>2</sub> = 2360 mg·m <sup>-3</sup> , NO = 400 mg·m <sup>-3</sup> , O <sub>2</sub> = 5%	Desulfurization = 98%; Denitrification = 99%
Ferrate <sup>VI</sup> solution <sup>21</sup>	Ferrate (VI) solution = 0.25 mM, T = 320 K, SO <sub>2</sub> = 2000 mg·m <sup>-3</sup> , NO = 700 mg·m <sup>-3</sup> .	Desulfurization = 100%; Denitrification = 64.8%
H <sub>2</sub> O <sub>2</sub> with Fe-based catalyst / ammonia <sup>10,22</sup>	H <sub>2</sub> O <sub>2</sub> = 30 wt%, Preheat temp. = 403 K, SO <sub>2</sub> = 17000 ppm, NO = 550 ppm, Ammonia = 1wt%, Washing temperature = 293 K	Desulfurization ~ 100%; Denitrification ~ 80%
UV/H <sub>2</sub> O <sub>2</sub> <sup>23,24</sup>	H <sub>2</sub> O <sub>2</sub> = 0.75 mol·L <sup>-1</sup> , Ca(OH) <sub>2</sub> = 5 mmol·L <sup>-1</sup> , T = 293K, SO <sub>2</sub> = 1000 ppm, NO = 400 ppm, O <sub>2</sub> = 6.0%, UV energy density per unit solution = 0.015 W·mL <sup>-1</sup>	Desulfurization = 100%; Denitrification = 81.8%
Fenton reagent <sup>9</sup>	H <sub>2</sub> O <sub>2</sub> = 11 wt%, Fe <sup>II</sup> = 2.8 mmol·L <sup>-1</sup> , T = 328K, SO <sub>2</sub> = 2400 mg·m <sup>-3</sup> , NO = 420 mg·m <sup>-3</sup>	Desulfurization = 100%; Denitrification > 90%
Urea/KMnO <sub>4</sub> <sup>25</sup>	Urea = 5 wt%, KMnO <sub>4</sub> = 7 mmol·L <sup>-1</sup> , T = 328K; SO <sub>2</sub> = 2900 mg·m <sup>-3</sup> , NO = 650 mg·m <sup>-3</sup>	Desulfurization > 98%; Denitrification = 43–52%
Pyrolusite slurry/ ozone <sup>26</sup>	Pyrolusite = 40 g·L <sup>-1</sup> ; T = 298 K, SO <sub>2</sub> = 2000 ppm; NO = 750 ppm, O <sub>2</sub> = 4%, O <sub>3</sub> injection = 900 ppm	Desulfurization ~100%; Denitrification ~ 75%
Sodium persulfate <sup>27</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> = 0.1 mol·L <sup>-1</sup> , T = 343 K, SO <sub>2</sub> = 1550 ppm, NO = 1000 ppm	Desulfurization ~100%; Denitrification = 77–83%

Table 1. Summary of selected wet scrubbing for simultaneous desulfurization and denitrification.

abatement of SO<sub>2</sub> and NO<sub>x</sub> emissions, respectively.<sup>9,10</sup> As of 2011, 61% of coal-fired power generating capacity in the United States has FGD, and nearly 66% in China.<sup>11</sup> 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,<sup>11</sup> with fewer than 18% in China.<sup>9</sup> In addition, separate control of SO<sub>2</sub> and NO<sub>x</sub> led to great capital and operational costs, large footprint, and reduced flexibility of optimal control economics.<sup>12</sup>

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 SO<sub>2</sub> and NO<sub>x</sub> into a single operational unit. One example is the SO<sub>x</sub>-NO<sub>x</sub>-Rox Box (SNRB) technology. The SNRB method incorporates dry sorbent injection for SO<sub>x</sub> removal and zeolite SCR for NO<sub>x</sub> reduction.<sup>12</sup>

Electron beam purification is another early approach for multicomponent pollutant control.<sup>13</sup> With the

advances in SCR technology, SO<sub>2</sub>, which acts as a contaminant, could be simultaneously treated with certain specific additives, such as copper and vanadium oxides.<sup>14</sup> Furthermore, wet scrubbers using strong oxidants<sup>9</sup> and transitional metal complexes<sup>15-17</sup> have also been proposed for simultaneous desulfurization and denitrification. In addition, hybrid processes are under development.<sup>18</sup>

### Wet scrubbing

The motivation behind simultaneous wet scrubbing of NO<sub>x</sub> and SO<sub>2</sub> is to take advantage of existing FGD scrubber system, thereby lowering capital and operational costs, along with smaller plant footprint. The absorbents using for NO<sub>x</sub>/SO<sub>2</sub> wet scrubbing can be categorized as strong oxidants and transitional metal chelates. The strong oxidants can convert NO and SO<sub>2</sub> into soluble NO<sub>2</sub> and SO<sub>3</sub>, respectively, followed by the absorption of SO<sub>2</sub> and NO<sub>2</sub> 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.

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The pilot-scale De-NO<sub>x</sub> project using wet scrubbing was reported several years ago. The U.S. Department of Energy supported the pilot tests of simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub> using Fe<sup>II</sup>EDTA in 1992.<sup>19</sup> Although excellent desulfurization and denitrification 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.<sup>20</sup>

Recently, Guo et al. studied the absorption of SO<sub>2</sub> and NO<sub>x</sub> into a Fe<sup>II</sup>EDTA spray in a horizontal reactor. This reactor was equipped with two sets of corrugated impellers at pH = 8.0.<sup>20</sup>

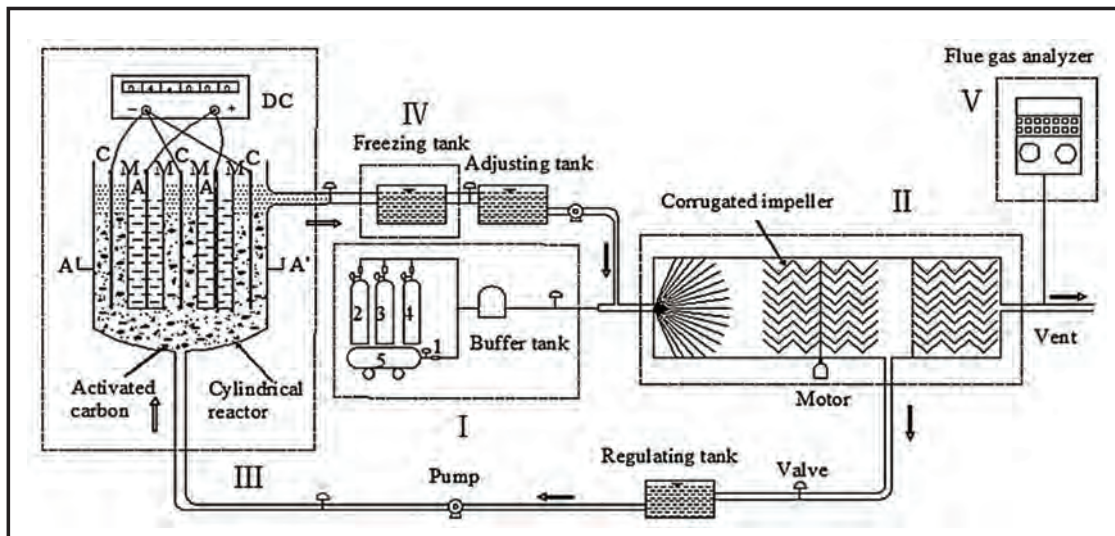


Figure 2. System for simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub>.

Notes: (1) mass flow meter, (2) N<sub>2</sub> cylinder, (3) NO cylinder, (4) SO<sub>2</sub> cylinder, (5) compared air cylinder: (A) anode, (C) cathode, and (M) proton exchange membrane (Adapted from Guo et al.<sup>20</sup>).

The produced liquid was processed in an electrochemical cell with activated carbon as a catalyst. In this approach, NO<sub>x</sub> and SO<sub>2</sub> were converted into N<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub>. 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 Fe<sup>II</sup>EDTA concentration of 100 mM, a liquid-to-gas ratio of 4 L·m<sup>-3</sup>, a rotating rate of 156 rpm, the voltage of absorbent regeneration of 1V, activated carbon of 25 g and temperature of 323 K. Simulated flue gas containing 326 parts per million (ppm) of NO, 900 ppm of SO<sub>2</sub>, and 5% of O<sub>2</sub> was treated continuously. The NO and SO<sub>2</sub> removal efficiencies remained at 99%

and 98%, respectively, in the 10 hours of operation. Highly pure Na<sub>2</sub>SO<sub>4</sub> was crystallized at 278 K. There was a negligible change in Fe<sup>2+</sup> concentration in the Fe<sup>II</sup>EDTA solution before and after crystallization. The catalytic electrochemical liquid treatment would greatly reduce costs, thereby making wet scrubbing using Fe<sup>II</sup>EDTA a promising solution to multicomponent gas cleanup.

## Conclusion

Heavy reliance on fossil fuels in the developing world are increasing SO<sub>2</sub> and NO<sub>x</sub> 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 SO<sub>2</sub> and NO<sub>x</sub>. Wet scrubbing using Fe<sup>II</sup>EDTA is an excellent candidate for this purpose. **em**

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