

Synergistic Hybrid DeNO_x Using Coal Reburn and Enhanced Dry Scrubbing

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Summary

Discussions/presentations addressing the emerging field of simultaneous removal of NO_x in SO₂ scrubbing operations invariably relate to wet collectors. Equal or superior in gas cleaning efficiency to wet scrubbing in all respects, dry scrubbers, particularly circulating fluid bed reactors, also so function, Graf, R et al (2001). Moreover, in the latter case, downstream use of fabric filtration provides superior performance in removal of fine particulate including any generated in operation of coal reburn. Applicable process designs include the Pahlman Process, which achieves action of permanganate oxidant using byproduct steel-industry waste...as well as alternative lime-based designs: (a) in use of in-duct formed chlorine dioxide gas accomplishing “full” preoxidation of acid gases, SO₂ and NO/NO₂ to SO₃ and N₂O₅; (b) economical use of hydrogen peroxide to preoxidize NO in employing the NO₂-reducing, oxidation-reduction scrubbing process mode; and (c) in use of ozone, (LoTO_x Process), or a high-reactivity, organic oxidant for “fully” preoxidizing NO_x to N₂O₅.

DeNO_x cost effectiveness of coal reburn can best be exploited by combined engineering design employing chemical process technology to achieve simultaneous removal, (e.g. of SO₂, SO₃, NO_x, and Hg⁰), in downstream dry scrubbing operation. Greatest synergism in performance is achieved in such trim-type, secondary deNO_x by scrubbing when, by dry process means, strictest stack emission limits are to be met for PM-2.5 as well as NO_x, Hg, SO₂, SO₃, etc. In the case of use of circulating fluid bed dry-scrubbing equipment substantial particulate agglomeration therein enhances the already/inherent, high efficiency of fabric filter operation downstream in collection of fine particulate as may originate from coal reburn use. In conjunction solely with low-cost primary deNO_x means including coal reburning stack emission may thereby be decreased to as low as 0.01 lb/MM Btu.

The most substantial dry-process developmental progress in SO₂/NO_x removal has been made in the advancement of the Pahlman Process, above, Nalbandian, H (2002). Early, commercial demonstration and application is pending. It effectively uses manganese oxide contained in ferrous/carbon, steel industry waste (Pahlmanite), functioning in the form of MnO₄ ions, in oxidation and sorption of acid gases. Capital costs are projected to range from US\$275 to US\$300 per kW for a 500 MW coal-fired plant, and operating and maintenance costs are forecast to be in the range of 2.15-2.45 mills/kWh. Operating and maintenance costs are partly offset by: (a) low parasitic energy requirement compared to an SCR and wet FGD combination; (b) resulting potential for increased boiler efficiency; and (c) sale of the system byproduct (e.g. nitric acid, ammonium nitrate/sulfate, potassium nitrate, sodium sulfate and sulfuric acid).

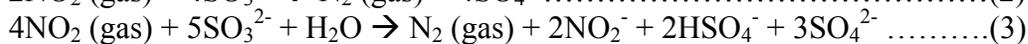
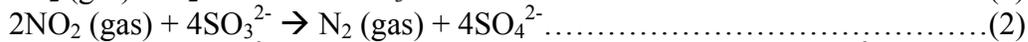
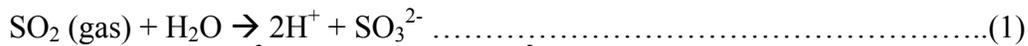
A very promising dry scrubbing technique utilizes gaseous ClO₂ as the in-duct formed, oxidizing agent, it being derived from commonly available, sodium chlorate crystal supply. By its nature ClO₂, introduced to flue gas spray cooled to less than 200°F, sequentially oxidizes SO₂ to SO₃, ultimately

followed by oxidation of NO to NO₂ and oxidation of NO₂ to N₂O₅. Dry scrubbing, using lime alkali sorbs:

- SO₃ gas even more efficiently than it sorbs SO₂, resulting in calcium sulfate reaction product
- N₂O₅ in the same ready manner in which common HCl gas is collected, yielding calcium nitrate and calcium chloride solids
- Chemically-reduced ClO₂ oxidant, yielding calcium chloride solids.

Residual NO₂ exiting the system to the boiler stack must be limited to approximately 15-25 ppm(v) so as not to impart an orange/brown coloration to the stack discharge plume. Thus, in a practical system design/operation for oxidizing NO to N₂O₅, conversion is carried out to the fullest extent so as to limit stack gas NO₂ concentration. There will, in addition to the low-solubility, principal, calcium sulfate dihydrate reaction product, be a significant amount of calcium nitrate and chloride, (each highly water-soluble), in the solid waste. Ultimate disposal of this reaction-waste (intermixed with the fly-ash catch and suitably moistened, optionally/advantageously using available plant wastewater for discard) may be via a typical “structural landfill” (as widely employed in ultimate disposal of waste FGD cake from wet magnesia buffered lime scrubbing systems after addition of fly ash). By this method of management of the gas cleaning solids yield, the soluble salts and other waste components are permanently prevented from reaching and impacting surface water and groundwater bodies... and an otherwise unusable land area so employed may be recovered for general use.

Japanese work in the 1970s, Ando, J (1976), emphasizes process technology for simultaneous NO_x removal by scrubbing via the oxidation-reduction process mode. It was therein shown that NO₂, formed artificially by augmented/artificial, upstream oxidation of flue-gas NO, e.g. using pre-treatment by chemical oxidant, reacts effectively with collector alkali, sulfite ion, (formed in conjunction with SO₂ absorption, and that has chemical-reducing properties as well), and can thereby be abated by chemical reduction, principally into gaseous N₂ as in reactions (1) and (2) below. (It was noted that a comparatively small amount of nitrite (and nitrate) usually forms by “side” reactions such as reaction (3):

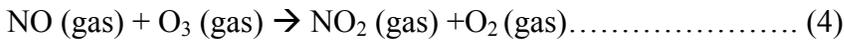


Under common, U. S., medium/high-sulfur, fuel-firing conditions, any of the FGD processes that, for alkaline reactant in removal of SO₂, use ammonium/magnesium/sodium sulfites, i.e. water-soluble alkalis, (all of which are also chemical reducing agents), can be utilized in applying the Japanese process development. And, uniquely, all such processes, not dry type only, can be managed to operate with no liquid effluent, thus precluding difficulties in management of wastewater containing nitrogen compounds. These FGD process operations, when converted to accomplish the oxidation-reduction, process sequence, as above, i.e. chemical-oxidation/chemical-reduction” or, in other words, “chemical-oxidation/chemical-deoxidation”, provide major opportunities for simultaneous SO₂/NO_x removal: Ellison, W (1995). Hydrogen peroxide, purchased and injected as a 60% solution in water, is believed to be a highly economical chemical oxidant for NO to NO₂ conversion. Relevant operations include

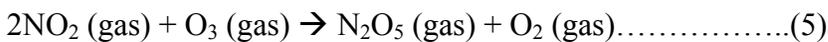
lime-based dry scrubbing, chemically augmented with sodium carbonate to provide adequate sulfite (and sodium) ion formation.

BOC Gases' proprietary NO_x oxidation process is a commercial preoxidation system arrangement in which ozone oxidant is used to convert NO (and NO₂) in the raw flue gas to highly water-soluble N₂O₅ gas, Ferrell, R J et al (2004):

Instantaneously:



Thereafter, with adequate flue-gas residence time and applicable flue gas humidification/cooling:



Extremely soluble, (akin to HCl gas), the N₂O₅ is efficiently removed in any scrubbing medium, dry or wet, (including even nitric acid solution):



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