

REMOVAL OF NO FROM COKE OVEN GAS

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This report deals with a recently developed process for the removal of NO from coke oven gas or similar gas mixtures. Coke oven gas contains a few ppm NO. NO and NO₂ react with cyclopentadiene to form gums at normal temperatures and easily decomposable nitrosate-complexes at low temperatures. Gums are known to be a source of troubles in gas distribution systems, nitrosate-complexes a cause of heavy explosions in low-temperature gas separation apparatuses.

The here-described method of removal of NO consists in adding to the coke oven gas ClO₂ diluted with air or nitrogen, preferably 2 vol. ClO₂ per vol. NO; ClO₂ oxidizes 95% and more of the NO within a few seconds. The products of reaction, mainly NO₂ and NOCl as well as unreacted ClO₂, are then eliminated by contacting the gas mixture with alkaline reducing means, e.g. sodium thiosulfate or arsenic acid dissolved in caustic soda or in bicarbonate (NaHCO₃ - Na₂CO₃).

Removal of NO by this process is possible because the velocity of the reaction between ClO₂ and NO in coke oven gas is extremely high whereas the constituents of coke oven gas react with ClO₂ much slower, hydrogen sulphide excepted.

We admixed approximately 100 ppm of ClO₂ to H₂, C₂H₄, N₂, NH₃, H₂S and NO-free coke oven gas and determined, after 2 or 20 seconds, the remaining quantity of chlorine dioxide. Within 2 or 20 seconds, no chlorine dioxide consumption was observed. Only in gas mixtures which contained H₂S some chlorine dioxide has reacted. This shows that the admixture of a few cm³ of chlorine dioxide per m³ of coke oven gas presents no danger of violent reaction.

Equations describing the reaction of ClO₂ with NO are known from the literature. However, it can be assumed that in coke oven gas the reaction mechanisms of the nitrogen oxides with chlorine-oxygen compounds in coke oven gas is different from the reaction mechanisms in the pure ClO₂ - NO-system. We observed the following: if a stream of chlorine dioxide-containing nitrogen is added to NO-containing hydrogen, white smoke rises from the point where the two streams mix and only a small portion of the NO, e.g. 10%, is converted. The white smoke seems to be ammonium chloride; NH₄⁺ ions and Cl⁻ ions can be found in the smoke. Conversion of the NO increases to approximately 98% if 10% of coke oven gas are added to the hydrogen-NO mixture. This shows that some component of the coke oven gas influences the mechanisms of reaction between ClO₂ and NO. While the addition of carbon monoxide to the system has no remarkable effect, the NO is oxidized quickly and completely as soon as 1-1.5 percent of oxygen are added to the NO containing hydrogen.

We have no clear idea as to how oxygen influences the reaction with ClO₂, NO, H₂ and N₂; as to how it hinders the formation of NH₄Cl and favors that of NO₂. This is the reason why we desist from giving reaction equations.

After preliminary laboratory studies had been confirmed on a larger scale of NO-removal from a hundred cubic meters per hour of synthesis gas we turned to practice the new method in an industrial plant *), where 2,500 cu. m/hr. of a cracking gas under 16 atm pressure had to be freed from about 0.5—2 ppm NO. This gas mixture is freed from the bulk of its CO₂ content by washing with water under pressure and the remaining 0.2—0.3% CO₂ are removed by means of soda lye in two subsequent washing towers.

The NO removal process is inserted between these two purification steps. Figure 1 shows the scheme of the arrangement. In the separator (1) any liquid water, drawn from the waterwash is carefully separated from the gas mixture. Then, per each liter of NO, 2 liters of ClO₂ admixed to 7—15 cu. m./hr. of nitrogen, are blown at (2) into the main gas stream in counter current and with high velocity, therefore also with high turbulence. During the time of 4—8 seconds, in which the gas passes the reaction tube (3), the ClO₂ has oxidized practically completely the NO in the gas mixture. In the soda lye of the caustic scrubbers (4) and (5) more than 90% of the reaction products NO₂, NOCl and also of the surplus ClO₂ are absorbed.

Naturally for any low temperature gas separation process the removal of these reaction products and of the surplus chlorine dioxide is as important as the removal of the NO itself and has to be driven as far as possible. To this end reducing agents, e.g. sodium thiosulfate or arsenic acid are added to the soda lye in at least a quantity sufficient to reduce all introduced ClO₂ - gas to the ClO₂⁻ ion (chlorous acid ion) resp., to reduce NO₂ gas to NO₂⁻ ion (nitrous acid ion). This means that per liter NO in the gas mixture practically 40 g Na₂S₂O₃ · 5H₂O are added to the soda lye filling of the second tower. (5). OH⁻ ions and S₂O₃²⁻ ions may be used up in the same time. When the soda lye of the first tower (4) has become neutralized by CO₂ it is replaced by the nearly fresh and reducing lye of the second tower (5) which is replenished with the complementary load of lye and reducing agent.

The gas which leaves the soda lye tower (5) contains as a rule not more than 2—3% of its original content of NO and often less. The two caustic scrubbers in series normally lower the initial CO₂ content of the gas mixture (2,000 ppm CO₂) to some few thousandth (1—3 ppm CO₂) and so they act as alkaline reducing scrubbers with the reaction products. In the gas behind these scrubbers only very small traces of NO₂, Cl₂, ClO₂ or similar substances could be found, e.g. 0.004 ppm ClO₂ and 0.002 ppm NO₂.

In the pilot plant a washing tower (6) had been provided with circulating alkaline thiosulfate-solution as a last barrier against any break through of traces of

*) The laboratory work and plant tests were carried out by Dr. H. Manhard

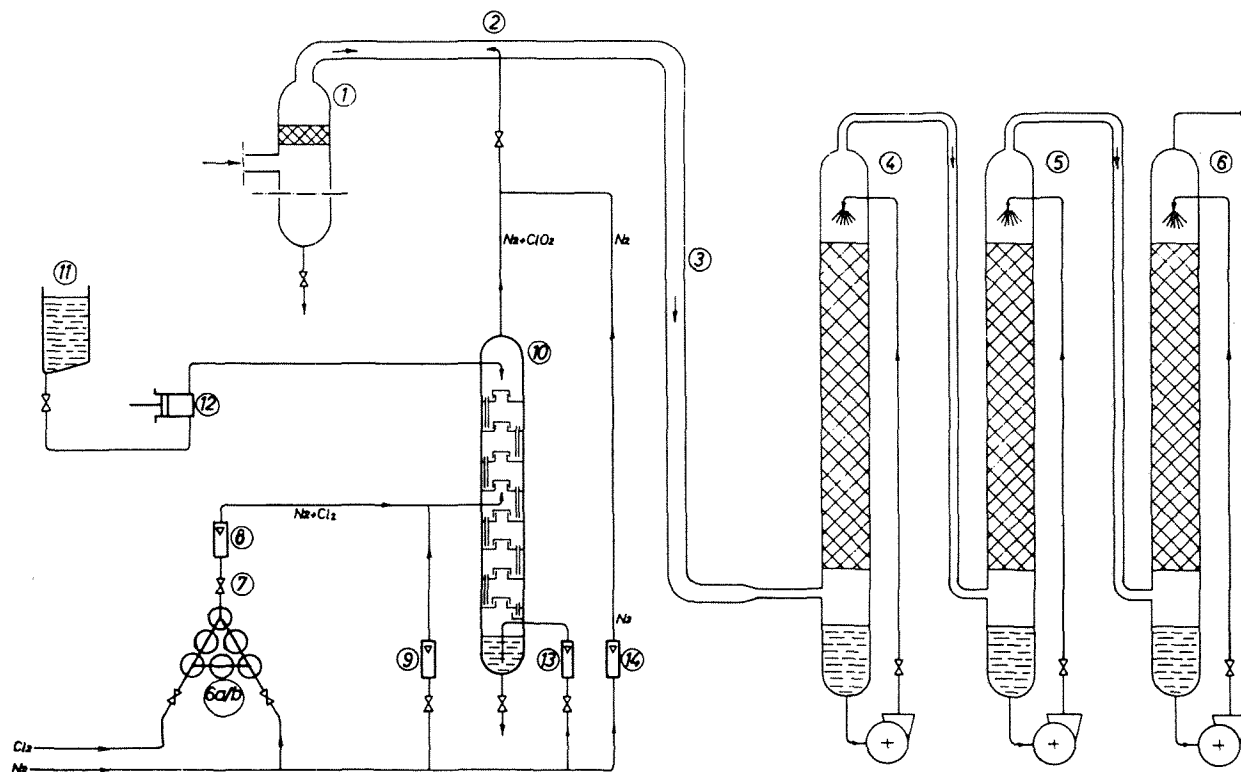


Figure 1. Removal of NO from coke oven gas with ClO_2 .

reaction remainders. Behind this tower no NO_2 nor ClO_2 at all could be detected even with our most sensitive testing method, that means less than $1.2 \cdot 10^{-4}$ ppm ClO_2 .

In normal low temperature practice adsorption means are provided at different temperature stages. Any traces of ClO_2 or NO_2 that incidentally would enter the separating device will be retained here.

The mixture of $\text{ClO}_2 - \text{N}_2$ to be introduced into the NO-containing gas must be available at a slightly higher pressure than the pressure of the gas mixture to be cleaned, e.g. 17 atm. abs. Therefore the mixture was produced under such pressure.

In interchangeable steel flask bundles (6a) and (6b) chlorine-nitrogen mixtures with about 2% Cl_2 were stored under pressures of 30 to 150 atmospheres and kept ready for use. Air can be used instead of nitrogen, if any increase of 0.1–0.2% O_2 in the gas mixture is allowable and if the mix proportion of air and gas is secured.

The necessary quantity of $\text{Cl}_2 - \text{N}_2$ was withdrawn over the reducing valve (7), measured in the rotameter (8), then diluted with nitrogen from rotameter (9) and introduced into the lower part of reaction column (10). A solution of NaClO_2 , stored in the container (11), was fed by the metering pump (12) to be head of the column (10) at a pressure of 17 atm. abs. The gaseous ClO_2 , developed by chemical reaction, was then stripped by nitrogen from the downtrickling liquid. The lean solution collected at the bottom of the column was stripped with a small quantity of nitrogen measured in rotameter (13).

The total quantity of nitrogen introduced into the washing column must at least be so great that the partial pressure of ClO_2 at the head of the washing column is considerably less than 0.1 kg/cm² absolute. A pressure of 0.1 kg/cm² is a safety limit for the self-decomposition of the ClO_2 gas. At a total pressure of 17 kg/cm², 0.6% ClO_2 is thus the maximal admissible concentration of ClO_2 . Practically, the concentration of ClO_2 is

smaller because by far more nitrogen is necessary for the stripping of the solution.

Through rotameter (14) so much nitrogen is added to the top gas of the column that the total quantity is about 0.2–0.5% of the quantity of the gas mixture to be purified.

An advantage of the use of chlorine gas as a raw material is its low price and the high degree of utilization of the NaClO_2 solution. Working with gaseous chlorine does, however, not exclude that gaseous chlorine might enter the gas to be purified if, accidentally, the counter-flow of the sodium chlorite lye would fail. The reducing capacity of the alkaline reducing wash agent being adapted to the moles ClO_2 , there is no doubt that the alkaline reducing wash in the towers (4) and (5) would take up chlorine gas which has gotten through.

However the production of ClO_2 from NaClO_2 solution is also possible without the use of chlorine, e.g., by adding to the NaClO_2 -solution an acid, e.g., HCl and besides the acid, an accelerator like FeSO_4 and stripping from the mixed solution the produced ClO_2 gas with air or nitrogen.

It is true, in such a reaction the yield from the NaClO_2 -solution is somewhat lower. But such reaction is easier to perform, to supervise and to automate. This reaction type has, furthermore, the advantage, that the stripping gas is always free from chlorine and that, therefore, in the strip gas stream, no corrosion problems for containers, tubing, valves, gaskets and rotameters will arise. In our pilot plant such a system is just now being tested.

As is shown in Figure 2 a metering pump set is installed with a common motor (6) driving four metering pumps (1–4) on the same shaft. Two of them (1) and (2) will feed reactant solutions (NaClO_2 or FeSO_4 ; HCl resp.) to reaction-column (5), the third (3) will expand the lean solution, in other words the sum of the liquids (1) and (2), from the bottom of the column (5), while the fourth (4) will deliver to spray nozzles (7) thiosulfate solution of a reducing capacity sufficient to remove the

products of reaction of NO and the surplus ClO_2 introduced into the main gas stream at (12).

The mix proportion of the various fluids can be determined by setting the stroke lengths of the various metering pumps while the total delivery can be adjusted to process requirements by common speed variation of the shunt motor (6), and this, if desired, automatically, responsive to instrument control signals (9) of the main gas flow (10) and/or its NO content (11). In this country automatic NO-analyzers are common practice on the market. In Europe self-made automatic analyzers are in use here and there.

If NO is to be removed from town gas or generator gas, which usually are produced and used at nearly normal pressures, the ClO_2 gas naturally will be also produced at low pressures. Nitrogen usually not being available in gas works, blower air will be used as strip gas. In town gas there is no need for washing out the carbon dioxide with soda lye. It would be too expensive.

The thiosulfate solution then is buffered with sodium carbonate. The pH value, the alkalinity of the carbonate-bicarbonate solution, at 2% CO_2 in the gas phase is sufficient to secure the reducing potential of the thiosulfate. In order to dispense with a special washing tower, the thiosulfate solution can be sprayed into the main gas stream and the lean liquid then taken out by a demister or a cyclon. Figure 2 shows by way of example the thiosulfate pump (4), the spray nozzles (7), and the demister (8).

The removal of 1 liter NO per hour from a gas mixture (e.g. 1 ppm in 1000 cu.m./hr.) requires per year and costs:

183 kg	NaClO_2 techn. grade 80%	DM 650.—
41 kg	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	DM 62.—
275 kg	HCl conc.	DM 55.—
360 kg	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$	DM 192.—
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		DM 959.—

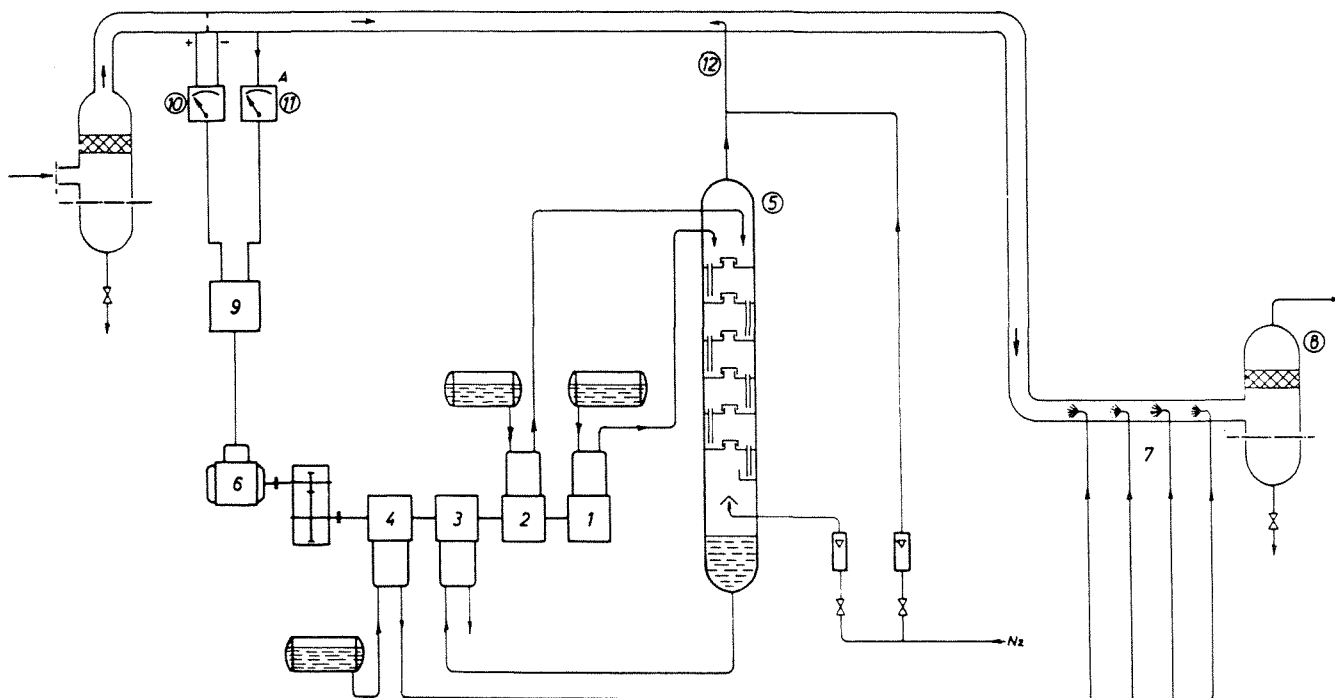


Figure 2. Removal of NO from coke oven gas with chlorine dioxide.