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Heat exchanger explosion at a nitrogen-wash unit

Stringent safety requirements are vital when considering hazards of the oxides of nitrogen.

A N UNEXPECTED EXPLOSION IN THE VICINITY of the $-130°$ to $-145°C$ section of the second heat exchanger at the Mekog nitrogen-wash unit occurred on July 13, 1959, causing severe damage. The explosion occurred while the unit was working under full load after being in normal service for 42 days. Prior to this, the unit had been completely thawed and washed with caustic solution. Despite the great damage, there were fortunately no personnel injuries.

Process under consideration

The normal process in the production unit concerned is as follows: A gaseous mixture is obtained by partial oxidation of fuel oil using steam and O_2. Soot is removed by scrubbing with H_2O, the gas is then purified of sul-

fur compounds by means of scrubbing at 17 atm. abs., after which the CO is converted.

A volume of 17,000 cu. m. of gas at 1 atm. and $15°C$ is then passed to a H_2O scrubbing circuit (Figure 1) where CO_2 is removed. The quantity of H_2O used is 1900 cu. m./hr., the quantity of make-up H_2O every 24 hr. is about 40% of the H_2O inventory. The gas is subsequently washed with caustic solution after which 10,500 standard cu. m. of gas/hr. remains.

The gas thus obtained contains 0.1% of O_2, less than 5 ppm of unsaturated hydrocarbons (mainly C_2H_4), and 0.1 to 0.5 ppm of NO, while C_2H_2 and dienes are only present in traces (less than 0.01 ppm of each). This gas passes into the nitrogen-wash unit

which consists of two parallel, interchangeable first heat exchangers ($+$15° to $-90°C$), one second heat exchanger ($-90°$ to $-185°C$), one third heat exchanger ($-185°$ to $-190°C$), and the wash column. There are also separators for ice and liquid fractions between the heat exchangers. The heat exchangers consist of vertical-tube bundles, and the incoming gas flows around the tubes through a space which is subdivided by means of horizontal baffle plates.

Because of the recognized danger of NO explosions in coke-oven gas splitters, great care was taken in operating the unit. The NO content of the incoming gas was determined every day in order to maintain an accumulation of NO less than the 5 kg. limit which was accepted in 1958. This limit seemed to be completely trustworthy in view of the extremely low hydrocarbon content and operating experience with coke-oven gas splitters of half this capacity, in which up to 4 kg. of NO repeatedly accumulated.

Circumstances of the explosion

The heat exchanger, which was 8.0 m. long, was torn apart laterally and snapped off. The tubes burst apart
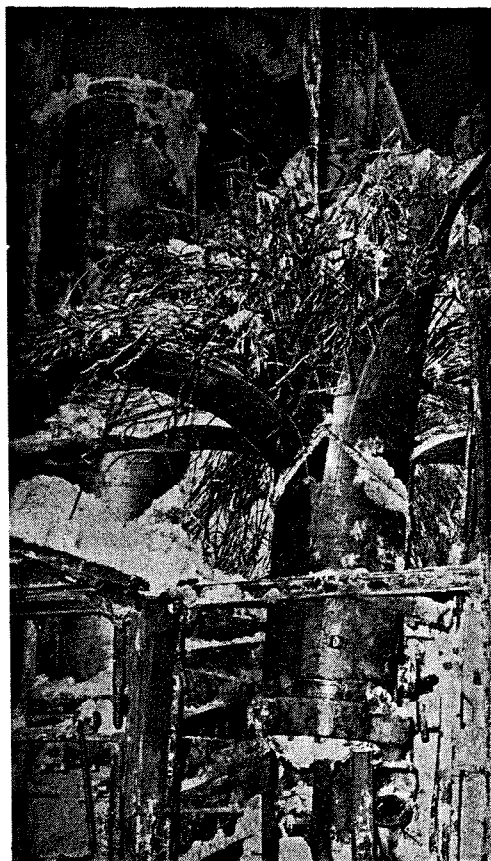
Exploded heat exchanger showing where shell was torn apart laterally and snapped off and where tubes burst.
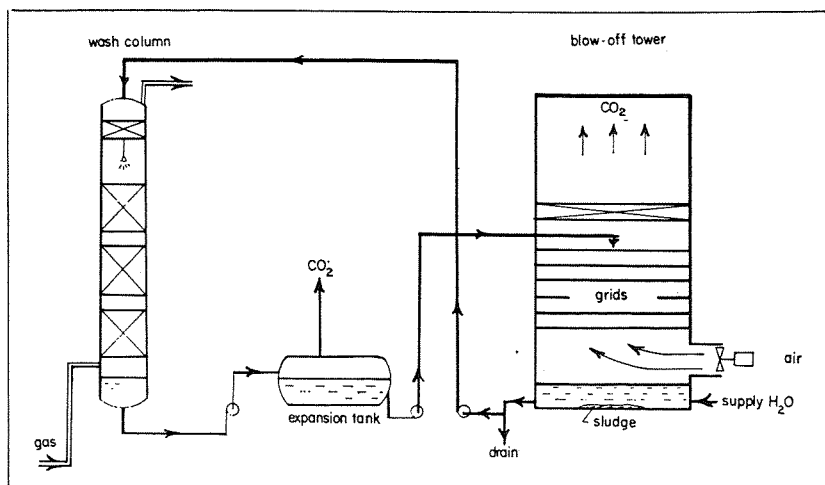

Figure 1. Flow through scrubbing unit where carbon dioxide is removed.

and were thrown out of the shell, as shown in the introductory photograph. The twisted part was about 1.5 m. long. At the break, the tubes were pressed together lengthwise, indicating an explosion in the space for the incoming gas.

According to an explosions expert, the general picture indicated the rapid explosive combustion, perhaps lasting 0.1 to 1 sec., of some 3-5 kg. of explosive material. At the time of the explosion, 5 kg. of NO had accumulated in the unit, the accumulation having been unexpectedly rapid.

It had been found that on warm summer days the gas desorbed an unusually large amount of NO from the scrubbing water (*i.e.*, 0.4 to 0.6 ppm) as shown in Figure 2. The

day before the explosion, as much as 0.8 ppm of NO was measured at the inlet; this, however, was considerably less than the maxima which have occasionally occurred in the coke-oven gas splitters (1 to 2 ppm).

During earlier operating periods of the nitrogen-wash unit there had been accumulations of 3.8 kg. of NO with a maximum NO content in the gas of 0.26 ppm, of 6.9 kg. of NO with a maximum of 0.6 ppm, and of 4.7 kg. of NO with a maximum of 0.6 ppm.

Possible explosion causes

Available facts indicate that in a nitrogen-wash unit for converted gas, explosions can occur spontaneously when 5 kg. of NO has accumulated
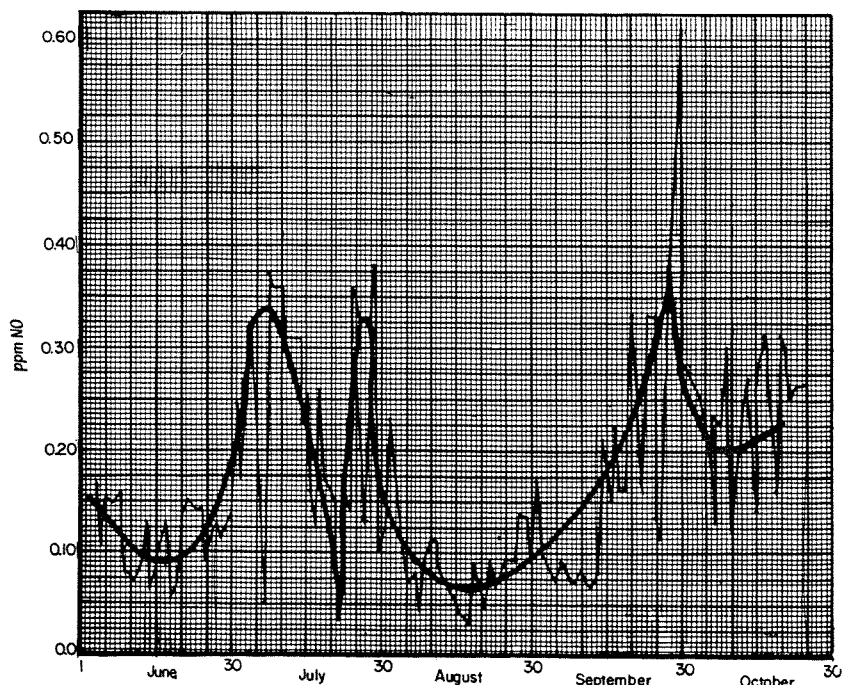

Figure 2. NO concentrations after water washing during summer months.

Key:
1. KMnO₄ solution
2. α-naphtylamine solution
3. sufanilic acid solution
4,5. open to the air, guarded by an active carbon filter
6. glass filters
7. glass cocks
8. capillary
9. capillaries and reagent-mixing vessel
10. glass spirals
11. exit KMnO₄ solution
12. rotameter
13. capillary
14. pressure regulator
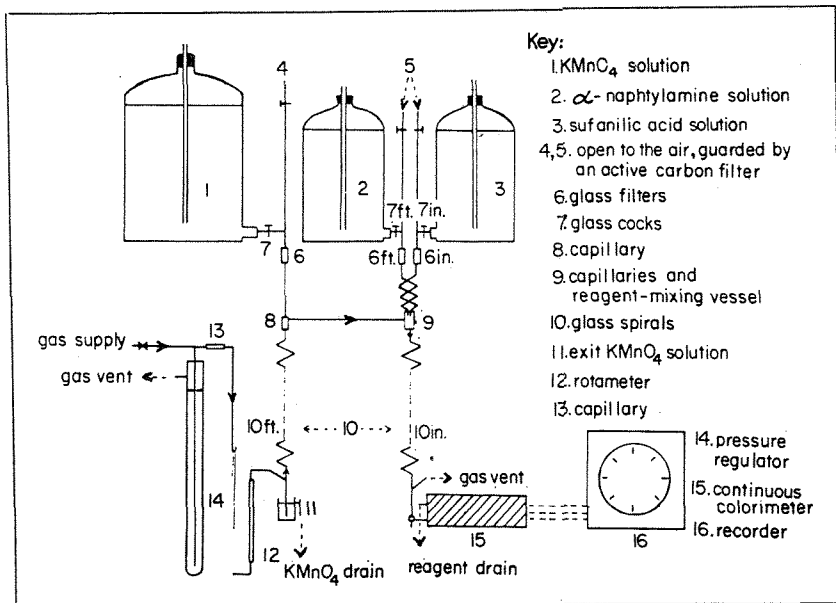15. continuous colorimeter
16. recorder

Figure 3. Flow system for continuous analysis of nitrogen oxide.

in the form of resins. Considerable amounts of N_2O, which seems to have been present, may also have contributed to the force of the explosion.

A study was made of the absorption of NO and N_2O in the gas during the CO_2-scrubbing process in the warmer months of the year, Table 1. Absorption of NO can be explained in various ways:

Table 1. Accumulation of oxides of nitrogen in the nitrogen wash.

	Oct. 1958	Jan. 1960	May 1960	Aug. 1960
total gas intake, cu. m.	31.10^6	20.10^6	26.10^6	19.10^6
total NO intake, liter.	5100	<200	409	850
total N_2O accumulated, l.	7440	100	38	960
accumulated N_2O/cu. m. gas intake, ppm.	0.24	0.005	0.0014	0.005

1. By the reduction of nitrate from the water as a result of inorganic conversion. Possible sources of the nitrate are NH_4NO_3 dust blown in from the nearby calcium ammonium nitrate plant and the nitrate content of the make-up water. The reducing agent might be traces of H_2S from the gas and ferrous sulfide from the tank sludge.

2. NO can be formed as a result of microbiological conversion of nitrates in the acid medium of the CO_2 washing towers by denitrifying bacteria (1). The presence of these bacteria has been proven at Mekog.

3. The formation of nitrite by nitrifying bacteria from NH_3 in the degassifier. At the time of the explosion, however, there was no clear evidence of the occurrence of this phenomenon.

The fact that NO accumulation in warm weather does not fluctuate markedly with the temperature of the H_2O, but fluctuates in periods of a few weeks, is a clear indication that the most pronounced NO-peaks in summer are attributable mainly to mi-

crobiological activity. The accumulated resins must have been derived chiefly from compounds of C_2H_4, etc., and NO; for the diene content is too low (0.01 ppm) to fix all the NO (about 0.5 ppm). It could not be determined whether the accumulated N_2O, which is present in about the same quantity as NO, was also partly bound to hydrocarbons.

Preventing explosions

The following steps were immediately taken to prevent explosions:

1. $Na_2Cr_2O_7$ was added to the CO_2 wash-water circuit until about 10 mg. of dichromate per liter was present. In this way the amount of NO in the gas was reduced from 0.6 to less than 0.1 ppm in 24 hr. By continuing this, in the winter months NO contents of 0.005 ppm and lower were attained in the gas.

2. The sludge was cleaned from the water tank of the CO_2 washing unit.

3. NO accumulation was limited to 1000 liters; alternately, as a temporary measure, the equipment was thawed and flushed with caustic every three months.

4. A maximum permissible NO content of 0.1 ppm was fixed and it was arranged that production should be stopped if this limit was exceeded.

5. The NO content was continuously checked and recorded. For this purpose an analyzer was developed with a sensitivity of about a few thousandths ppm of NO, calibrated by means of standard sodium nitrite solutions and also with a standard gas with known doses of NO in the range of 0.006-0.1 ppm.

The analyzer, Figure 3, indicates NO by oxidation with permanganate to NO_2, followed by colorimetric determination with Griess reagent, a mixture of α-naphthylamine and sulfanilic acid. The liquids are passed at constant rates from flasks by glass filters and resistance capillaries (to stabilize the flow) to the reacting spirals. The colorimeter has a compen-

Table 2. Plant conditions for comparing behavior of NO resins.

	N_2 WASH UNITS	COKE-OVEN GAS SPLITTERS
Gas load	10,500 m³/hr.	5,000 m³/hr.
Pressure	17 atm.	13 atm.
Gas composition:		
NO, ppm	0.1-0.5, max. 0.8	0.3-1.0, max. 2.0
N_2O	present	present
O_2	0.1%	0.1%
C_2H_4	1-7 ppm	1.5-1.8%
C_3H_6	<0.5 ppm	0.1%
C_2H_2	<0.01 ppm	0.05-0.1%
Saturated C-H excl. CH_4	2-7 ppm	about 2.0%
Max. NO load	5000 g.	4000 g.

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sating photoelectric setting to register minor extinction differences.

For the future, the possibility is being studied of removing the NO and, if possible, also the unsaturated hydrocarbons and N_2O from the gas at low temperatures by means of an adsorbent. Molecular sieves and activated carbon are being considered for this purpose.

Behavior of NO resins

It is possible to make a comparison of the behavior of NO resins in coke-oven gas splitters and in units for washing converted gas with N_2 since we have operating experience with both types. The conditions in the plant are shown in Table 2.

It is apparent from this table that the gas for the coke-oven gas splitters contained more NO and much more unsaturated hydrocarbons than the converted gas. Nevertheless, there were no particular difficulties under these conditions in the coke-oven gas units, whereas in the nitrogen wash unit, a spontaneous explosion occurred during normal operation.

Without going into details on the many differences between the two units, it can be stated that one difference must be considered fundamental, namely that in the coke-oven gas splitters any NO resins formed will always be amply moistened by the large excess of condensing hydrocarbons. In view of the uncommonly low vapor pressure of the hydrocarbons in the unit for converted gas, the resins formed there will actually remain dry. We now think it probable that this difference is the cause of the greater unstability of the resins in our nitrogen-wash unit.

For this reason we believe that for gases with a low hydrocarbon content still more stringent requirements should be made as regards NO content and accumulation than in the case of coke-oven gas units. #

LITERATURE CITED

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Questions and answers

KERRY—American Air Liquide, N. Y., N. Y.: The problem of contaminants in N_2 scrubbing units dates back over thirty years. Although considered only recently in this country, a great deal of published information is available in Europe where intensive study has been done on the reactions of NO or NTO with dienes. The way they solve them in coke oven gases is to actually induce the formation or the chemical reaction of NO or NTO with the

dienes in empty reactors before the coke oven gas plant itself (*i.e.*, the exchanger system). They do that by permitting the feed gas to go through an empty tower right after the compressor. After a period of time the empty reactor is washed down with caustic, and these gums are removed.

The percentage of NO encountered in coke oven gas operation is extremely low (0.1 is very high, while 0.05 is more acceptable). Obviously you can not afford to shut a plant down every several months just to wash it down. With respect to treatment of other hydrocarbon gases, engineers want to know the quantities of NO, heavy hydrocarbons, and C_2H_2. In most cases, the NO, very fortunately, is extremely low. As far as we are concerned, we can only afford to ignore NO if it's magnitude is about 0.01%. With concentrations beyond that, steps have to be taken to treat NO and to remove it. NO can come into a feed gas which has been prepared by partial oxidation not necessarily through combustion, but through external means such as water wash-

ing. If such a thing does happen, NO obviously has to be removed, and I think low temperature absorption may be practical.

In Europe most of the hydrocarbon separation units use the front exchangers to remove water, in other words, as driers in terms of sequence or switch changes. We prefer to use driers ahead of them. While driers are certainly no cure-all insofar as absorption of contaminants, we feel that they may absorb some of the dienes that cause trouble. This is no solution if the NO goes beyond 0.01%.

Acetylene is another problem that has been looked at for a good many years. If the C_2H_2 content is serious enough, we always recommend that the feed gas be hydrogenated unless, of course, there is sufficient C_2H_4 in the feed gas. In that case, we normally put in a special exchanger which is nothing more than an C_2H_4 reflux condenser. We use C_2H_4 to wash out C_2H_2 since the two form an azeotrope. However, you must have a quantity of C_2H_4, in the order of 20-25 times the C_2H_2 content.

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Nitrogen wash incident

Process safety modifications include replacement of carbon steel pipe subjected to low temperatures, better instrumentation and control systems.

ON THE AFTERNOON OF MARCH 12, 1960, approximately 70 ft. of a schedule 40 carbon steel line containing H_2 at a pressure of 325 lb. was suddenly subjected to liquid N_2 temperatures causing the line to rupture with explosive violence. Despite the fact that fragments were thrown in all directions with sufficient force to embed themselves into the lagging of adjacent equipment, no one was injured and little damage was done to nearby lines or equipment.

Just prior to the line rupture, the operation of the N_2 wash system had not been stable or satisfactory. In fact, only 4 hr. earlier it had been necessary to back feed gas out of the boxes because of cold warm-ends on the heat exchangers.

After the cold warm-ends had recovered, feed gas was reintroduced and shortly thereafter trouble began. The first symptoms of trouble were cycling temperatures and gas compositions from the wash column. As had been done many times in the past, control instruments were placed in manual in an effort to break this vicious temperature and composition cycle that was obviously becoming more extreme as time went on. Finally, the temperature alarm in the carbon steel piping sounded, which indicated that the temperature had fallen to $-20°C$.

The operator pressed the toggle switch in the 60 point potentiometer to read the temperature, and found it to be $-120°C$ and falling rapidly. He