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TO: F. E. Adley

FROM: C. P. Skillern

July 25, 1957

NITROGEN OXIDES IN THE ENVIRONS OF PUREX AND REDOX STACKS

A limited survey of the concentration of NO_2 near the Purex and Redox process stacks was conducted to determine the general relationships between the stack emission rates and the persistence and amounts of this gas at the ground level. It had been observed that when certain adverse meteorological conditions existed there was obvious contact of the stack gas plume and NO_2 with the ground. Because of the potential danger of an individual inhaling this gas, grab samples were collected to determine the concentrations of NO_2 at ground level. Subsequent to the preliminary grab sampling, a continuous recording of NO_2 concentration was obtained with a recently developed NO_2 monitor.(1)

Nitrogen dioxide is an insidious gas which may be respired with minor irritation to the upper respiratory tract or lungs, but it will solubilize in the lung fluid and form nitrous or nitric acid. This insult to the body may go unnoticed until the individual receives an acute amount of NO_2 and then may develop a fatal edema of the lung. An upper limit of 5 ppm for the concentration of NO_2 was established by the American Conference of Governmental Industrial Hygienists as the

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(1) HW-47559, C. P. Skillern, A Portable Multi-Range NO_2 Gas Monitor.

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maximum allowable concentration (MAC) for an eight-hour work day. For shorter exposures the body will tolerate a higher concentration, and 25 ppm(1) is suggested as safe for a few minutes. Experience indicates 200-700 ppm(2) is rapidly fatal, and in a case simulating conditions(3), where a welder received a lethal exposure, the concentration was measured between 200-500 ppm.

In metal dissolution, NO_2 (90%) was evolved with a minor amount of NO (10%) present. This was checked by drawing the gas over silica gel, which removed 65% of the NO_2 selectively(4). The metal dissolving at Purex and Redox releases a relatively large amount of these gases. Nitric oxide, when it comes in contact with the oxygen of the air, is probably converted rapidly to NO_2 because NO, in concentrations greater than 100 ppm in the presence of O_2, is quickly converted to NO_2. Nitric oxide can be considered a source of NO_2 even at lower concentrations in the presence of O_2, but the conversion is much slower. Nitric oxide, itself, is only mildly toxic, exhibiting mainly a narcotic effect.

The NO_2 monitor used in this study utilized the color sensitivity associated with the diazotization of N-1 naphthylethylenediamine dihydrochloride. The resulting color intensity of the solution was then measured photometrically (540 mμ) and recorded. The instrument detects NO_2 concentration from 0.25 ppm up to 5000 ppm with provision to extend it up to 15,000 ppm. The range of this instrument made it effective during this study, because it was applicable to measurements of stack and environmental conditions.

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(1) Hygienic Standards, Industrial Hygiene Quarterly, p. 232, June, 1956.

(2) Henderson and Hagard, Noxious Gases, Rheinhold, 1943.

(3) Adley, F. E., "Exposure to Oxides of Nitrogen Accompanying Shrinking Operations," J. Ind. Hyg. & Tox. 17, Jan. 1946.

(4) HW-30331, W. E. Gill, Unpublished data.

The initial phase of the study was to measure the amount of NO_2 and NO being emitted from one of the stacks while the NO_2 gas monitor was being developed. Grab samples were collected from the sampling manifold at the 200 ft. level to study the rate of NO_2 emission during various periods of the dissolving cycle. These samples were collected in evacuated flasks and the NO_2 determined by the phenol-disulfonic method. Generally, it was found, by grab sampling techniques, that the amount of NO_2 being evolved was a function of the concentration of the acid in the dissolving solution, and the temperature.

The NO_2 gas concentrations at the T and B plants were previously found to contain bi-modal peaks which were attributed to the heat of reaction from concentrated acid being introduced directly on the slugs.(1) This process heated by the dissolution reaction was cooled by cold water jackets in the walls of the dissolution reaction was cooled by cold water jackets in the walls of the dissolution chambers. This process was cooled twice in the old T and B plant process.

Purex and Redox plants utilize a process where the heat evolved in the dissolution of the metal can be controlled and brought to a definite level by dilution of the acid. The amount of NO_2 evolved from the stack was found to be uniform after building up, then tailing off as the process was completed.

The monitor was applied to the Purex stack. Typical recordings are shown in Figure 1. The initial rise in concentration continues for approximately 1½ hours. This is followed by several hours of some variation 25 to 50 ppm and then a tailing off period that can last up to six hours. When two dissolvers are placed in operation they are additive.

Continuous monitoring was conducted at the Army Camp 518th AAA Bn. Delta Battery, which is located 5000 feet southwest from the Purex stack. The NO_2 monitor was operated in this area for a period of one month. In Figure 2 the results of the recordings made in this area are given. During this time the concentration varied from a trace up to 8 ppm, and the duration of the contact

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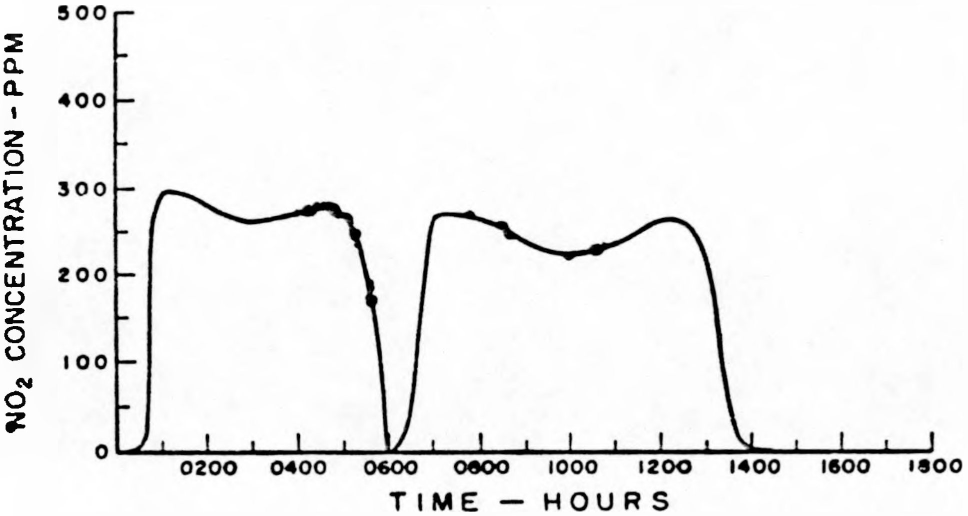
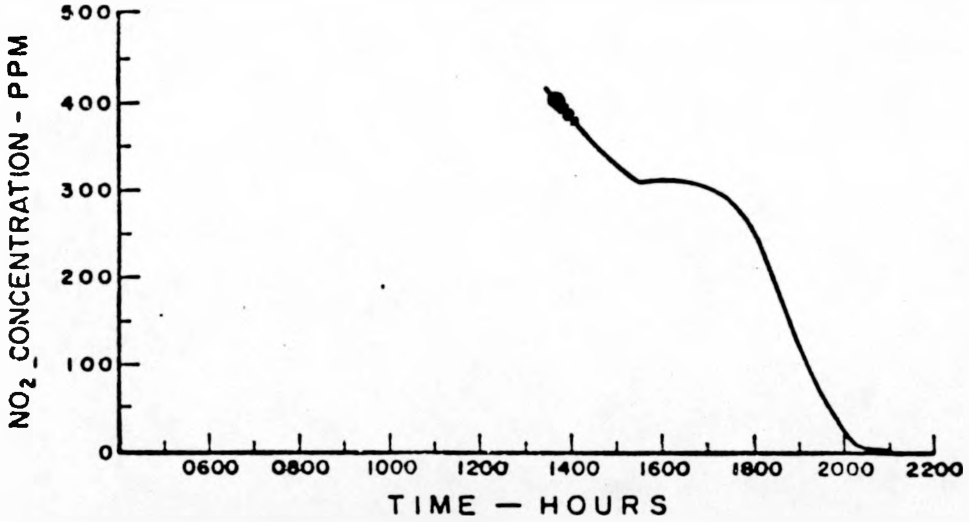
(1) HW-25128, H. B. Perry, Ground Exposures to Oxides of Nitrogen From 200-B and 200-T Process Stacks.

FIGURE - 1
TYPICAL PUREX STACK CONCENTRATIONS OF NO_2
DURING METAL DISSOLUTION



DISSOLUTION ONE DISSOLVER 1st & 2nd CUTS
AUGUST 17, 1956



FINAL PHASE OF TWO DISSOLVERS (A, B)
SEPTEMBER 7, 1956

NO_2 Concentrations

May 30-June 30, 1956

Army Camp 518th AAA Bn. Delta Battery
5,000 ft. S.W. Purex Stack

Date	Time	Dissolver Operation	Direction & Wind Speed mph*	ppm	Time	Duration
5/30/56	0030 - 0828 0930-1640	Normal Operation	NW 5	3-5	0215	30 min.
5/31/56	0730-2040 2350-0705 (6/1)	Normal Operation	NW 5	4-8	2345	5 min.
6/1/56	1830-0317 (6/2)	Normal Operation	WSW 10	1	2100	3 hrs.
6/5/56	1825-0050 (6/6)	Normal Operation	[illegible] 5	1-2	1945	5 min.
6/6/56	2310-0600 (6/7)	Normal Operation	SW 10	1-2	0030	30 min.
6/11/56	0155-1530	Normal Operation	NNW 2	1-2	0715	10 min.
6/15/56	1800-0315	Normal Operation	WSW 10	1-2	2230	60 min.
6/21/56	0415-0925	Normal Operation	W 10	0.5-2	0745	1-2 min.
6/25/56	0925-1615	Normal Operation	Var. 10	3	2000	45 min.
6/28/56	----		NW 8-18	3-5	0205	5 min.
6/29/56	Continuous Dissolving	Healing Out 2 Dissolvers	NW 10	2-3	1115	5 min.
"	"	"	"	"	1245	"
"	"	"	"	1	1300	30 min.
"	"	"	"	2-3	1445	15 min.
"	"	"	"	8	1540	"
"	"	"	"	1	1800	6 min.
"	"	"	"	5	2100	1 hr., 15 min.
6/30/56	Continuous Dissolving	Healing Out 2 Dissolvers	Var. 3	5	0930	15 min.
"	"	"	Var. 5	3	1200	10 min.
"	"	"	Var. 3	1	1300	8 min.
"	"	"	Var. 3	1	1900	15 min.

* Meteorological Station Data.

Figure 2

of the plume with the ground varied from one minute up to a three-hour period. The first two NO_2 contacts with the monitor were made when two dissolvers were in operation and the concentration was generally higher during that time. A larger number of contacts were made during the hours of darkness. The wind direction, as supplied from the Meteorological Station, was generally out of the northwest. One contact was made when dissolving was just completed at Purex and might be attributed to residual NO_2. Samples collected when the wind was from this direction were found to have higher concentrations.

The typical dissolution cycle of Redox stack was recorded and is seen in Figure 3. The Redox plant usually operates one or two dissolvers. Occasionally, three dissolvers will be in operation. A dissolution cycle was seldom found when three dissolvers were operating at the same time. However, an occasion arose on October 28, 1952, as seen in Figure 3.

Environmental samples were collected at the 2614-[illegible] Building by the NO_2 monitor and grab samples about 800 feet southeast from the Redox stack and other areas adjacent to Redox, Figure 4. The concentrations varied from 0 up to 138 ppm. A grab sample containing 78 ppm NO_2 was collected at a distance of 1000 feet from the stack. Grab samples were collected only when a plume was detected by olfaction.

Summary and Conclusions

The concentration of NO_2 effluent from Purex and Redox will average about 300 and 1500 ppm (0.565 mg/l and 2.82 mg/l), respectively, per dissolver at any time during the dissolving cycle except at the start and during tailing off. The average emission rate per dissolver from each stack was 420 lbs/hour at Redox Plant and 255 lbs/hour at Purex Plant.*

Samples collected in the environmental areas varied from zero up to 138 ppm. Ground contact 5000 feet from the Purex stack was found to persist up to 3 hours. Nitrogen dioxide contacts made by the NO_2 monitor 5000 feet from Purex

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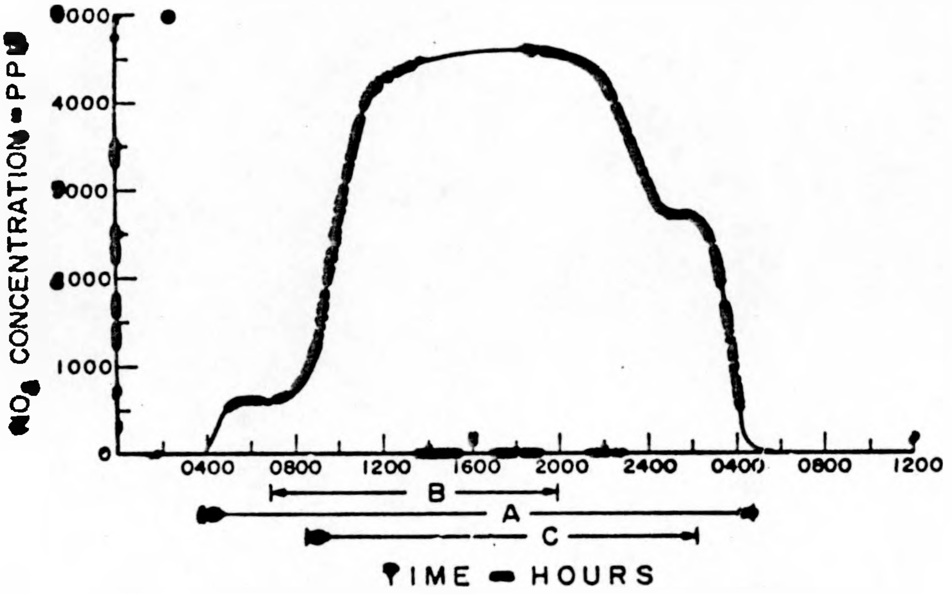
*The emission rates were based upon an airflow of 40,000 cfm for Redox stack and 120,000 cfm for Purex stack.

FIGURE - 3
TYPICAL REDOX STACK CONCENTRATIONS OF NO_2
DURING METAL DISSOLUTION



3 DISSOLVERS IN OPERATION
OCTOBER 28, 1956

ENVIRONMENTAL SAMPLING OF REDOX STACK

(Grab Samples)

Date	Sampling Location Distance - Yards	Wind Direction* Speed - mph	Meteorological* Dilution Factor	Dissolvers Operating	Concentration ppm
10/3/55	500 East	WNW 6	500	2	12
"	400 East	WNW 6	500	2	11
"	1800 Northwest	SE 3	450	2	12
"	10 South	NW 2	400	2	138
10/19/55	150 North	W 2	300	1	17
"	700 North	S 6-7	450	1	18
"	650 North	S 6-7	450	1	5
"	750 North	S 6-7	450	1	14
"	10 South	SW 3	[illegible]	1	90
5/1/56	300 South	S 5	---	1	2.0
5/3/56	400 Southwest	[illegible] 5	---	1	4.8
5/9/56	300 South	S 5	---	2	18
5/14/56	300 South	W 5	---	3	15
5/14/56	300 South	N 5	---	3	3**

* Meteorological Station Data.

** Contact made at 2614-W Bldg. with the NO_2 Monitor.

Figure 4

were generally at night and when the wind was from the northwest. One contact was made at the army camp when the dissolvers were not in operation at Purex, which was probably due to residual NO_2. The army camp received 9.5 hours exposure to NO_2 when the monitor operated in the area 720 hours.

The MAC for NO_2 is 5 ppm for an 8-hour work day. No criterion has been established for exposures to higher concentration except that there are numerous cases in the literature of fatalities following short exposures to concentrations that were respirable.

The concentration of NO_2 contacting the ground was found readily measurable in the environs of the Purex and Redox process areas. A complete air pollution investigation would require much more information. The toxic character of the gas represents a hazard, but a larger program would be necessary for complete analysis rather than the limited survey completed at this time. A re-study would be advisable after the new NO_2 scrubbers are placed in operation.

C. P. Skillern

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Industrial Hygiene Operation

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