

THE BEHAVIOUR OF CONTAMINANTS IN AN AIR SEPARATION PLANT

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Following an explosion in the vapourizer of an air separation plant of Dominion Foundries and Steel, Limited, Hamilton, Ontario¹, the Ontario Research Foundation was requested to carry out a study on the source and behaviour of contaminants in their three oxygen plants. This article is a summary of some of the results.

Analysis of process streams

Concurrent analyses were made at a number of points in the plants and at the air intake to obtain a contaminant balance. The range of concentrations

found after a number of trials is given in Table I. Examination of the differences in concentrations at various stages indicated that some accumulation was occurring in the cold equipment but owing to the nature of the sampling methods and the transient conditions existing in the cold section of an air plant no reliance could be placed on the quantitative value of these estimates. On the other hand, estimates of catalytic filter efficiency could be obtained with greater reliability. For operation of the filter at 300–330° F., this was found to be 40–80% for acetylene at a concentration level of 0.01–0.05 ppm.; partial oxidation of C₃–C₅ hydrocarbons, particularly unsaturates, was also indicated.

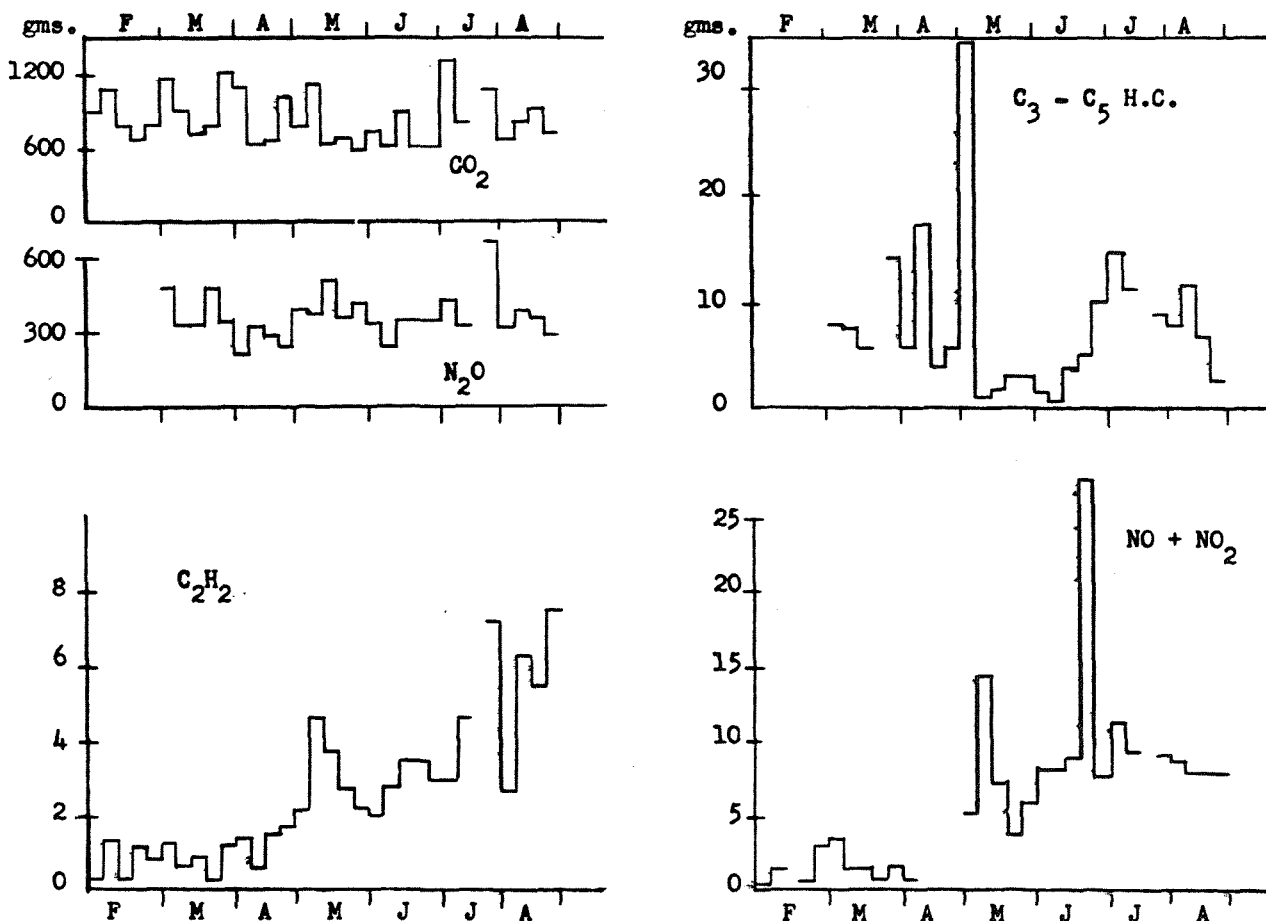


Figure 1. Weekly variation of contaminants on rich liquid filter.

TABLE I

CONCENTRATION OF CONTAMINANTS IN PROCESS STREAMS

	Before Rich	L.P. Column,*	L.P. Column,**
	Liquid Filters	Main Vapourizer No. 1 Plant	Main Vapourizer No. 3 Plant
	p.p.m.	p.p.m.	p.p.m.
Acetylene	0-0.1	0	0
C ₃ -C ₅ Hydrocarbons	0-0.1	0-1	0-0.1
Oxides of Nitrogen	0-0.04	0-0.01	0-0.01

* Gaseous take off of product O₂ from main vapourizer and no catalytic filter.

** Liquid take off of produce O₂ from main vapourizer.

Contaminant accumulation

The alternative approach of analysing the derime gases, in which much higher concentrations exist, was adopted as a means of providing data on contaminant accumulation in the various units of the plant.

The amounts of contaminants frozen on the walls of the regenerators after approximately one year of service are listed in Table II. The values are given as a range due to the variation in the flow rate of the derime gas. The C₃-C₅ hydrocarbons consisted primarily of butanes; propane, pentane, propylene and butene were also present. Both nitric oxide and nitrogen dioxide were also detected. These amounts do not necessarily represent the total quantities of such materials which had condensed on the walls of the regenerators over the year since, on the reverse cycle, when the regenerators are swept with nitrogen, a portion of them would probably have been revolatilized. The presence of materials with higher vapour pressures than C₄-C₅ hydrocarbons and nitrogen dioxide is unexpected in that their concentrations in the atmosphere are generally below that at which they would condense at the end conditions of the regenerators, viz. -170°C., 6 atms.

Main vapourizers

The amounts of materials held on the walls of the main vapourizers of these plants after one year of operation are given in Table III. Prior to the derime, the No. 1 Plant operated with gaseous take off from the main vapourizer and had no catalytic filter.

The C₃-C₅ hydrocarbons were all saturated paraffins, primarily n-butane and isopentane, except

in the No. 1 Plant where traces of 1-butene and isobutylene were found. Nitric oxide was present as part of the oxides of nitrogen. The amounts found are not thought to have constituted a significant explosion hazard in the main vapourizer. However, they are indicative of the occurrence of solid accumulations over long periods, even at the relatively low contaminant levels encountered at this plant site. The lower values for hydrocarbons frozen in the vapourizers of the No. 2 and No. 3 Plants tend to substantiate the designed purpose of liquid take off which is to reduce potential hydrocarbon accumulation in the main vapourizer.

The 300-700 grams of carbon dioxide found in the No. 2 Plant probably arose during difficulties at start up when carbon dioxide blockage of the low pressure column occurred. No reason was apparent for the distinctly different ratios of hydrocarbons to oxides of nitrogen obtained in the No. 2 and No. 3 Plants.

Silica gel filters

In preliminary work, contaminants held in the silica gel filters and the auxiliary vapourizer had been estimated on two or three occasions. However, in order to evaluate their efficiency and interdependence under random air pollution conditions a program was undertaken in which the rich liquid, liquid oxygen and auxiliary vapourizer were consecutively examined over a number of months. The No. 1 Plant, in which an auxiliary vapourizer and catalytic filter had been installed, was selected for this series of tests. During the tests, the auxiliary vapourizer was operated with a purge of 0.5% of the oxygen product.

Test results

The results from the derime tests from February to August, 1961, are tabulated in Tables IV, V, VI, and VII. The amounts on the rich liquid filters, which contain 800 lbs. of silica gel, are expressed as the total material derimed for a one-month period of operation, generally five filter switchings. The values for the liquid oxygen filter (800 lbs. gel) and the auxiliary vapourizer, which are derimed each month, are given for the corresponding period. The variation of the quantity of contaminants adsorbed on the rich liquid filters over the period of study with each filter operation is shown in Figure 1.

Carbon dioxide

It is apparent that the amount of carbon dioxide on the rich liquid filters remained consistently at

TABLE II

CONTAMINANTS HELD ON WALLS OF REGENERATORS (EXCLUDING H₂O AND CO₂)

	No. 1 Plant	No. 2 Plant	No. 3 Plant
	10/59-5/60 gms.	5/60-1/61 gms.	9/59-9/60 gms.
Oxides of Nitrogen (NO + NO ₂)	Present	15-45	4-60
Nitrous Oxide (N ₂ O)	100-200		30-400
Hydrocarbons (C ₃ -C ₅)	35-70	50-500	10-130
Acetylene	2-5		n.d. <1

TABLE III

CONTAMINANTS HELD ON WALLS OF MAIN VAPOURIZER

	No. 1 Plant*	No. 2 Plant**	No. 3 Plant**
	10/59-10/60 gms.	5/60-1/61 gms.	9/59-9/60 gms.
Acetylene	0.02	0.013	n.d. <0.006
Hydrocarbons			
C ₂	poss. trace	poss. trace	n.d.
C ₃ -C ₅	63	<2	10-15
Oxides of Nitrogen (NO + NO ₂)	-	7	0.004
Nitrous Oxide (N ₂ O)	present	2.1	n.d. <0.07
Carbon Dioxide	300	300-700	3-10

* Gaseous take off of product O₂ from main vapourizer and no catalytic filter.

** Liquid take off of product O₂ from main vapourizer.

about 4000 grams per month, Table IV, with a weekly range of 600-1300 grams. This quantity represents about 97% of that held in the three units and is equivalent to an average concentration in the rich liquid feed to the filters of 0.4 ppm. The amount of nitrous oxide on the rich liquid filter was also fairly consistent at 1000-2000 grams per month with a weekly range of 230-660 grams. This represents approximately 95% of the nitrous oxide retained in the three units and is equivalent to an average air concentration of 0.06-0.12 ppm. The latter concentration is possibly one third of the natural concentration of nitrous oxide in the atmosphere² and the difference is probably due primarily to nitrous oxide removed in the regenerators but also to a small amount removed in the liquid oxygen purge and the product oxygen.

Oxides of nitrogen

Values for acetylene and oxides of nitrogen (NO + NO₂) on the rich liquid filters and the average concentration in the intake air equivalent to the amount found are given in Table V. Both materials have shown a trend to higher values during the summer months. The range in weekly values varies by a factor of as much as twenty as illustrated in Figure 1. Only trace amounts of acetylene were found occasionally on the oxygen filter and in the auxiliary vapour-

izer. Oxides of nitrogen in the latter two units were also detected in trace amounts on several occasions, but due to interfering materials reliable results could not always be obtained.

The quantities of C₃-C₅ hydrocarbons, and the equivalent concentration in the air, are given in Table VI. Table VII contains the average constituent analysis of this fraction. The weekly values for the rich liquid filters varied by a factor of 30 while the variation in the monthly values for the oxygen filter and auxiliary vapourizer was only by factors of 3 and 10 respectively. There was no apparent relation between either the total amount on the filter, the distribution between the different units, or the atmospheric wind conditions.

Routine plant analyses of total hydrocarbons in the purge liquid from the auxiliary vapourizer gave a nominal analysis of 30-60 ppm. with only one or two exceptions. Chromatographic verification of a number of the routine tests showed that the major portion of the nominal value represented residual oxygen, krypton, xenon, carbon dioxide, nitrous oxide and ethane and only 0-5 ppm. was actually C₃-C₅ hydrocarbons.

Need for deriming

On the assumption that the average concentration of C₃-C₅ hydrocarbons in the purge liquid is

TABLE IV

CARBON DIOXIDE AND NITROUS OXIDE DERIMED

	Carbon Dioxide			Nitrous Oxide		
	Total R.L. Filters	LOX Filters	Auxiliary Vapourizer	Total R.L. Filters	LOX Filters	Auxiliary Vapourizer
	gms.	gms.	gms.	gms.	gms.	gms.
February	4200	100	-	1810	8	-
March	4770	57	-	1930	40	-
April	3430	82	21	1030	69	0.8
May	3800	88	19	2010	120	0.8
June	3480	68	8	1630	66	trace
July	4300	81	60	1900	67	3
August	3900	-	23	1670	-	0.7

TABLE V

ACETYLENE AND OXIDES OF NITROGEN DERIVED

	Acetylene		Oxides of Nitrogen (NO + NO ₂)	
	Total R.L. Filters gms.	Equivalent Total Conc. in Air p.p.m.	Total R.L. Filters gms.	Equivalent Total Conc. in Air p.p.m.
February	3.9	0.0004	5.1	0.0005
March	4.1	0.0004	8.5	0.0007
April	5.1	0.0005	-	-
May	15.4	0.0012	37	0.0024
June	14.6	0.0012	60	0.0043
July	19.6	0.0019	39	0.0034
August	27	0.0025	40	0.0032

5 ppm., the hydrocarbons removed from the plant by purging is 120 grams per month which is equivalent to an average level in the air intake of 0.005 ppm. On relating this to the amounts found on the filters and vapourizer, it follows that 40-70% of the hydrocarbons which are carried to the high pressure column either as a vapour or entrained solid at an average concentration of 0.008-0.015 ppm., are retained in the plant and must be removed by deriming.

The liquid oxygen filter shows somewhat greater efficiency for hydrocarbons than the rich liquid filter, which is undoubtedly a reflection of the absence of excessive amounts of carbon dioxide and nitrous oxide. However, significant quantities are still carried to the auxiliary vapourizer where they deposit on the walls. The amounts found on the vapourizer may not create too severe a hazard, depending on whether the material is deposited in all the tubes or localized in one or two tubes, but they are indicative of the rate at which hydrocarbons can accumulate in this unit even at low concentrations.

Ethylene has been found on the rich liquid filters on several occasions but has not been found on the liquid oxygen filter. Ethane has not been detected on the filters although it has been found in the rich liquid and liquid oxygen. This may reflect the low adsorbitivity of silica gel for ethane, particularly in the presence of other contaminants^{3,4}.

Conclusions

In considering the results of the analytical program to date it is apparent that there is much to be learned concerning the contaminant problem in air

TABLE VI

C₃-C₆ HYDROCARBONS DERIVED

	Total R.L. Filters gms.	LOX Filters gms.	Auxiliary Vapourizer gms.	Equivalent Total Conc. in Air p.p.m.
February	-	78		
March	34	29		
April	31	38	20	0.004
May	46	47	56	0.0048
June	20	91	11	0.0044
July	46	98	121	0.0115
August	35		74	

separation plants. In particular, there is a need for greater knowledge of the physical and chemical properties of contaminants at low temperatures, the effect or irregular variation in process operation and the ability of process equipment to minimize the effect of wide variations in air pollution conditions. With the continued improvement of analytical procedures and instrumentation, a more detailed appraisal of these problems should be obtained.

From the present analytical study a number of general conclusions may be drawn. In part, there is already an appreciation in the industry of some of these factors:

(1) The efficiency of contaminant removal by air heat exchangers cannot be predicted solely on the basis of contaminant vapour pressure data.

(2) The efficiency of catalytic filters is reduced at low concentrations.

(3) Rich liquid silica gel filters are very effective in removing small quantities of acetylene but are only partially effective in removing C₃-C₆ paraffins. Their effectiveness for the latter is further re-

TABLE VII

CONSTITUENTS IN C₃-C₆ HYDROCARBON FRACTIONS (AVERAGE FRACTION OF TOTAL FOUND FOR EACH CONSTITUENT)

Constituent	Rich Liquid Filter	Liquid Oxygen Filter	Auxiliary Vapourizer
Propane	0.03	0.08	0.03
n-Butane	0.50	0.50	0.71
Isobutane	0.24	0.21	0.21
n-Pentane	0.09	0.07	0.02
Isopentane	0.14	0.14	0.03

duced by the presence of large amounts of carbon dioxide and nitrous oxide on the filter.

(4) There is considerable probability that solid accumulations of contaminants will occur on the walls of vapourizers even though the average concentration in the bulk liquid phase is well below the solubility limit. In the case of auxiliary vapourizers, significant quantities may be deposited at quite low intake concentrations over a one-month period. This emphasizes the need for regular deriming of these units.

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DISCUSSION

GARRICK: Your results, as shown in the paper, on catalytic oxidation at those temperatures are probably correct. And, if you hold it at about 330°C., you are probably getting very close to the 100% range and it has been our experience that low concentrations have a minimum effect on the oxidation percentages.

SEFTON: We have examined the efficiency of the catalytic filters for hydrocarbon oxidation on a number of occasions. Due to the sampling and analytical methods for the C₃-C₆ hydrocarbons, not too much reliance can be placed on the results for these hydrocarbons at the low concentrations encountered. However, with respect to acetylene, greater accuracy was obtainable. The oxidation of acetylene has been as good as 70-80% where at other times it has only been 30-40%. As I noted, these were at concentrations of 0-0.5 p.p.m.

WELLS: How did you determine the amounts of these materials that were given off during the derime? Did you continuously monitor your exhaust from the derime and measure the flow of derime air?

SEFTON: We put a pitot tube on the total derime flow and passed a portion of this stream through a silica gel trap immersed in liquid oxygen. The total amount of contaminants frozen on the silica gel trap was then determined and since the ratio of the derime flow to the sample rate remained relatively constant, to within 10% to 20%, this quantity could be related back to that which was present in the unit being derimed.

GIBSON: Would you care to guess whether these contaminants in the reboiler are in the liquid or vapor portions of the reboiler and would frequent raising the level help to dispel this?

SEFTON: We just don't know where they are located—just that they are in the main vaporizer somewhere. It may be at a spot in contact with liquid or it may be in the vapor space.

STEVENS—Canadian Industries: In your conclusions, you conclude this emphasizes the need for regular deriming of these units. Would you care to add how often they do derime?

SEFTON: At this particular plant, the auxiliary vaporizer is derimed once a month. The optimum period

would of course depend on the particular contaminant conditions.

JENKINS: I get the impression that most vaporizer explosions have taken place at the top of the vaporizer with the exception of one or two where NO or CO₂ have combined with acetylene and sunk to the bottom.

BOYNE—Monochem: What percentage of your gaseous capacity is the auxiliary vaporizer? Is it a 100% capacity unit, or is it a partial capacity unit?

SEFTON: All of the oxygen product is withdrawn from the main vaporizer as a liquid and is passed to the auxiliary vapourizer where it is completely vapourized excepting the purge to waste.

BOYNE: Do you periodically flush your auxiliary vaporizer with an excess quantity of liquid?

SEFTON: No.

WHITE—Smith Douglass: We have had some discussion on whether we should wash with a caustic solution after deriming. Were there indications on this study that the deriming did not take out all of the hydrocarbons and perhaps we may need a caustic wash?

SEFTON: Our studies indicated that all the hydrocarbons were removed by deriming.

POWELL: I don't think you mentioned how you were actually performing your analyses—whether it was infrared or other methods and what kind of reliability do you find in the method that you are using?

SEFTON: The contaminants which were collected on the cold silica gel trap, were stripped from the gel in a vacuum system and the resultant gaseous sample then analysed on a gas chromatograph (silica gel and benzyl ether columns).

POWELL: Do you find the reproducibility of this good?

SEFTON: Yes. The reproducibility in stripping the sample from the gel trap and analysing chromatographically was perhaps ten to fifteen percent. Coupled with the variation in the derime flow rates the total error is probably 20-30%.