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HW--56399

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TITLE

COMPOSITION OF PUREX DISSOLVER OFF-GAS

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JUL 14 1958

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COMPOSITION OF PUREX DISSOLVER OFF-GAS

By

J. F. Facer

Purex Technology Operation
Research and Engineering
CHEMICAL PROCESSING DEPARTMENT

June 9, 1958

HANFORD ATOMIC PRODUCTS OPERATION
Richland, Washington

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COMPOSITION OF FUREX DISSOLVER OFF-GASIntroduction

The composition of dissolver off-gas was determined for seven different ~~dissolving of uranium in nitric acid (both with one and two dissolvers in~~ operation) at irregular intervals during February, March, and April, 1958. Samples were taken at the Purex 293-A facility absorber inlet, scrubber inlet, and scrubber discharge. The absorber was operated with and without reflux, and the scrubber was operated with water or with approximately 10% sodium hydroxide.

This memorandum describes the sampling procedures and analytical methods and gives the gas analyses found.

Summary and Conclusions

Typical gas compositions were 10, 4, and 2% NO + NO₂, respectively, for the gas entering the absorber, entering the scrubber, and leaving the scrubber. The gas leaving the scrubber indicated a small decrease in NO and NO₂ concentrations and a small increase in O₂ concentration over the period of a dissolving.

Ninety to one hundred percent of the NO₂ entering the absorber was absorbed there, and eighty to one hundred percent of the NO₂ entering the scrubber was removed there. No significant difference was observed in the composition of scrubber off-gas whether water absorption or caustic scrubbing was used. The composition of the off-gas from the scrubber appeared to be limited by the rate of NO oxidation rather than by the efficiency of the 293-A facility.

Discussion

Special analytical techniques were developed and/or evaluated by members of the Process Chemistry Operation. It was necessary to take three samples for each gas analysis because the gas composition changed on standing and because different laboratories had the equipment required for the analytical techniques used.

NO₂ was separated from other gas constituents by passing the gas sample through silica gel. Laboratory tests indicated that silica gel should absorb greater than 90% of the NO₂ in mixtures of air, NO, and NO₂, and this was confirmed for a plant sample containing approximately 1.5% NO₂ by using two silica gel tubes in series. NO₂ absorption on silica gel varies with the gas flow rate and NO₂ concentration, and any NO₂ which passes through the silica gel train will be reported as NO. A single test with absorber inlet gas, containing approximately 6% NO₂, indicated that 75% of the NO₂ was absorbed by silica gel. Such accuracy appears adequate for the desired analyses, but a larger silica gel train should be employed for any further tests.

Sample #1 submitted to H.L.O. Analytical Laboratories for spectrochemical analysis was obtained by drawing dissolver off-gas through a 70 cc Hobermann-type bulb for one to three minutes. The gas temperature, dew point, and ~~pressures up and downstream from the sample bulb were recorded to be used in~~ calculating the corrected sample volume and water content. In the event of any appreciable condensation or entrainment in the bulb during sampling, the sample was rejected and another sample was taken.

Twelve to twenty-four hours usually elapsed between taking the spectrochemical samples and preparing them for analysis. During this period, essentially all of the nitric oxide reacted with oxygen to form nitrogen dioxide. Condensables, such as water, carbon dioxide, and nitrogen dioxide were removed by freezing before transferring the non-condensable gases to the mass spectrograph for analysis. Gases determined by the spectrochemical analysis were N_2O , O_2 , N_2 , A, residual NO , and "mass 4". In addition, the condensables were titrated with caustic to determine the total mols of NO_2 .

Sample #2, submitted to the Purex Analytical Laboratory for NO plus NO_2 determination, was collected by using an evacuated 500 cc balloon flask. The pressures before and after sampling, gas temperature, and dew point were recorded to be used in calculating the corrected sample volume and water content. The laboratory added 25 ml. of 0.05 M H_2SO_4 - 0.0005 M H_2O_2 solution to oxidize any NO to NO_2 , and the nitrate concentration of the resulting solution was determined spectrophotometrically by the phenol-disulfonic acid⁽¹⁾ method.

Sample #3, submitted to the Purex Analytical Laboratory for NO_2/NO ratio determination, was collected by using an evacuated system, consisting of a 5 cc., 6 mm. I.D. tube filled with silica gel in series with a 500 cc balloon flask containing 25 ml. of 0.05 M H_2SO_4 - 0.0005 M H_2O_2 solution. The pressure in the sample container system before and after sampling, the gas temperature, and the dew point were recorded for possible use in calculating the corrected gas volume and water content.

The silica gel was leached with 0.05 M H_2SO_4 - 0.0005 M H_2O_2 as soon after sampling as feasible, and the nitrate in the resulting solution was determined spectrophotometrically by the phenol-disulfonic acid method. The nitrate in the solution in the balloon flask was determined by the same method. Because of the unknowns introduced by silica gel adsorption and NO oxidation, the volume of the NO_2/NO ratio sample could only be estimated.

A composite gas analysis was calculated from the three sample analyses. Analysis of sample #1 gave the percentages of non-condensable gases in that gas remaining after oxidizing the NO to NO_2 with oxygen from the sample and freezing out the water and NO_2 . Analysis of sample #2 gave the percentage of NO plus NO_2 . Analysis of sample #3 gave the ratio of NO_2 to NO . Titration of the condensables from sample #1 provided a rough check of the percentage of NO plus NO_2 . The water content was calculated with the assumption that the gas was saturated at the temperature at which it left the previous solution contactor (i.e., downdraft tower, absorber, or scrubber).

Composite gas analyses are given in Table I.

No satisfactory explanation has been found for the 2 - 3% hydrogen analyses of samples taken on April 9, 1958. The mass spectrograph calibration for hydrogen was checked within a day of the high analyses and was found to be correct. ~~The 0.5% H₂ found in all other samples is believed to be more~~ nearly representative of dissolver off-gas composition.

The abnormally high NO + NO₂ composition of the first scrubber discharge sample on April 22, 1958, was confirmed by the results from titration of the condensables in the mass spectrograph sample. However, an estimate of the NO + NO₂ composition in the NO₂/NO sample indicated a normal NO + NO₂ composition, so the two high samples may show some operational irregularity.

Gas velocities were calculated from a three point pitot tube traverse. Line pressures were obtained from recorders at the panel board for the 293-A facility. The barometric pressure was obtained from the Meteorology Station. Gas temperatures were measured at the pitot traverse points.

The NO plus NO₂ content of gas samples taken before March 22, 1958, were not obtained either because of misunderstandings or because of inadequate analytical techniques. Rather than throw out the data, compositions were calculated by using the NO₂/NO rates and the following assumptions which are believed to be approximately correct. Subsequent analyses have given good substantiation for the calculated compositions.

- 1) 5.5 mols of nitric acid are required to dissolve one mol of uranium. 3.5 mols of this nitric acid are added to the dissolver, and the other two mols are recovered in the downdraft tower.
- 2) For each mol of uranium dissolved, 1.75 mols NO₂ and 1.75 mols NO are evolved.
- 3) Dissolution requires five hours.
- 4) 90% of the NO₂ throughput is recovered in the downdraft tower.
- 5) 60% of the NO₂ throughput is recovered in the absorber without reflux water, and 90% of the NO₂ throughput is recovered in the absorber with reflux water.
- 6) 75% of the NO₂ throughput is recovered in the scrubber when it is used as an absorber, and 100% of the NO₂ throughput is recovered when the scrubber is used with sodium hydroxide.
- 7) The gases are saturated with water vapor at the temperature leaving the downdraft tower, absorber, and scrubber.
- 8) The off-gas composition does not vary appreciably throughout the cut downstream of the scrubber. These numbers are the average concentrations of this gas.

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These calculated gas compositions are given in Table II. The March 24 and 25, 1958, values show fair agreement with the March 24 and 25, 1958, analyses shown in Table I.

(1) HW-27229, Analytical Manual for Reactor Process Water

JF Facer/pms

TABLE I

COMPOSITION OF DISSOLVER OFF-GAS

Test Date	3 - 24/25 - 58				4 - 9 - 58				4 - 22 - 58			
Sample Point	Absorber Inlet	Scrubber Inlet	Scrubber Discharge	Absorber Inlet	Scrubber Inlet	Scrubber Discharge	Absorber Inlet	Scrubber Inlet	Absorber Inlet	Scrubber Inlet	Scrubber Discharge	Scrubber Discharge
Hours since solution began boiling	2.8	2.9	0.6 1.6 2.6 3.5 4.6		3.4	3.1	1.0 2.8 5.7		4.1	3.9	1.7 3.7 5.8	
Gas Flow SCFM	1305	1180	1195 1152 1146 1158 1208	1284	1250	1234 1244 696*	615	692	501 624 509			
Vol. %												
H ₂ O	5.7	3.8	6.3 6.0 5.7 5.1 4.2	5.5	3.7	4.8 4.6 3.1	3.7	2.5	3.9 2.5 3.4			
NO	3.7	1.9	1.9 1.6 0.9 0.6 0.6	3.7	1.1	1.9 2.2 0.3	3.1	1.2	6.5 0.6 0.7			
NO ₂	12.2	3.6	4.1 3.9 1.7 1.1 1.1	6.2	2.7	2.5 2.0 2.0	6.0	1.5	5.0 1.1 1.2			
H ₂	10.1	10.1	10.1 10.1 10.1 10.1 10.1	10.1	10.1	10.1 10.1 10.1	10.1	10.1	10.1 10.1 10.1			
A	0.7	0.8	0.8 0.8 0.8 0.8 0.8	0.6	0.8	0.8 0.8 0.8	0.7	0.8	0.7 0.8 0.7			
O ₂	10.5	9.5	11.6 10.6 9.6 12.2 12.8	9.5	9.9	9.8 9.4 13.6	14.0	12.9	11.6 12.3 12.8			
N ₂	66.3	79.2	74.3 76.4 60.5 80.5 79.7	71.8	78.4	77.7 77.4 77.1	72.0	80.4	71.6 82.1 80.4			
H ₂	0.5	0.5	0.5 0.5 0.5 0.7 0.5	2.7	3.4	2.9 2.9 2.8	0.4	0.6	0.5 0.6 0.7			
Conditions:												
B Dissolver		1st Cut				1st Cut				2nd Cut		
C Dissolver		2nd Cut				1st Cut				Off		
Absorber		NaOH				Reflux Off				2.5 gpm H ₂ O		
Scrubber						2.5 gpm H ₂ O						

*B Dissolver cut was completed prior to final sampling.

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TABLE 1

CALCULATED GAS COMPOSITIONS

Test Date	<u>2-11-58</u>	<u>2-17/18-58</u>	<u>3-17-58</u>	<u>3-20-58</u>	<u>3-24/25-58</u>
Conditions:					
A Dissolver	1 st Cut	Off	Off	Off	Off
B Dissolver	Off	2 nd Cut	Off	1 st Cut	1 st Cut
C Dissolver	Off	Off	2nd Cut	Off	2nd Cut
Absorber		Reflux On		Reflux Off	
Scrubber	NaOH	2.5 gpm H ₂ O	NaOH	2.5 gpm H ₂ O	NaOH
To Absorber:					
% H ₂ O	6.2	5.7	5.6	5.8	5.7
NO	2.0	3.3	2.7	3.5	2.3
NO ₂	6.6	5.6	7.7	10.2	7.5
O ₂	12.5	12.8	11.2	8.4	11.6
N ₂	71.9	71.7	72.0	71.2	72.0
A	0.9	0.9	0.9	0.9	0.9
CFM	740	720	620	475	1315
To Scrubber:					
% H ₂ O	3.6	4.2	4.1	4.6	3.8
NO	1.2	1.0	1.0	2.1	1.1
NO ₂	1.7	2.6	2.8	6.2	2.2
O ₂	13.4	12.9	11.4	8.3	12.1
N ₂	79.1	77.7	79.8	77.9	79.6
A	1.0	1.0	1.0	1.0	1.0
CFM	590	675	570	440	1210
From Scrubber:					
% H ₂ O	5.0	4.2	4.6	4.0	5.5
NO	0.1	0.9	0.4	1.5	0.4
NO ₂	1.1	1.4	0.7	2.4	0.8
O ₂	13.0	12.9	11.4	8.4	11.8
N ₂	79.9	79.6	81.7	82.8	80.6
A	1.0	1.0	1.0	1.0	1.0
CFM	675	660	550	415	1180

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END

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