Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

DPSP-69-1403 RTR-1117

Gerics

conci et

794



DISTRIBUTION:

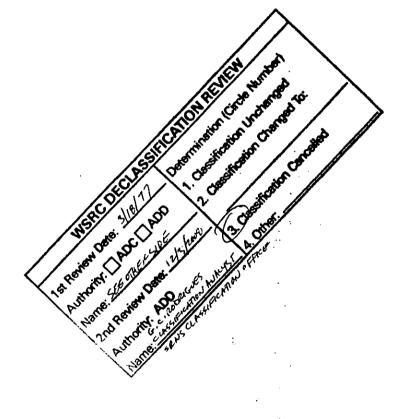
F.	₽.	Allen
H.	₩.	Bellas
F.	E.	Kruesi
C.	H.	Ice
E.	C.	Nelson
s.	Mirshak	
G.	F.	Merz
₩.	s.	Durant
-		
	H. F. C. E. S. G.	H. W. F. E. C. H. E. C. S. Mil G. F.

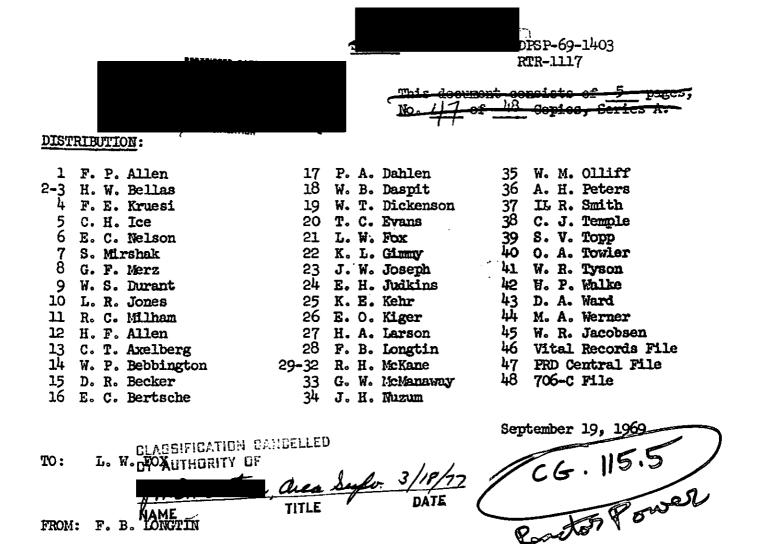
			Dahlen		3: 3(
			Daspit		-
			Dickenson		3
	_	-	Evans		3
			Fox		3% ¥
			Gimmy		
23	J.	W.	Joseph		ŧ.
			Judkins		ľ
0 E	٣	t:	Kahn	1	ŀ

35	W.	Μ.	011iff
36	Α.	H.	Peters
37	$\mathbf{I}\mathbf{F}$	R.	Smith
38	C.	J.	Temple
39	s.	٧.	Topp
40	0.	A.	Towler
41	W.	R.	Tyson
42	W.	P.	Walke
ፑሪ	Ð.,	A.	Ward



21 C L 2





AIR RADIOLYSIS

INTRODUCTION:

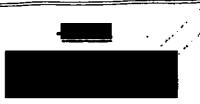
The rate of production of oxides of nitrogen in the CO₂ space of 100 Area reactors was needed to understand recent instances of corrosion² in the reactor Process Room. The method of calculating this production rate can also be of use in other problems such as the amount of nitrogen oxides generated and exhausted through the containment filters in a meltdown accident. ALCON AND AC 2° I THURSDAY Land Carta Nation Carta Nation

• The main products of air radiolysis by gamma rays are N_20 and $NO_2^{(0)}$.

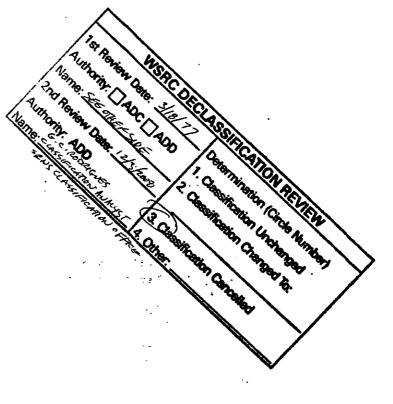
- - (1) gn mols $NO_2 = 7.2 \times 10^{-13} (grams of air) (gamma dose in r)$ <u>.</u>

(2) gm mols
$$N_2 0 = 6.2 \times 10^{-13}$$
 (gm. air) (gamma dose in r)

o Production in the CO, space is at a rate of approximately 0.23 gm mols NO, and 0.20 gm mols No per hour for full core charges at 2000 MM.



, ¢²



٠.

• .

× .

.



SUMMARY, contd.

- o (2) contd.
- With 30,000 cfm air flow through the process room, the concentration of NO₂ in process room air would be about 160 ppb, or 48 ppb in the stack exhaust (flow = 100,000 cfm).
- Contact with air containing 160 ppb of NO₂ could produce a concentration of up to .0042N HNO₂ in any moisture condensed on surfaces in the process room. In contact with acid solutions of this strength, carbon steel corrodes at a rate of about O.1 inch per year, with evolution of hydrogen which could contribute to cracking.

CONCLUSION:

Production of NO, by air radiolysis in the CO, space is sufficient to cause substantial corrosion damage in the Process Room in locations where condensed water is present.

DISCUSSION:

BASIS:

The radiolytic yields of NO₂ and N₂O from irradiation of air with gamma rays, fission fragments and reactor radiations are summarized in reference 1. For gamma rays the yields are 0.76 NO_2 molecules and 0.69 N_20 molecules per 100 ev absorbed.

A gamma dose of 1 r produces 1 esu of positive ions and 1 esu of negative ions in 1 cm² (S.T.P.) of dry air. This amounts to $1.684^{\circ} \times 10^{-1}$ ion pairs each formed by absorption of 34 ev of gamma energy. Thus a dose of 1 r results in absorption of 5.47×10^{-2} ev/gm of air. It will produce $0.76 \times 5.47 \times 10^{11} =$ 4.16×10^{11} NO₂ molecules and $0.69 \times 5.47 \times 10^{11} = 3.77 \times 10^{11}$ M 0 molecules per gram of air. In gram mol units this is 6.9×10^{-13} mols of NO₂ and 6.2×10^{-13} mols of N₂O per gm of air. Equations 1 and 2 of the "Summary" section express these results.

Reference 1 also gives yields of NO₂ and N₂O for irradiation of air by fission fragment and reactor irradiation of 1.2 and 0.3 molecules per 100 ev absorbed, respectively. At neutron fluxes up to around 10^{12} n/cm² sec the resulting production of N₂O and NO₂ is calculated to be negligible (about 2%) compared to that by a 10° r/hr gamma² field. (See Appendix I for details.)

CO_ SPACE_PRODUCTION:

The CO₂ space consists of an annulus $1\frac{1}{2}$ " thick next to the tank wall and an annulus 7/8" thick next to the concrete biological shield. The inner annulus has an air volume of about 100 cu. ft (air context ~ 3190 gm), a gamma flux of 10° r/hr and a fast neutron flux of about 10¹² r/cm²sec at 2000 MW. The outer annulus has a volume of about 60 cu. ft. and much lower radiation intensities (Reference 2). Consequently almost all of the production of N₂0 and NO₂ occurs in the inner annulus.





CO, SPACE PRODUCTION, contd.

The rate of NO, production in the inner annulus is $(7.2 \times 10^{-13})(3190)(10^8 \text{ r/hr}) = 0.23 \text{ gm mols/hr}$, as calculated from Equation 1. Similarly the production rate for N₂0 is $(6.2 \times 10^{-13})(3190)(10^9) = 0.2 \text{ gm mols/hr}$.

Production will continue at this rate indefinitely as long as there is a supply of air to the CO₂ space. This supply need only be fast enough so that the O₂ is not exhausted. The rate of production will decline somewhat as the O₂ concentration is reduced by radiolysis, but not markedly until the O₂ concentration drops below 10%. (Reference 1) Material balance calculations show that a flow of 3.2 cubic feet per hour through the CO₂ space would be sufficient to maintain 10% O₂ in that space.

When the CO, space is not sealed, normal air circulation draws all of the NO₂ and N₂O into the Process Room, where it is diluted by a ventilation flow of about 30,000 cfm. This amounts to 2.27×10^{6} mols/hr or 6.55×10^{7} gms/hr of air. The resulting concentration of NO₂ is 161 ppb or 10⁻⁵ percent by volume. Its partial pressure in the Process Room will be about 10-7 atmos.

When this air stream reaches the stack, it has been further diluted to a flow of about 100,000 cfm. The resulting NO₂ concentration should then be 0.3 x 160 = 48 ppb.

NITRIC ACID FORMATION:

A nitric acid solution will form wherever air containing NO₂ is in contact with moisture such as may condense on solid surfaces in the Process Room. The reaction producing nitric acid is:

$$2NO_2 + H_2 O = HNO_2 + H^+ + NO_3$$
(3)

In the presence of air further nitric acid may be formed by oxidation of HNOg.

The standard free energies per nol of the above substances are known (e.g. Reference 3) and from them the free energy change for the above reaction is calculated to be:

$$\Delta F^{\circ} = -9,395 \text{ cal.}$$
 (3a)

From this free energy the equilibrium constant for the reaction is calculated as:

$$\frac{(H+)(HNO_{2})(NO_{3}^{-})}{P_{NO_{3}}} = 10^{6.86}$$
(3b)

In this equation (H+), (HNO₂) and (NO₃⁻) are the concentrations (mols/liter) of the indicated species dissolved in water, while P_{NO_2} is the partial pressure of NO₂ in the air in atmospheres.

If no other chemical reactions occur and there are no other sources of H+, HNO_2 or NO_2 , then $(HNO_2) = (NO_2) = (H+)$ and equation 3b becomes

$$(H+)^3 = 10^{6.86} P_{NO_2}^2$$
 (4)





MITRIC ACID FORMATION, contd.

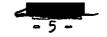
For
$$P_{NO_2} = 10^{-7}$$
 Equation 4 gives as the equilibrium concentration of (H+)
(H+) = $10^{-2 \cdot 38}$ M

or pH = 2.38. At this pH general corrosion of carbon steel in contact with acid solutions occurs at a rate of ~ 0.1 inches per year. Furthermore, in corrosion at this pH hydrogen is evolved, which can cause hydrogen embrittlement. (5)

OTHER SOURCES OF ACTD

Reactor blanket gas conceivably could contain both oxides of nitrogen (from radiolysis of the small percentage of N₂ normally present) and nitric acid volatilized from the moderator. This gas is known to leak into the Process Room. The blanket gas carries condensed moisture which would cause corrosion of carbon steel or aluminum over which it flows, if it contained much NO₂ or nitric acid. Corrosion of aluminum has been observed in the Process Room. Aluminum parts of the 100 cfm canned centrifugal blanket gas blower in K showed no corrosion after several months of operation including tests at higher than normal blanket gas content of N₂. Thus it appears that blanket gas leakage cannot be an important contributor to Process Room corrosion problems.





DPSP-69-1403 RTR-1117

APPENDIX I - Production by Reactor Radiations

Assumptions

Neutron cross section of air N 1 barn/molecule

= 0.021 cm²/gm 1 mev = 10^{4} cev

Neutron energy

Calculations

Therefore air will absorb $(0.021)(10^{12}) = 2.1 \times 10^{10}$ neutrons per gm sec from a fast neutron flux of 10^{12} r/cm²-sec. The energy absorbed will be 2.1 x 10^{12} cev/cm²sec. This will produce NO, at a rate of 2.64 x 10^{14} molecules per second per gram of air, or 9.46 x 10^{17} molecules/gm hr or 1.57 x 10^{-6} mole/gm hr.

A gamma field of 10^8 r/hr produces NO at a rate of 6.9 x 10^{-5} mols/gm hr. Thus for most purposes the production by a neutron flux of 10^{12} r/cm sec is negligible.

REFERENCES :

- 1. Steinberg, M., "Chemonuclear and Radiation Chemical Process Research and Development" Isotopes and Radiation Technology, Vol. 4 No. 2, Winter 1966-1967, pp. 143-155.
- 2. Works Technical Department "Monthly Progress Report".
 - a) DPSP-62-1-3, pp. 97-102, March 1962 (SECRET).
 - b) DFSP-62-1-11, pp. 66-69, November 1962 (SECRET).
 - c) DPSP-63-1-1, pp. 74-77, January 1963 (SECRET).
- 3. Latimer, W. W., Book, "Oxidation Potentials", 2nd Edition, Prentiss-Hall, Inc., 1952, pp. 39, 91.
- 4. Uhlig, H. H., Book, "The Corrosion Handbook", Jolen Wiley & Sons, Inc., N. Y.∆ 1948, pp. 129, 133-134.

