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CG. 115.5
Reactor Power

TO: L. W. FOX

FROM: F. B. LONGTIN

# AIR RADIOLYSIS

## INTRODUCTION:

The rate of production of oxides of nitrogen in the $CO_2$ space of 100 Area reactors was needed to understand recent instances of corrosion 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.

## SUMMARY:


- The main products of air radiolysis by gamma rays are $N_2O$ and $NO_2$.
- The rates of production are given by the equations:

  (1) gm mols $NO_2 = 7.2 \times 10^{-13}$(grams of air)(gamma dose in r)

  (2) gm mols $N_2O = 6.2 \times 10^{-13}$(gm. air)(gamma dose in r)

- Production in the $CO_2$ space is at a rate of approximately 0.23 gm mols $NO_2$ and 0.20 gm mols $N_2O$ per hour for full core charges at 2000 MW.


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SUMMARY, contd.

o (2) contd.

o With 30,000 cfm air flow through the process room, the concentration of $NO_2$ in process room air would be about 160 ppb, or 48 ppb in the stack exhaust (flow = 100,000 cfm).

o Contact with air containing 160 ppb of $NO_2$ could produce a concentration of up to .0042N $HNO_3$ 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 0.1 inch per year, with evolution of hydrogen which could contribute to cracking.

CONCLUSION:

Production of $NO_2$ by air radiolysis in the $CO_2$ 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 $NO_2$ and $N_2O$ 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 $N_2O$ 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 $cm^3$ (S.T.P.) of dry air. This amounts to $1.684^{6} \times 10^{12}$ ion pairs each formed by absorption of 34 ev of gamma energy. Thus a dose of 1 r results in absorption of $5.47 \times 10^{13}$ ev/gm of air. It will produce $0.76 \times 5.47 \times 10^{11} = 4.16 \times 10^{11}$ $NO_2$ molecules and $0.69 \times 5.47 \times 10^{11} = 3.77 \times 10^{11}$ $N_2O$ molecules per gram of air. In gram mol units this is $6.9 \times 10^{-13}$ mols of $NO_2$ and $6.2 \times 10^{-13}$ mols of $N_2O$ per gm of air. Equations 1 and 2 of the "Summary" section express these results.

Reference 1 also gives yields of $NO_2$ and $N_2O$ 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/$cm^2$ sec the resulting production of $N_2O$ and $NO_2$ is calculated to be negligible (about 2%) compared to that by a $10^8$ r/hr gamma field. (See Appendix I for details.)

$CO_2$ SPACE PRODUCTION:

The $CO_2$ space consists of an annulus 1½" 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 content ~ 3190 gm), a gamma flux of $10^8$ r/hr and a fast neutron flux of about $10^{12}$ r/$cm^2$-sec 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 $N_2O$ and $NO_2$ occurs in the inner annulus.

$CO_2$ SPACE PRODUCTION, contd.

The rate of $NO_2$ production in the inner annulus is $(7.2 \times 10^{-13})(3190)(10^8\ r/hr) =$ 0.23 gm mols/hr, as calculated from Equation 1. Similarly the production rate for $N_2O$ is $(6.2 \times 10^{-13})(3190)(10^8) = 0.2$ gm mols/hr.

Production will continue at this rate indefinitely as long as there is a supply of air to the $CO_2$ space. This supply need only be fast enough so that the $O_2$ is not exhausted. The rate of production will decline somewhat as the $O_2$ concentration is reduced by radiolysis, but not markedly until the $O_2$ concentration drops below 10%. (Reference 1) Material balance calculations show that a flow of 3.2 cubic feet per hour through the $CO_2$ space would be sufficient to maintain 10% $O_2$ in that space.

When the $CO_2$ space is not sealed, normal air circulation draws all of the $NO_2$ and $N_2O$ into the Process Room, where it is diluted by a ventilation flow of about 30,000 cfm. This amounts to $2.27 \times 10^6$ mols/hr or $6.55 \times 10^7$ gms/hr of air. The resulting concentration of $NO_2$ 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 $NO_2$ concentration should then be $0.3 \times 160 =$ 48 ppb.

NITRIC ACID FORMATION:

A nitric acid solution will form wherever air containing $NO_2$ is in contact with moisture such as may condense on solid surfaces in the Process Room. The reaction producing nitric acid is:

$$2NO_2 + H_2O = HNO_2 + H^+ + NO_3^- \qquad (3)$$

In the presence of air further nitric acid may be formed by oxidation of $HNO_2$.

The standard free energies per mol 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:

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

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

$$\frac{(H+)(HNO_2)(NO_3^-)}{P_{NO_2}{}^2} = 10^{6.86} \qquad (3b)$$

In this equation (H+), ($HNO_2$) and ($NO_3^-$) are the concentrations (mols/liter) of the indicated species dissolved in water, while $P_{NO_2}$ is the partial pressure of $NO_2$ in the air in atmospheres.

If no other chemical reactions occur and there are no other sources of H+, $HNO_2$ or $NO_3^-$, then $(HNO_2) = (NO_3^-) = (H+)$ and equation 3b becomes

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

NITRIC ACID FORMATION, contd.

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

$$(H+) = 10^{-2.38}\ \underline{M}$$

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 ACID

Reactor blanket gas conceivably could contain both oxides of nitrogen (from radiolysis of the small percentage of $N_2$ 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 $NO_2$ 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 $N_2$. Thus it appears that blanket gas leakage cannot be an important contributor to Process Room corrosion problems.

APPENDIX I - Production by Reactor Radiations

Assumptions

Neutron cross section of air $\sim$ 1 barn/molecule

$= 0.021\ cm^2/gm$

Neutron energy  1 mev = $10^4$ cev

Calculations

Therefore air will absorb $(0.021)(10^{12}) = 2.1 \times 10^{10}$ neutrons per gm sec from a fast neutron flux of $10^{12}$ $r/cm^2$-sec. The energy absorbed will be $2.1 \times 10^{14}$ $cev/cm^2$ sec. This will produce $NO_2$ at a rate of $2.64 \times 10^{14}$ molecules per second per gram of air, or $9.46 \times 10^{17}$ molecules/gm hr or $1.57 \times 10^{-6}$ mols/gm hr.

A gamma field of $10^8$ r/hr produces $NO_2$ at a rate of $6.9 \times 10^{-5}$ mols/gm hr. Thus for most purposes the production by a neutron flux of $10^{12}$ $r/cm^2$sec is negligible.

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