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SUBSTITUTION OF OXIDES OF NITROGEN FOR SODIUM NITRITE

INTRODUCTION AND SUMMARY

Sodium nitrite is added to SRP canyon process solutions to produce nitrous acid, which is an oxidant used for valence adjustment and oxidation of unwanted reducing agents. Unfortunately, sodium nitrate is formed in producing the nitrous acid, and contributes significantly to high- and low-activity waste volumes in both canyons. Gaseous oxides of nitrogen (NO_x) appear to be an attractive alternative to sodium nitrite. Past experience indicates they are a good source of nitrous acid, and make no contribution to waste. Approximately \$415 M per year could be saved in interim waste storage costs alone with the use of NO_x. The purpose of this memorandum is to discuss the chemistry of nitrous acid, the SRP application of NO_x, environmental effects, and outline a development program for NO_x replacement of sodium nitrite.

DISCUSSION

Nitrous Acid Chemistry

Nitrous acid is used in SRP process solutions for valence adjustment and oxidation of reducing agents. It is introduced into these nitric acid solutions by the addition of sodium nitrite:

$$NaNO_2 + H^+ + NO_3^- \rightleftharpoons HNO_2 + Na^+ + NO_3^- \tag{1}$$
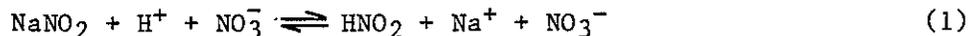
Nitrous acid is a weak acid, $K_a = 6 \times 10^{-4}$ at 30°C[1] for:

$$K_a = \frac{[H^+][NO_2]}{[HNO_2]} \tag{2}$$

This means that in all acidic solutions in canyon processing, HNO_2 is essentially undissociated. Nitrous acid is also unstable in normal canyon aqueous solutions:

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + 2NO + H_2O \tag{3}$$
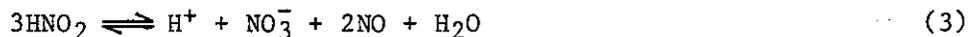
$$K_a = \frac{[H^+][NO_3^-] \ P^2_{NO}}{[HNO_2]^3} \tag{4}$$

$$K_a = 40 \ \frac{L\text{-}atm}{mol} \ at \ 30°C^{[1]}$$

There is very low nitrogen oxide partial pressure in most SRP canyon process solutions, which shifts the equilibrium to the right in equation (3).

The major problem with sodium nitrite use is that the sodium nitrate produced on the right side of equation (1) contributes to canyon waste volumes. The situation is made worse by the fact that where the oxidation reactions are relatively slow, excess sodium nitrite must be added to make up for the instability of the HNO_2.

There are several different gaseous oxides of nitrogen, or combinations of them, that might be used to produce nitrous acid. Reversing reaction (3), nitrogen oxide gas can be used to replace the sodium nitrite to generate nitrous acid:[2,3]

$$2NO + H^+ + NO_3^- + H_2O \rightleftharpoons 3HNO_2 \tag{3r}$$
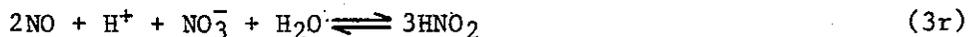
Bubbling NO through the solution increases NO partial pressure, shifting equilibrium to the right in reaction (3r) [increasing equilibrium HNO_2 concentration in equation (4)]. Also, no penalty

has to be paid for using excess NO (environmental aspects will be discussed later). From the NO dissolution mechanism:

$$HNO_2 + 2NO \longrightarrow N_2O_4 + H_2O \qquad \text{rate controlling} \qquad (5)$$

$$N_2O_4 + 2NO \longrightarrow 4HNO_2 \qquad \qquad \text{rapid} \qquad (6)$$
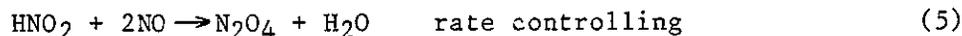
and from the rate expression:

$$\frac{d[HNO_2]}{dt} = \underset{\text{(formation)}}{k_1[H^+][HNO_3^-][HNO_2]} - \underset{\text{(decomposition)}}{k_2 \frac{[HNO_2]^4}{p^2_{NO}}} \qquad (7)$$

it can be seen that the formation of nitrous acid from NO gas is autocatalytic. Thus, the formation of nitrous acid may be difficult in solutions which contain significant concentrations of either sulfamic acid or hydrazine, both of which are nitrous acid scavengers. Experimental work is necessary to determine if this particular oxide of nitrogen will perform adequately in these solutions, which make up the bulk of the potential applications.

Nitrogen dioxide (NO_2 or N_2O_4) has also been studied for use in producing nitrous acid,[3,4] although it does so indirectly:

$$H_2O + NO_2 \longrightarrow HNO_3 + NO \qquad (8)$$

The NO then reacts to form HNO_2 by reaction (3r) above. A mixture of NO and NO_2, corresponding to the composition N_2O_3, may provide the best reactants for nitrous acid[1]:

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \qquad (9)$$

Because of the uncertainty about which oxide(s) of nitrogen will provide the best source of HNO_2, the reagent of choice is referred to throughout this paper as NO_x.

SRP Application

In 1981, a study of alternatives to sodium nitrite for production of nitrous acid was made.[5] It surveyed the use and/or study of alternatives both at SRP and elsewhere. In-situ generation of nitrous acid by photolysis of nitric acid and the use of NO_x were recommended as feasible options for SRP application. Development work will have to be done before the photochemical method could be implemented, particularly in the area of suitable photolysis equipment. On the other hand, NO_x gases could be used with existing technology. The NO_x could be introduced into process tanks using dip tube jumpers similar to those used now for

liquid level/specific gravity measurements. In some applications, if a slow rate of NO_x feed was sufficient, NO_x might actually be used to replace air in this instrumentation.

A major concern at SRP in the past has been the handling and storage of NO_x gases on the second or third level of the canyons because of the toxicity of these gases.[6] This is a legitimate concern, but a safe and economical system should not be impossible to design considering all of the 400-Area experience with H_2S here, and the technical expertise and experience available through the Engineering Department.

Environmental Concerns

At first glance, it may appear that using NO_x in the canyons in place of sodium nitrite would increase NO_x emissions. However, this probably is not the case. Because of the instability of nitrous acid, a significant amount of NO_x is released from solution upon sodium nitrite addition to nitric acid solutions. A part of the experimental development work will be to determine if any more NO_x would be released using NO_x as oxidant.

Incentives

In-canyon use of sodium nitrite is listed in Table 1. The actual consumption varies significantly with changing production routes and processing rates. It is estimated that replacing sodium nitrite with NO_x gases could save $185 M/yr in 221-H (at 100 M kg Al/yr fed to first cycle) and $230 M/yr in 221-F (at 1500 MTU/yr) in interim waste storage costs. Pertinent data used in these calculations are listed in Table 2. No attempt was made to estimate the savings in saltcrete production, but considerable savings would be achieved there also.

Program

It is recommended that the following work be performed to develop NO_x substitution for sodium nitrite to the point of implementation.

1) Perform laboratory experiments to determine:

   a) which oxide of nitrogen or combination will provide best performance

   b) if NO_x generation of HNO_2 will perform adequately in solutions containing holding reductants.

   c) conversion efficiency (mole to mole conversion of NO_x to HNO_2) in simulated and actual plant solutions

   d) Compare NO_x emissions from NO_x use with that from sodium nitrite addition to nitric acid solutions.

2) Develop a safe and efficient NO_x storage and feed system compatible with SRP canyons. Cost should not outweigh benefit of sodium nitrite elimination.

3) Evaluate in situ NO_x generation via photochemistry.

4) Demonstrate NO_x use in actual plant solutions on a small scale in SRL and in actual plant tests.

REFERENCES

1. D. M. Yost and H. Russel, Jr. Systematic Inorganic Chemistry. Prentice-Hall, Inc., New York (1944).

2. M. R. Berret and A. D. Kelmers. "The Reduction of Pu(VI) to Pu(IV) in Nitric Acid by NO or NO_x Gases." ORNL/TM-6552 (November 1978).

3. G. S. Nichols. "Replacement of Sodium Nitrite with Nitrogen Dioxide." DPST-62-1-5, p. II-9 (May 1962).

4. Personal Communication with J. H. Gray concerning studies made at the Allied General Nuclear Services reprocessing plant at Barnwell.

5. C. A. Hines to H. D. Harmon. "Replacement Alternatives for Sodium Nitrite in the Separations Processes." DPST-81-365 (June 1, 1981).

6. DPSOP 158-2. "SRP Industrial Hygiene Manual; Hazardous Materials," p. 4148.

TABLE 1

Usage of Sodium Nitrite in F & H Canyon Process

Location	Purpose	Estimated[1,2] Amount Used
221-H HAW Evaporator Feed	Oxidize ferrous sulfamate before evaporation	3,200 kg/yr
221-H LAW Evaporator Feed	Oxidize ferrous sulfamate before evaporation	12,800 kg/yr
221-H Frame Waste Evaporator Feed	Oxidize FS, hydrazine; suppress Ru volatility	37,000 kg/yr
221-F 2AF Feed Adj.	Pu valence adjustment; oxidize FS/HAN	35,400 kg/yr
221-F 1AN Feed Stream to 1A Contactors	Pu valence adjustment	8,300 kg/yr

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1   Based on 1500 MTU/yr in 221-F and 100M kg Al/yr in 221-H

2   Flowsheet information from: C. E. Pickett, R. A. Langendorf, 221-H, D. M. Cooper, Operating Procedures, 221-F.

TABLE 2

Data Used in Economic Calculations

Purex Process

LAW: Sp. gr. = 1.22; 28% solids

First Cycle operating at 11 MTU per day rate

H-Area

HAW: Sp. gr. = 1.33; 38.2% solids

LAW: sp. gr. = 1.29; 36% solids

Frame Waste: sp. gr. = 1.3; 37% solids

Interim Waste Storage Cost: $5.60 per gallon