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**CONTROL OF HIGH LEVEL RADIOACTIVE WASTE-GLASS MELTERS -  
PART 6: NOBLE METAL CATALYZED FORMIC ACID DECOMPOSITION,  
AND FORMIC ACID/DENITRATION (U)**

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## **NOBLE METAL CATALYZED FORMIC ACID DECOMPOSITION, AND FORMIC ACID DENITRATION**

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### **ABSTRACT**

A necessary step in Defense Waste Processing Facility (DWPF) melter feed preparation for the immobilization of High Level Radioactive Waste (HLW) is reduction of Hg(II) to Hg(0), permitting steam stripping of the Hg. Denitration and associated NO<sub>x</sub> evolution is a secondary effect of the use of formic acid as the mercury-reducing agent. Under certain conditions the presence of transition or noble metals can result in significant formic acid decomposition, with associated CO<sub>2</sub> and H<sub>2</sub> evolution. These processes can result in varying redox properties of melter feed, and varying sequential gaseous evolution of oxidants and hydrogen. Electrochemical methods for monitoring the competing processes are discussed. Laboratory scale techniques have been developed for simulating the large-scale reactions, investigating the relative effectiveness of the catalysts, and the effectiveness of catalytic poisons. The reversible nitrite poisoning of formic acid catalysts is discussed.

### **SUMMARY AND CONCLUSIONS**

It is concluded that electrochemical monitoring should be evaluated in pilot-scale facilities as a means of on-line monitoring of DWPF feed preparation reactions, and can be used to indicate upset conditions when high H<sub>2</sub> evolution rates are present. This would permit interruption of operations before accumulation of significant hydrogen concentrations. Sensors are relatively simple and small in size, and could be fitted into the feed preparation sample loops, with the sensors located at sampling stations. Electrochemical reference junctions are also required. Probes to measure pH are desirable.

It is concluded that the DWPF formic acid digestion process can be considered to be made up of two separate reaction sequences. First, the addition of formic acid

reduces the pH, and causes reduction of nitrite to NO. It is concluded that monitoring of pH and Eh (redox potential) could be an effective way to monitor the progress of the nitrite reduction, to determine batching errors and to estimate the duration of NO evolution. Second, noble-metal-catalyzed formic acid decomposition releases CO<sub>2</sub> and H<sub>2</sub>. Eh values are comparable to published values for NO and H<sub>2</sub> evolution, respectively.

Shifts in pH and Eh caused by nitrite destruction or formic acid catalytic decomposition follow predictable paths. Redox potentials, which are measured using reference electrodes and converted to the standard hydrogen electrode (Eh), show an oxidative surge when formic acid is added to simulated waste containing nitrite. This surge is attributed to the evolution of NO gas. Hydrogen evolution is accompanied by low values of Eh, consistent with those expected by electrochemical calculations.

## EXPERIMENTAL

Titration were conducted using a Corning model 150 ion analyzer in automatic end point sensing mode and commercial electrodes (Orion Pt redox probe, PAR graphite electrode, Orion Ag/AgCl double junction reference electrode with KNO<sub>3</sub> outer junction filler, Beckman glass pH electrode). Electrodes were calibrated at room temperature using standard pH 4 and 10 buffers, and ZoBell Eh buffer [2]. No drift in Eh occurred, and values were considered accurate to +/- 0.005 V. Some pH drift occurred, and pH values are considered accurate to -0.0 / +0.1 units. A correction of +0.222 V was applied to convert the Ag/AgCl standard electrode referenced data to Eh. Wires and strips of commercial purity Pd, Ru, Rh, Ag, and Cu were used as sensing electrodes for catalysis studies.

Platinum redox electrodes are the most commonly used type because of their inertness in most natural and industrial solutions. However, Pt can act as a catalyst for nitrogen reactions. As examples, the reduction of nitric acid on a platinum electrode in the presence of nitrous acid evolves hydrogen [3], and 0.01 M NaNO<sub>2</sub> raises the Pt potential by 0.17 V at pH 6.8, an effect which is specific to Pt and not for other electrode materials (Au, Pd, Ni, graphite) [3]. Similarly, the measured potential of N<sub>2</sub>O/NH<sub>2</sub>OH.H<sup>+</sup> reactions has been reported as 0.70 to 0.75 V higher than calculated potentials for reactions of hydroxylamine with nitrous acid [3]. For these reasons, redox measurements for the experiments were taken with both Pt and graphite electrodes.

## DISCUSSION

Nomenclature and symbol conventions are based on those used in Reference 1. The familiar acid/base reactions can be written in terms of pH, thus giving an indication of the pH range over which certain species of interest are dominant. For the nitrite destruction portion of waste digestion reactions:



for which

$$\log ([\text{NO}_2^-]/[\text{HNO}_2]) = -3.35 + \text{pH} \quad (2)$$

$$\text{or } \log ([\text{HNO}_2]/[\text{NO}_2^-]) = +3.35 - \text{pH} \quad (3)$$

$$\text{or } [\text{HNO}_2]/[\text{NO}_2^-] = 10^{(3.35 - \text{pH})} \quad (4)$$

thus, for typical pH's seen during melter feed preparation, nitrous acid  $[\text{HNO}_2]$  varies from  $\ll 0.1\%$  of the nitrite content for caustic pH's, to the predominant species at pH values  $< 3.35$ . For the stronger nitric acid, nitrate is the predominant ion under all conditions, and nonionized nitric acid can be ignored:

$$[\text{NO}_3^-]/[\text{HNO}_3] = 10^{\text{pH}} \quad (5)$$

For redox reactions (which include electron transfers) it is necessary to include terms for the oxidation potential:



for this and many other nitrogen oxidation reactions the oxidation potentials have been evaluated [1]. In this case at 25 °C:

$$E_0, \text{ volts} = 0.835 - 0.0591 \text{ pH} + 0.0295 \log ([\text{NO}_3^-]/[\text{NO}_2^-]) \quad (7)$$

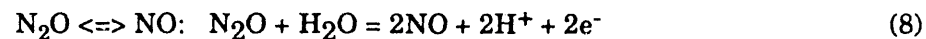
$$\text{or } E_0, \text{ volts} = 0.835 - 0.0591 \text{ pH for } [\text{NO}_3^-] = [\text{NO}_2^-]$$

where  $E_0$  is the redox potential, which is referenced to the standard hydrogen electrode at pH = 0, and termed Eh. Note, this potential shifts 30 mV for each decade shift in the nitrate to nitrite ratio, and 60 mV for each shift by one pH unit. Thus, in a solution where nitrite and nitrate are the major redox species, the oxidation potential of the solution (at 25°C) can be measured relative to a standard half cell and compared to Equation 7, and used to monitor the ratio.

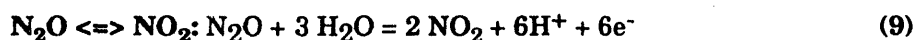
Probing of actual washed High Level Waste sludge indicated a redox potential of +0.262 V [4], which is in reasonable agreement with the +0.236 V equilibrium Eh calculated for the waste tank conditions using equation 7.

### GENERAL NITROGEN REACTIONS

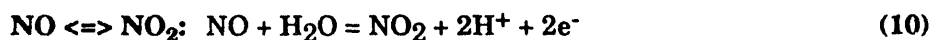
Part of the difficulty in characterizing denitration or denitritation reactions is that a number of gaseous products can be evolved and removed at different rates, causing both pH and Eh shifts [1,3,5-10]:



for which  $E_0 = 1.591 - 0.0591 \text{ pH} + 0.0295 \log (p\text{NO}_2^2/p\text{N}_2\text{O})$

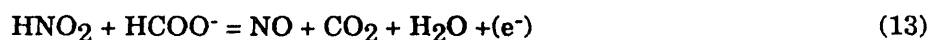


for which  $E_0 = 1.229 - 0.0591 \text{ pH} + 0.0098 \log (p\text{NO}_2^2/p\text{N}_2\text{O})$



for which  $E_0 = 1.049 - 0.0591 \text{ pH} + 0.0295 \log (p\text{NO}_2/p\text{NO})$

Thus, in reactions of formic acid with nitrates and nitrites, competing reactions are common resulting in  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NO}_2$  mixtures [5]:



Nitrogen dioxide ( $\text{NO}_2$ ) is more corrosive than nitric acid, and is a powerful oxidizing agent because of polarization effects [3]:



Nitric oxide can be oxidized to this more corrosive form by air [3]:



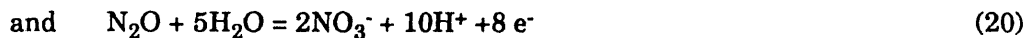
The rate for this is  $dx/dt = k [\text{O}_2] [\text{NO}]^2$  where  $k = 2.09 \times 10^{-6} (\text{mole/L})^{-2} \text{ min}^{-1}$ . The reaction is accelerated by light or gamma radiation. In addition,  $\text{NO}_2$  is unstable, and [11]:



The  $\text{NO}_x$  produced can be evolved and reabsorbed, especially if the condensate is not strongly acidic. The solubilities of the redissolved  $\text{NO}_x$  species are functions of pH and the redox potential [1]:

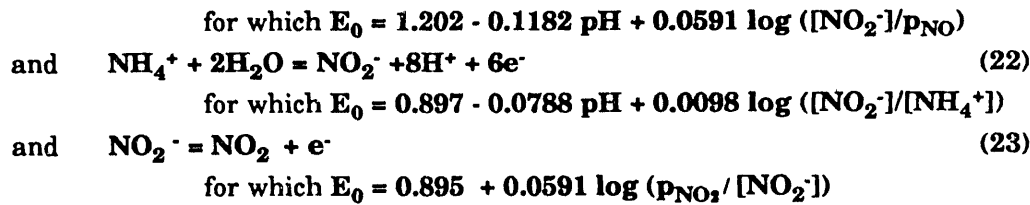


for which  $E_0 = 1.396 - 0.0886 \text{ pH} + 0.0148 \log ([\text{NO}_2^-]^2/p\text{N}_2\text{O})$

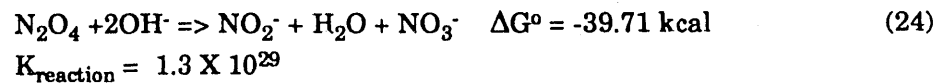


for which  $E_0 = 1.116 - 0.0739 \text{ pH} + 0.0074 \log ([\text{NO}_3^-]^2/p\text{N}_2\text{O})$

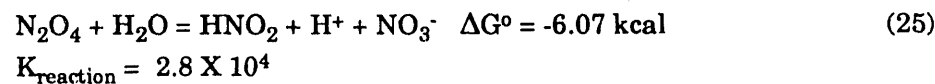




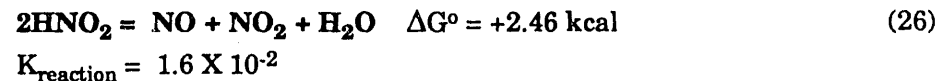
Overall, the redissolution of the evolved gases is very strongly driven if there is solution available that has not been well mixed with acid. In particular, for the very aggressive tetroxide (and similarly for nitrogen dioxide) [11]:



So from a thermodynamic stand point equation 24 goes to completion. For reabsorption on to neutral pH mixtures the reaction is less vigorous, but still proceeds, and increases the subsequent requirements for reducing agents [22]:



Once the feed has been acidified, any gas phase passing through the reacting feed will tend to come to equilibrium with the solution [11]:



where the redox potentials for the two half reactions are nearly identical:

$$E_{1/2} = 1.093 - 0.0591 \text{ pH} + 0.0591 \log(p_{\text{NO}_2}/[\text{HNO}_2]) \quad (27)$$

$$E_{1/2} = 1.004 - 0.0591 \text{ pH} + 0.0591 \log([\text{HNO}_2]/p_{\text{NO}}) \quad (28)$$

and for the combination

$$E_0 = 1.049 - 0.049 \text{ pH} + 0.0296 \log(p_{\text{NO}_2}/p_{\text{NO}})$$

The positive free energy of this reaction is so small that there is a very appreciable amount of NO and NO<sub>2</sub> that can dissolve in any gas bubbled through the acidified solution. Thus, there will be substantial NO and NO<sub>2</sub> evolved until the nitrite is exhausted whenever the pH of the feed is < 5. In experiments with 0.2 to 0.5 M NaNO<sub>2</sub> treated with HCOO<sup>-</sup> at pH from 2.8 to 5.6 at 20°C, the Eh was +0.694 to +0.723 V, which is compatible with NO<sub>x</sub> mixtures of equations 19, 21, 23.

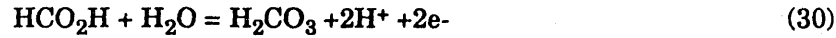
## FORMIC ACID REACTIONS

Formic acid hydrolyzes under similar conditions to those for nitrous acid:

$$[\text{HCO}_2^-]/[\text{HCOOH}] = 10^{-3.74 + \text{pH}} \quad (29)$$

and can be oxidized to carbonate ion, etc. The predominant reactions are [1]:

At pH < 4.20 formic acid to carbonic acid



$$\text{for which } E_0 = -0.156 - 0.0591 \text{ pH} + 0.0295 \log ([\text{H}_2\text{CO}_3]/[\text{HCO}_2\text{H}])$$

At 4.20 < pH < 6.38 formate ion to carbonic acid



$$\text{for which } E_0 = -0.267 - 0.0295 \text{ pH} + 0.0295 \log ([\text{H}_2\text{CO}_3]/[\text{HCO}_2^-])$$

At 6.38 < pH < 10.34 formate ion to bicarbonate ion



$$\text{for which } E_0 = -0.078 - 0.0591 \text{ pH} + 0.0295 \log ([\text{HCO}_3^-]/[\text{HCO}_2^-])$$

Above pH 10.34 formate ion to carbonate ion



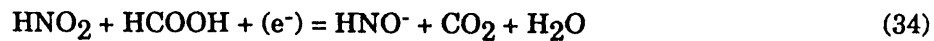
$$\text{for which } E_0 = +0.227 - 0.0886 \text{ pH} + 0.0295 \log ([\text{CO}_3^{2-}]/[\text{HCO}_2^-])$$

These equations indicate the predominant species for the pH ranges, but the other species are also present in lower concentrations. These equations can be plotted on axes of Eh vs pH and used to describe the reducing strength of formic acid solutions.

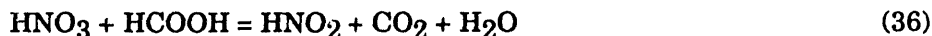
## FORMIC ACID - NITRIC ACID REACTIONS

When HCOOH was fed into boiling  $\text{HNO}_3/\text{NaNO}_3$  solutions (similar to those of DWPF feed preparation) the evolved gases were 68% NO / 4%  $\text{NO}_2$  / 28%  $\text{N}_2\text{O}$  [10]. These results are similar to results of large scale testing on simulated waste. When  $\text{HNO}_3/\text{NaNO}_3$  solutions were fed into boiling HCOOH (similar to reverse of normal DWPF processing), the evolved gases were 22% NO / 3%  $\text{NO}_2$  / 75%  $\text{N}_2\text{O}$  [10]. Thus, the reverse strike process should produce less oxidizing  $\text{NO}_x$  mixtures than the direct strike process. Similar effects were seen by Orebaugh [5], who also measured shifts with time as concentrations of the mixture shifted.

Of concern for potential denitration are the reactions where formic acid can increase the amount of nitrous acid [5]:



where (24) and (25) are autocatalytic, and have  $\text{HNO}_2$  as an essential intermediate [12]. Kinetic information has been published for these reactions, but have focussed on high nitrate concentrations [5,7]. Equations 24 and 25 can be summarized as:



Denitration requires threshold concentrations of  $10^{-1}$  to  $10^{-2}$  M  $\text{HNO}_2$  to proceed [8]. Nitrous acid scavengers (hydroxylamine, sulfamic acid, hydrazine) increase the induction time required for the denitration steps. Ferrous ion consumes  $\text{HNO}_2$ , and can slow the denitration [8]. It can therefore be expected that  $\text{Cu}^+$  might have an effect similar to  $\text{Fe}^{++}$ . Similarly, sludge might participate in the reactions.

### FORMIC ACID - NITROUS ACID REACTIONS

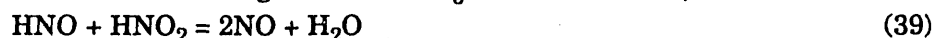
In dilute mineral acids nitrous acid disproportionates [12] by:



In formic acid in addition to the above disproportionation the most likely sequence of reactions is [12]:



which is the limiting reaction in  $[\text{H}_3\text{O}^+] = 0.1$  to  $3.0$  N, and



for an overall reaction of



which gives the correct overall stoichiometry for formic acid consumption [10]. The reaction rate for this in 1.2 M  $\text{HCOOH}$  (5.5%, comparable to DWPF feed preparation) is :

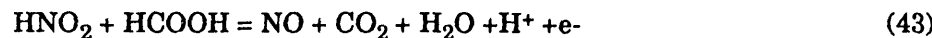
$$-d(\ln [\text{HNO}_2])/dt = 0.0060 (\text{min.}^{-1} \text{ mole}^{-1} \text{ l}) [\text{HCOOH}] \quad (41)$$

which is not dependent upon acidity for solutions up to 2.5 N  $[\text{H}_3\text{O}^+]$  [12]. The corresponding equilibrium half reactions are:



for which  $E_o = 1.004 - 0.0591 \text{ pH} + 0.0591 \log([\text{HNO}_2]/p_{\text{NO}})$

and



for which  $E_o = -1.401 - 0.0591 \text{ pH} + 0.0591 \log([\text{HNO}_2] [\text{HCOOH}]/$

$p_{\text{NO}} p_{\text{CO}_2})$  for an average corresponding to equation 38 of:

$$E_o = -0.199 - 0.0591 \text{ pH} + 0.0296 \log([\text{HNO}_2]^2 [\text{HCOOH}]/ p_{\text{NO}}^2 p_{\text{CO}_2}).$$



## NO AND NO<sub>x</sub> PRODUCTION BY FORMIC ACID

The most critical nitrite reactions which can be monitored using pH and Eh methods appear to be those that result in HNO<sub>2</sub> production and NO<sub>x</sub> evolution, since NO<sub>x</sub> is an oxidant, can be reabsorbed to produce high local concentrations of HNO<sub>2</sub> and HNO<sub>3</sub>, and can increase the effective nitrate and nitrite contents for reduction reactions.

Because of the moderate nitrite content of washed sludge, about 0.2 M, HNO<sub>2</sub> production is primarily by formic acid causing a pH shift in the sludge, by equations 1 and 4, and can be considered instantaneous.

For formic acid reduction of equation 36, active NO<sub>x</sub> evolution will occur with simultaneous carbon dioxide evolution, and  $p_{NO} = 0.7$ . For the precipitate hydrolysis solutions being studied, the [HNO<sub>2</sub>] is about 0.1 for pH near 3 (Equation 4). Thus by equation 40, for reverse strike digestion of sludge with formic acid, producing NO:

$$E_0 = 1.004 - 0.0591 \text{ pH} + 0.0591 \log (0.1/0.7) = 0.954 - 0.0591 \text{ pH} \quad (44)$$

In the absence of NO<sub>x</sub> evolution the Eh of the solution is expected to reflect the nitrite/nitrate ratio by equation 7, and since the nitrite/nitrate ratio begins at about 1:

$$E_0 = 0.835 - 0.0591 \text{ pH} \quad (45)$$

should approximate the Eh prior to the NO evolution (in the absence of other reducing agents), resulting in a shift which is the difference of equations 29 and 30

$$E_{\text{shift, NO}_x \text{ evolution}} = +0.119 \text{ Volt} \quad (46)$$

NO is not the only NO<sub>x</sub> which may evolve, however, and the regions of relative predominance of the gaseous substances have been calculated [1]:

$$N_2O \rightleftharpoons NO : \quad E_0 = 1.582 - 0.0591 \text{ pH (at 1 atm.)} \quad (47)$$

$$N_2O \rightleftharpoons NO_2 : \quad E_0 = 1.226 - 0.0591 \text{ pH (at 1 atm.)} \quad (48)$$

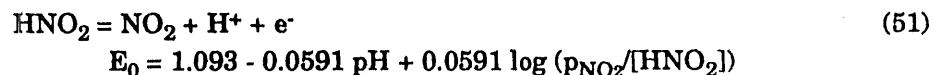
$$NO \rightleftharpoons NO_2 : \quad E_0 = 1.049 - 0.0591 \text{ pH} \quad (49)$$

Therefore it may be also advantageous to note that for:



$$E_0 = 1.297 - 0.0591 \text{ pH} + 0.0148 \log ([HNO_2]^2/p_{N_2O})$$

and similarly for:



which means that using the same assumptions as those for equation 31:

$$E_{\text{shift, N}_2\text{O evolution}} = +0.437 \text{ Volt} \quad (52)$$

and

$$E_{\text{shift, NO}_2 \text{ evolution}} = +0.299 \text{ Volt} \quad (53)$$

Noting that deviations from equation 7 can occur when other redox species are present .

### METAL CATALYZED FORMIC ACID DECOMPOSITION

The metal catalyzed decomposition of formic acid has been studied by several methods [13-16]. The catalytic activities are affected by the preparation of the catalysts: When a salt of the metal is added to formic acid / formate solution instead of the metal, all the Pt metals show higher catalytic activities than the finely divided metal itself [13]. Ru is reported to require an incubation time before hydrogen is evolved [16]. The catalytic activity decreases rapidly as the active catalysts are alloyed with other materials [21]. The order of the reaction is approximately 1 when  $\text{HCOO}^-$  is the major formate specie [17], as in washed HLW digestion. It has been concluded, based on gas phase reactions, that the reaction is a two step process, with the kinetics controlled by the heat of formation of the metal formate [18]: First the formate or formic acid is adsorbed on the catalyst's surface:



Then the formate decomposes:



However, for aqueous decomposition it may be equally important to form and evolve the hydrogen, which should be inversely proportional to the hydrogen overpotential required for the electrochemical decomposition of water, and proportional to the exchange current available on the metal's surface:



Table 1 ranks various catalytic metals by their hydrogen overpotential and exchange currents. The free energy released during formic acid decomposition to  $\text{H}_2$  and  $\text{CO}_2$  is -9,160 cal/mole, equivalent to 0.047 Volt. Thus, Ag and the elements below it in Table 1 require thermal activation energy, and are limited in the rate that they can evolve  $\text{H}_2$ . For this reason amalgams of the noble metals are not expected to be active catalysts.

Table 1. The Relative Effectiveness of Catalysts for Formic Acid Decomposition When Ranked by Hydrogen Overpotential and Exchange Current.

<u>Element</u>	<u>H<sub>2</sub> Overpotential,</u> Volts [22]	<u>log Exch. Curr.,</u> Amp/cm <sup>2</sup> [23,24]
Pd	0.00000	-3.0
Pt	0.000002	-3.1
Ru	0.00043	
Rh	0.004	-3.6
Ag	0.097	-7.2
Ni	0.1375	-5.2
Cu	0.19	-6.5
C	0.335	
Hg	0.570	-12.3

Pd catalysts have been patented for destroying formates in waste streams [25]. The first evidence of formic acid decomposition caused by fission product noble metals during digestion of simulated radioactive waste feed was discussed by PNL, with detection of both NO and NH<sub>3</sub> production [26]. Electrodes of Pt, Rh, and Ir in normal solutions of formic acid have been reported to give lower potential readings than the standard hydrogen electrode, with Pd giving the same potential as the hydrogen electrode [15].

In SRL test solutions of 0.5 M NaCOOH and 0.5 M NaNO<sub>3</sub> at pH 4.2, simulating HLW, Cu underwent active dissolution, and Pd showed a tendency to activate as the temperature approached boiling. NO<sub>2</sub><sup>-</sup> showed a tendency to (reversibly) deactivate the Pd as the NO<sub>2</sub><sup>-</sup> concentration increased above 40 mM, but was not capable of stopping the decomposition once it started on finely divided Pd (from PdCl<sub>2</sub>) above 72°C. PdCl<sub>2</sub> reacted to form a black precipitate which evolved gas at a rate of over 15 cc s<sup>-1</sup> g<sup>-1</sup> Pd. The solution Eh measured with a graphite electrode ranged from -0.064 to -0.311 during the hydrogen evolution, compatible with the Eh of NH<sub>4</sub><sup>+</sup> or H<sub>2</sub> evolution. The difference between the highest observed H<sub>2</sub> evolution potential, and the lowest NO<sub>x</sub> evolution potential was 0.63 volts, making the two reactions clearly distinguishable with an Eh probe, even without pH measurement.

When soluble noble metals were added to simulated waste with mercury, the pH shift resulting for formic acid destruction by Pd was one pH unit less than that of the Pd without Hg, showing Pd poisoning. Rh and Ru caused 1.5 pH less shift with Hg present, indicating that they were more effectively poisoned by Hg.

## ACKNOWLEDGEMENTS

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**Physical and Chemical Effects Which May Reduce the Catalytic Activity of Noble Metal Fission Products in Actual High Level Waste**

Amalgamation with mercury

Alloying with other fission products (e.g. Te, Se)

Actual particle size

Microencapsulation by  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}\cdot 3\text{H}_2\text{O}$ ,  $\text{MnFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ , etc.

**Three Laboratory Scale Methods Have Been Developed and Demonstrated for Catalysis Studies on Simulated and Actual High Level Waste**

Eh-pH monitoring for  $\text{NO}_x$  and  $\text{H}_2$  evolution

Digestion bomb heating / Ion chromatography & pH

HCOOH decomposition

Denitrition

Denitration

pH shift

poisoning of catalyst

Gas burette with Eh monitor

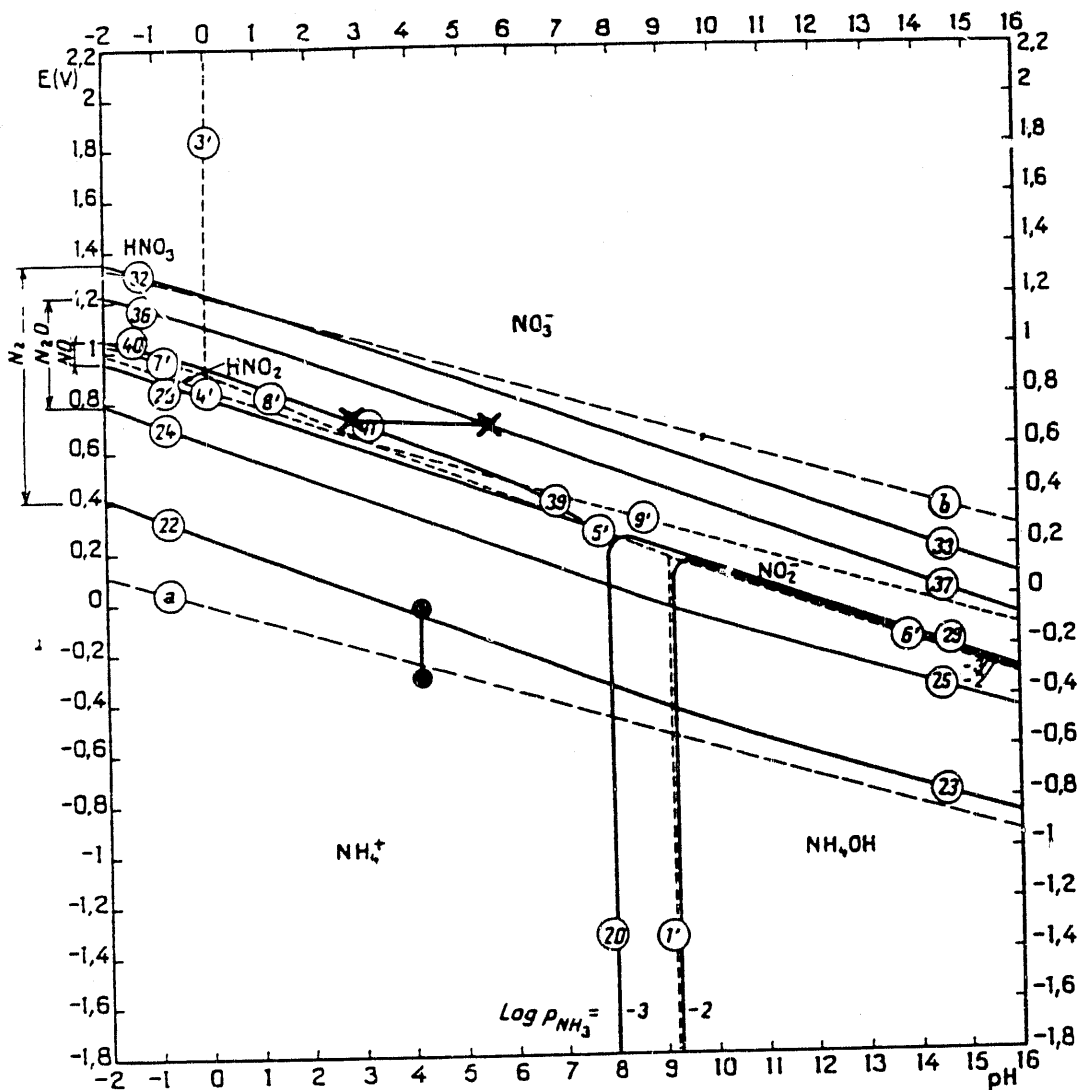
Gas evolution rate

Eh vs. gas evolution rate

poisoning of catalyst

**Eh-pH Diagram of Nitrogen with Experimentally Determined (Simulated HLW)  
 NO<sub>x</sub> evolution X-----X and CO<sub>2</sub>/H<sub>2</sub> evolution ●-----●**

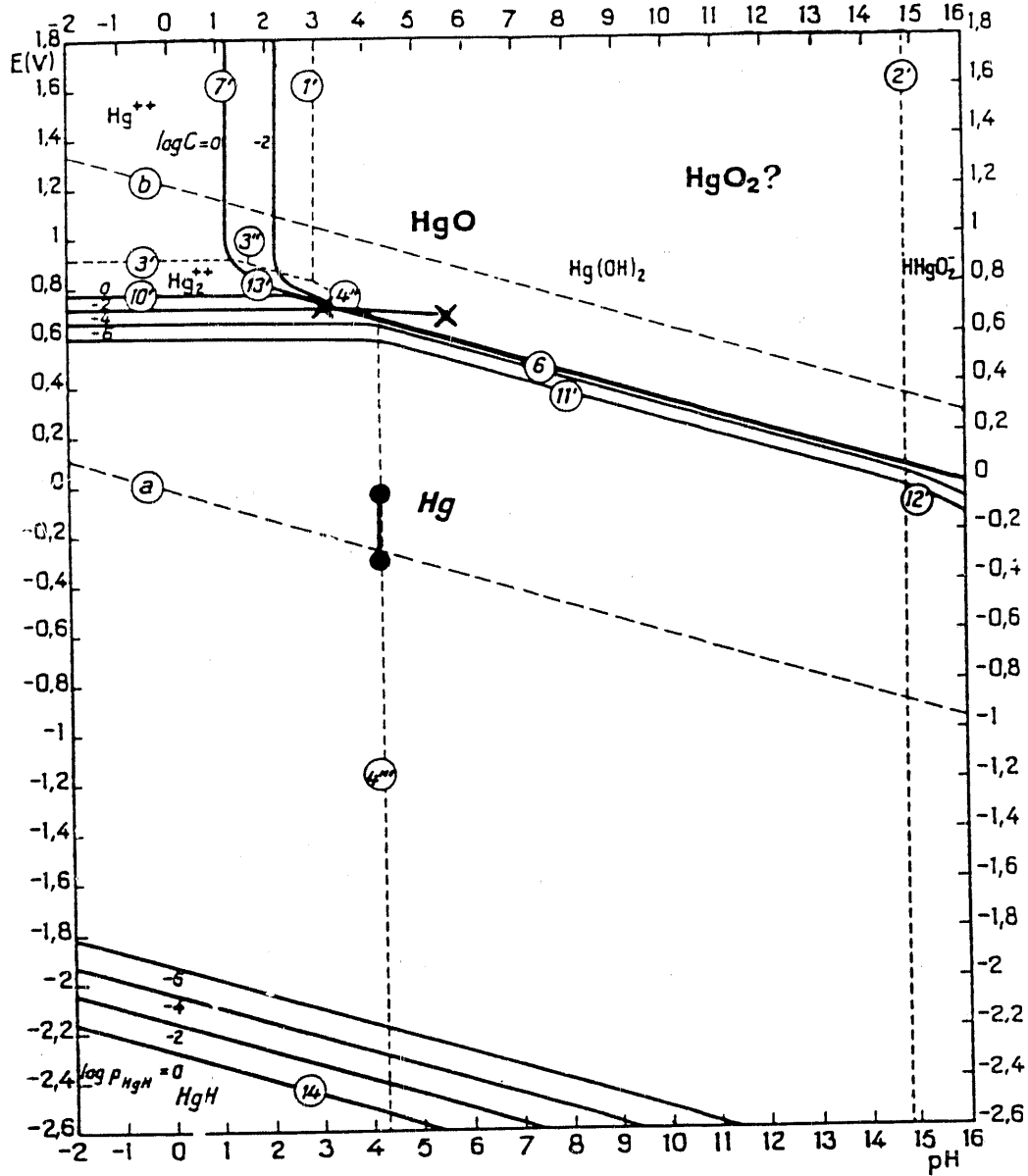
Note the large difference between the regions, indicating that only small amounts of NO<sub>x</sub> and H<sub>2</sub> are simultaneously released in a well mixed system. The two regions are far enough apart that pH probably does not need to be measured if Eh is used as an alarm for H<sub>2</sub> evolution.



Background Figure from M. Pourbaix,  
*Atlas of Electrochemical Equilibria in Aqueous Solutions* [1]

**Eh-pH Diagram of Mercury with Experimentally Determined (Simulated HLW) NO<sub>x</sub> evolution X-----X, and CO<sub>2</sub>/H<sub>2</sub> evolution ●-----●**

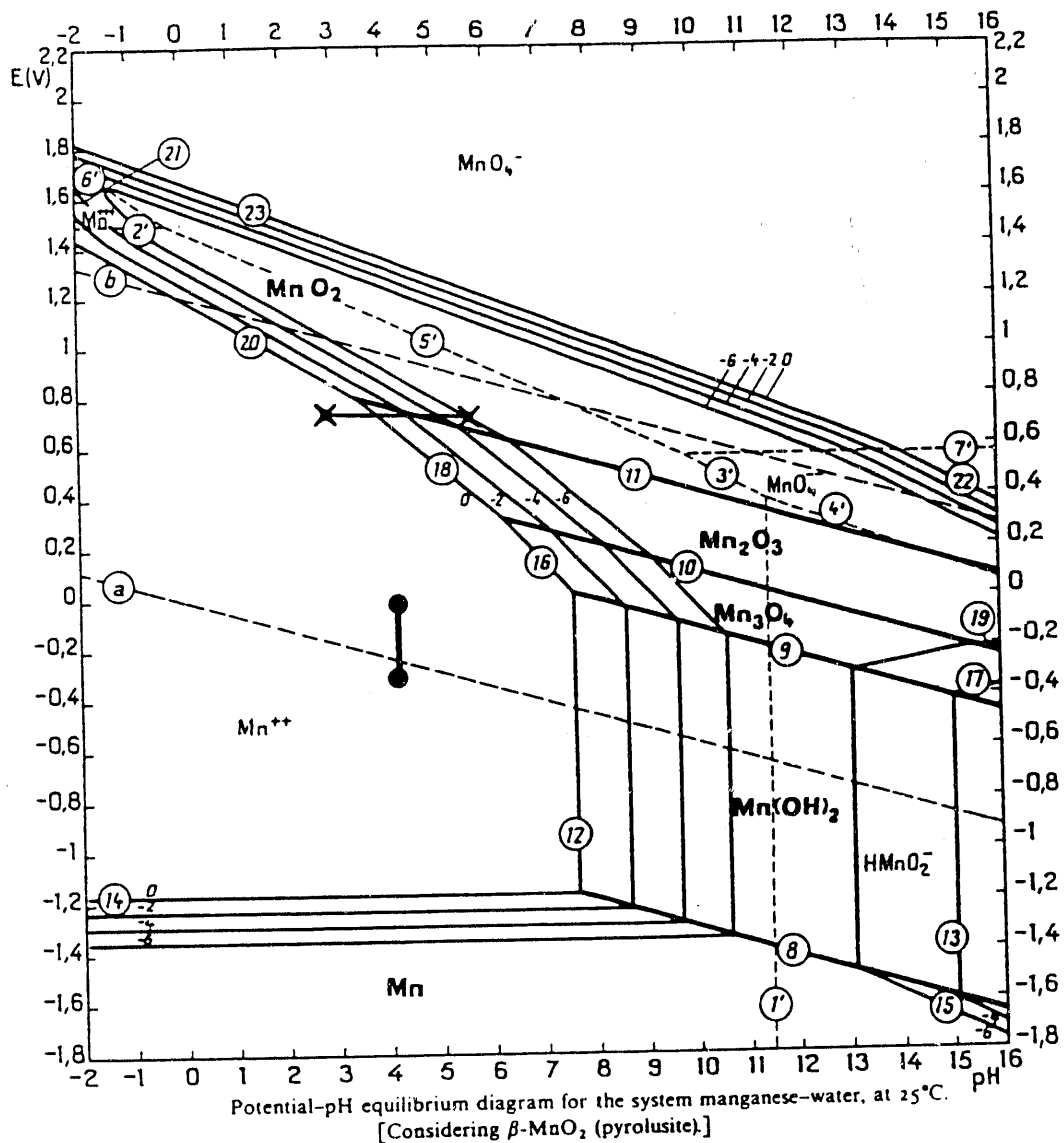
The redox potential does not need to approach that of hydrogen generation in order to reduce mercury.



Background Figure from M. Pourbaix,  
*Atlas of Electrochemical Equilibria in Aqueous Solutions* [1]

Eh-pH Diagram of Manganese with Experimentally Determined (Simulated HLW) NO<sub>x</sub> evolution X-----X and CO<sub>2</sub>/H<sub>2</sub> evolution ●-----●

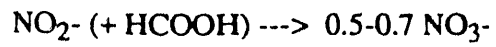
Note the large difference between the Mn(IV) ---> Mn(II) and the H<sub>2</sub> evolution, indicating that the two regions are far enough apart that pH probably does not need to be measured if Eh is used as an alarm for H<sub>2</sub> evolution during Mn digestion. Mn(IV) must be reduced to minimize foaming in the melter.



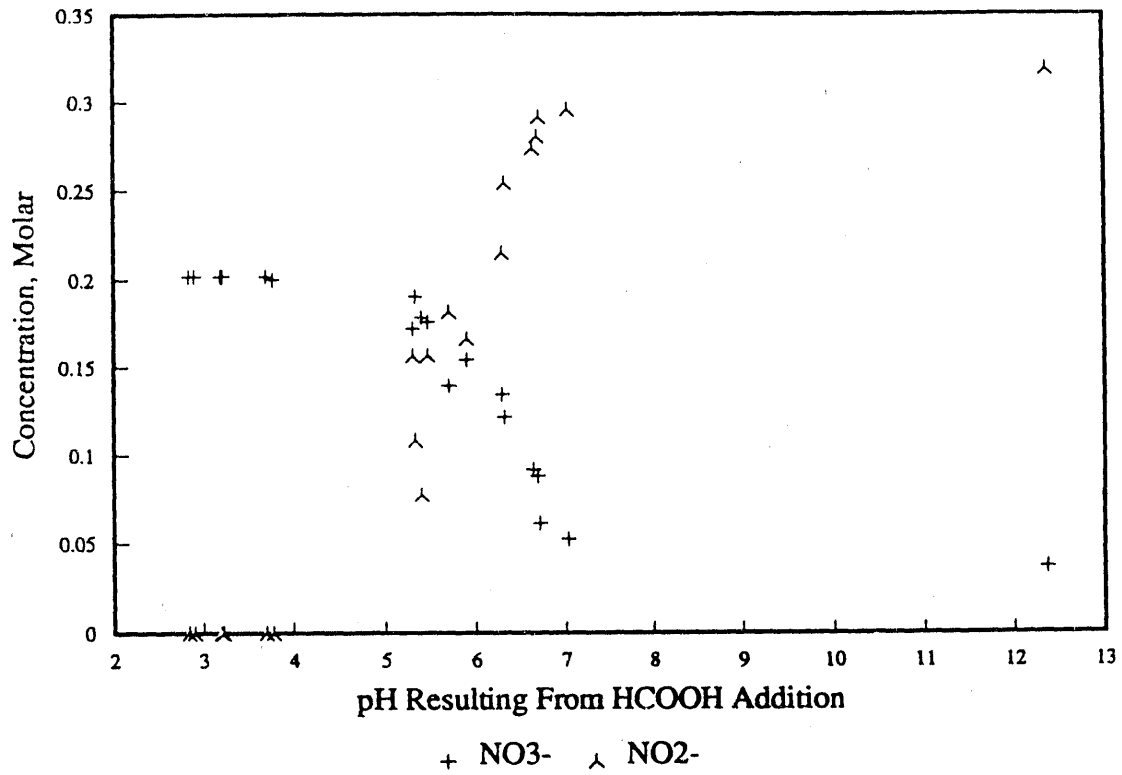
Background Figure from M. Pourbaix,  
*Atlas of Electrochemical Equilibria in Aqueous Solutions* [1]



When Nitrite is reacted with formic acid under reflux conditions, the condensate contains nitrate from absorbed NOx. Thus, there is a net reaction of

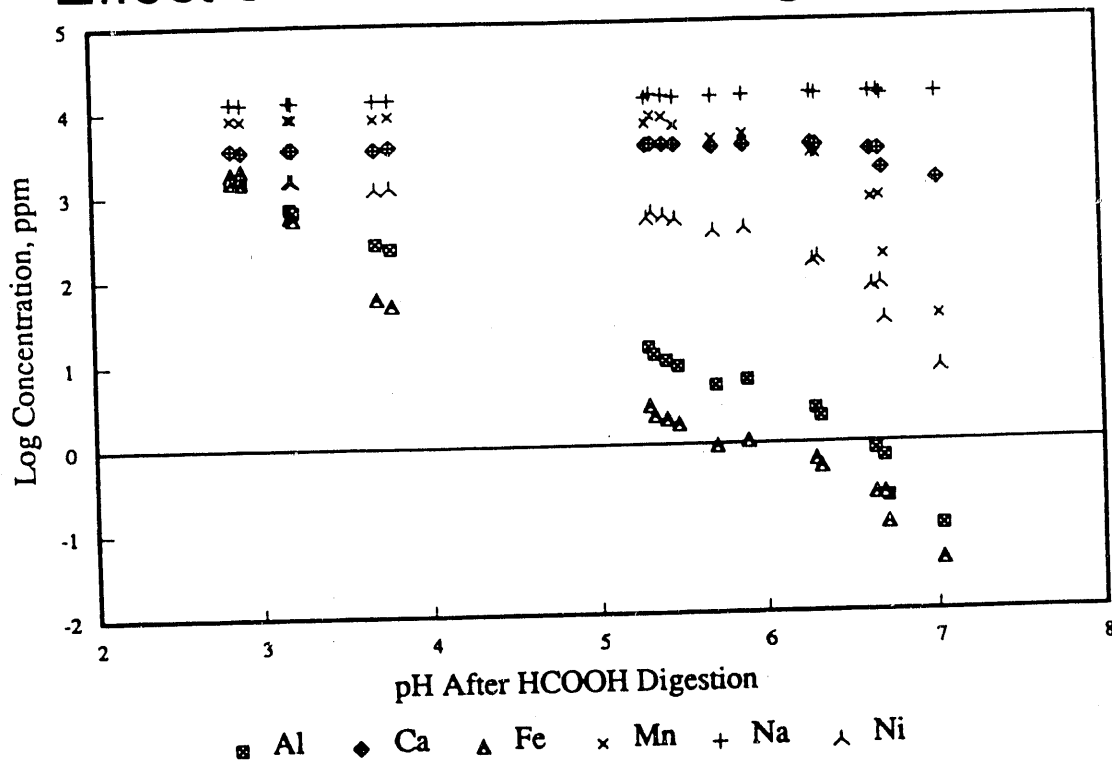


Effect of pH on Nitrite Destruction and Nitrate Production



The solubility of transition metals is a strong function of pH, influencing their ability to cause homogeneous catalysis.

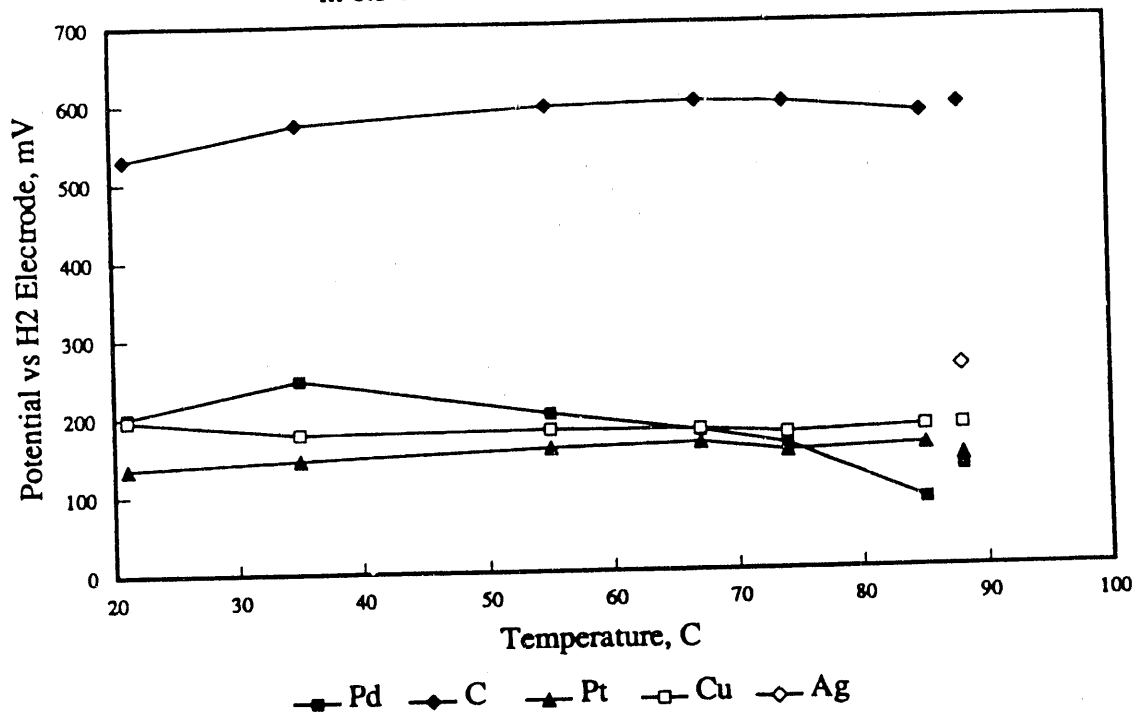
## Effect of HCOOH on Sludge Solubility



Experiments indicate that electrochemical methods are useable to characterize the catalytic activity of the various candidates for H<sub>2</sub> evolution via HCOOH decomposition, and in determining the effectiveness of poisons for these catalysts. Using solid electrodes, Pd has been identified as the most likely cause of the decomposition: The Pd potential decreases as temperature is raised, showing an increased tendency for hydrogen evolution, and may have a break at about 80°C.

## Electrochemical Potentials of Catalysts

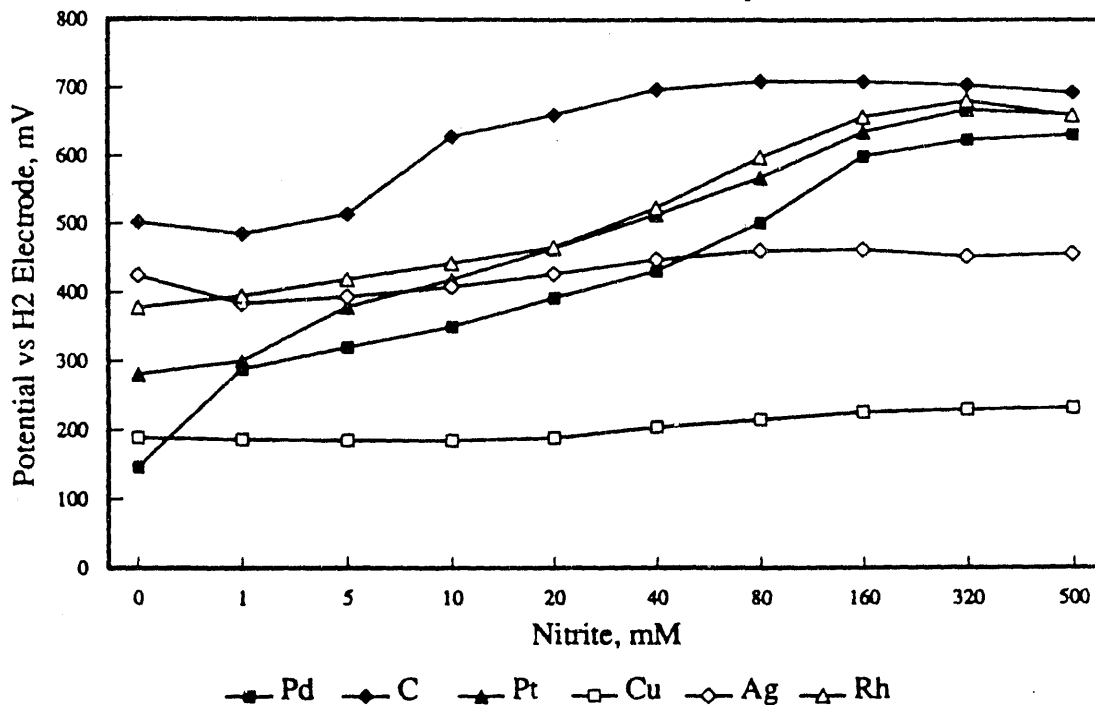
in 0.5 M NaNO<sub>3</sub> + 0.5 M NaCOOH, pH 4.1



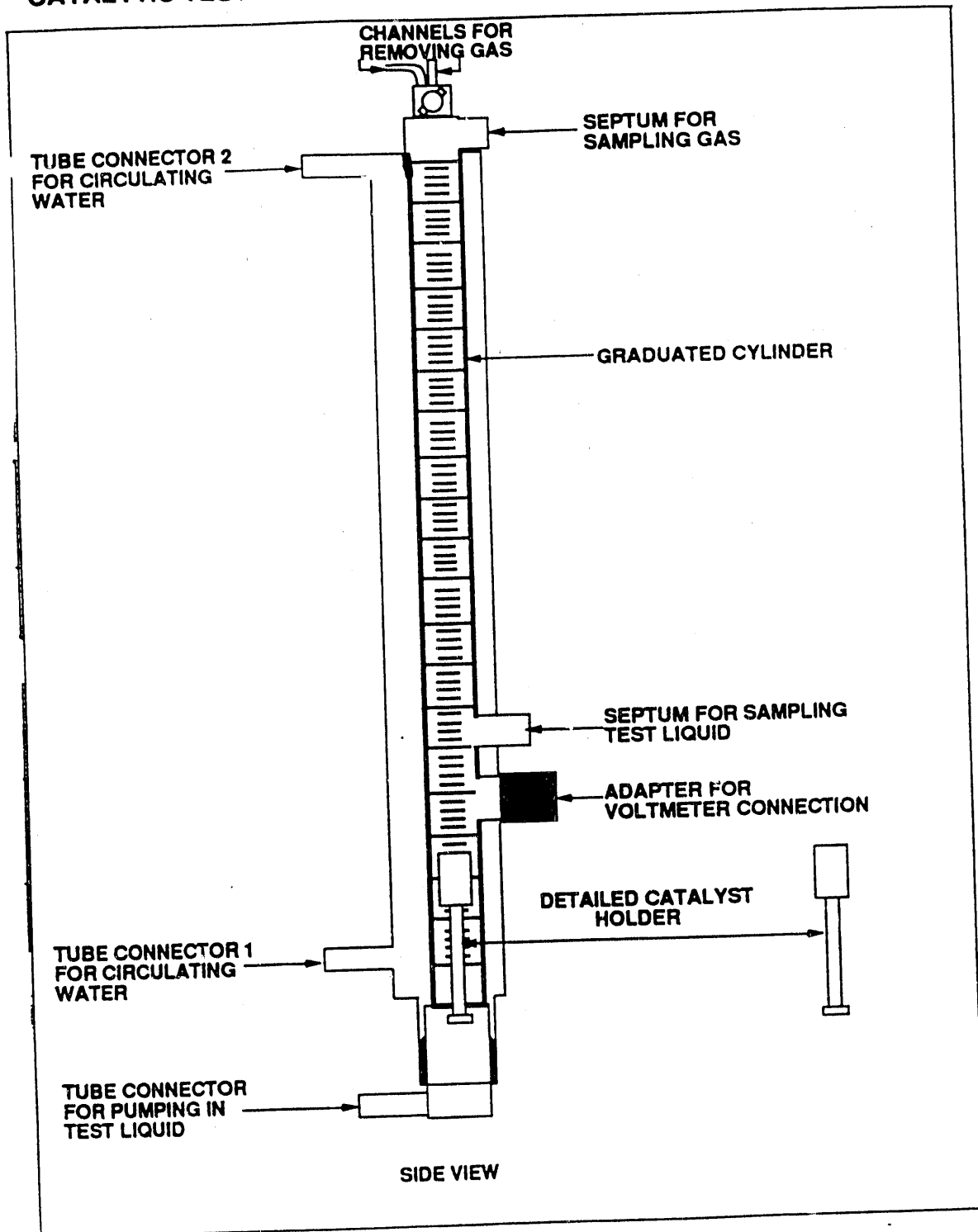
Room temperature tests were conducted to examine the effectiveness of nitrite as a poison for solid catalysts. The test was conducted in a stirred beaker exposed to the air, and Cu actively dissolved in the solution. The copper potential was unaffected by the increased nitrite concentration, indicating that nitrite did not stop the dissolution. The potential of the copper is that which would be expected for copper dissolution. Similarly, the potential for silver at high nitrite concentrations stabilized at that corresponding to silver dissolution. The third notable feature in this figure is that the noble metal lines Pd, Pt, and Rh slope upward at > 5 mM nitrite. This indicates a tendency for nitrite absorption, implying that above these concentrations these materials are progressively poisoned by increasing nitrite concentrations.

## Electrochemical Potentials of Catalysts

0.5 M NaNO<sub>3</sub> + 0.5 M NaCOOH, pH 4.1, 22 C

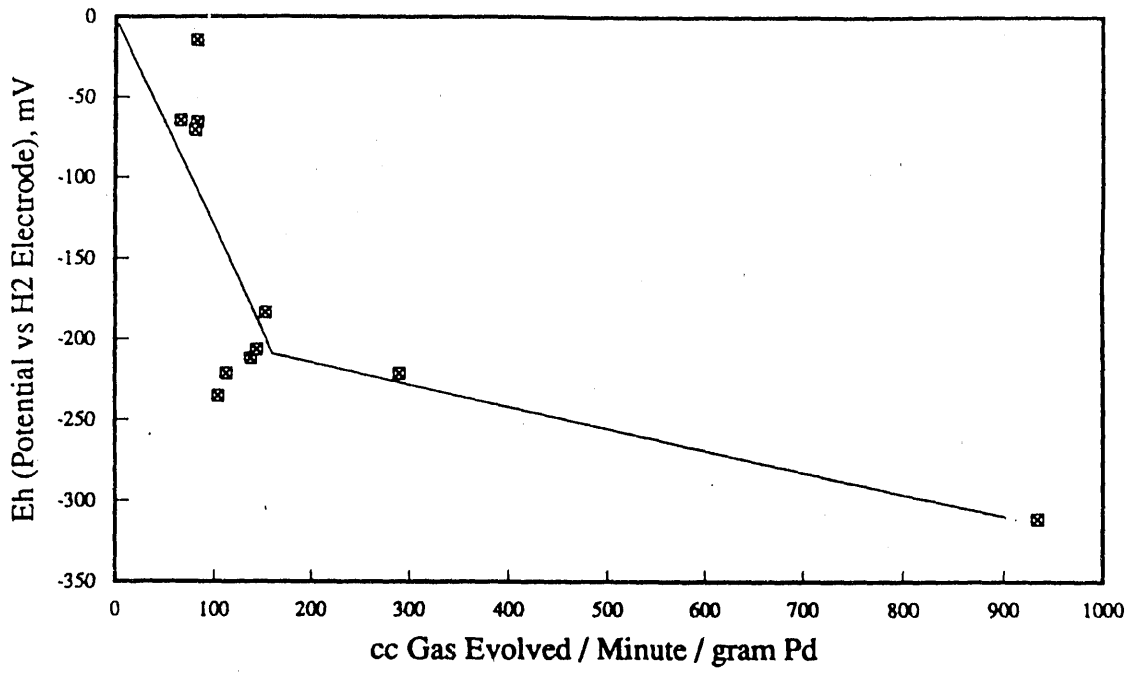


# CATALYTIC TEST CHAMBER



Gas evolution rate is a function of temperature and solution redox potential.  
Carbon electrode used to monitor solution potential.

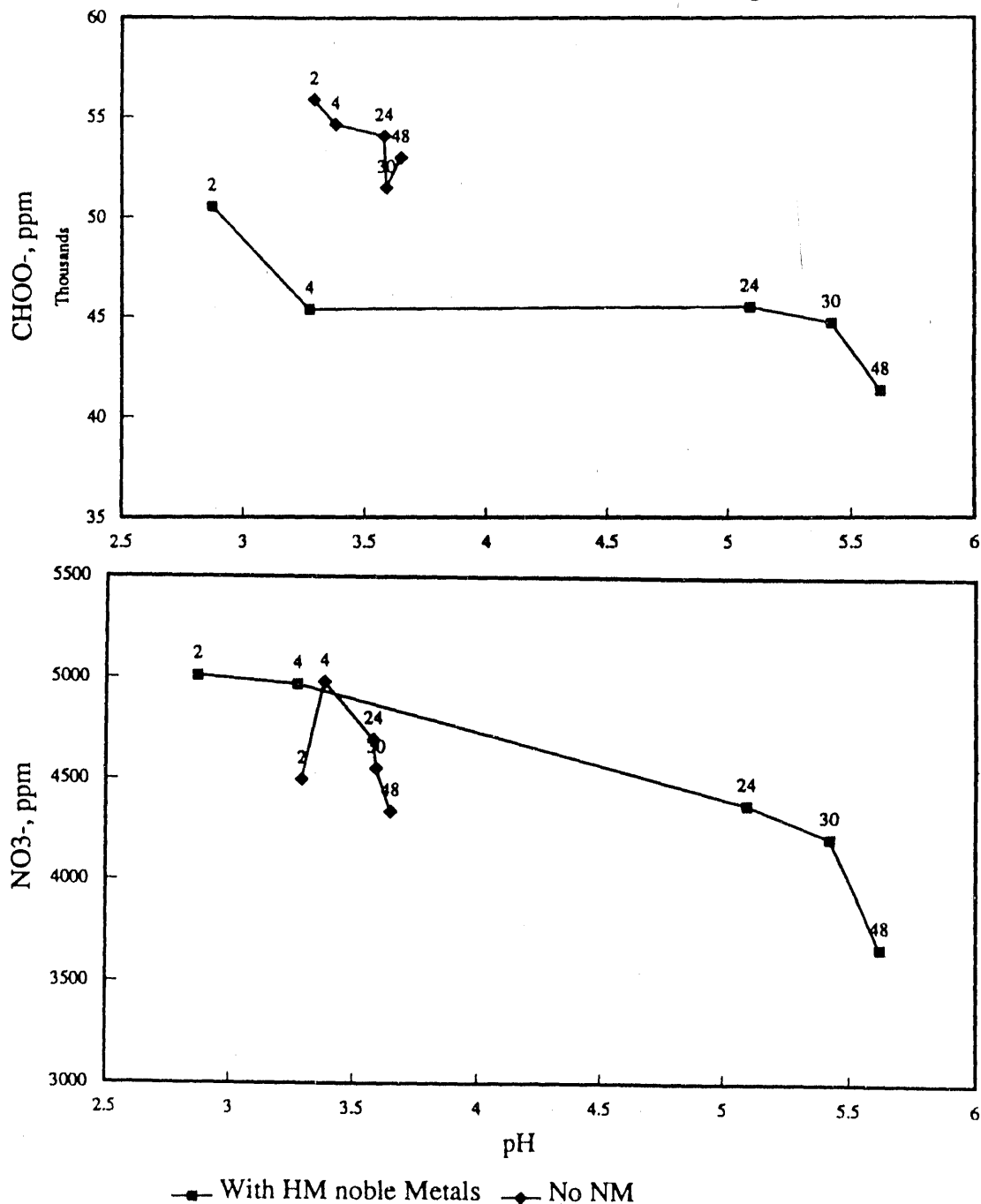
### Electrochemical Potentials of H<sub>2</sub> / CO<sub>2</sub> Evolution in 0.5 M NaNO<sub>3</sub> + 0.5 M NaCOOH, pH 4.2, 72-90 C



Experimental work has included developing small scale methods for screening the possible effects and treatments. The sealed Teflon pressure vessels used in microwave digestion were used as a relatively closed system for simulating the SME/Condenser. Using ion chromatography it was possible to follow the shifts in formic acid concentration and pH as the decomposition proceeds. The figure shows the decrease in formic acid concentration, and simultaneous shift in pH. The denitration process was essentially complete after two hours. There was a measureable decrease in nitrate concentration in the samples with noble metals, indicating that partial noble metal catalyzed formic acid denitration could also be occurring. Initial solutions were about 8,000 ppm  $\text{NO}_3^-$ , and 60,000 ppm  $\text{CHOO}^-$ .

## Effect of Noble Metals on Formic Acid Decomposition

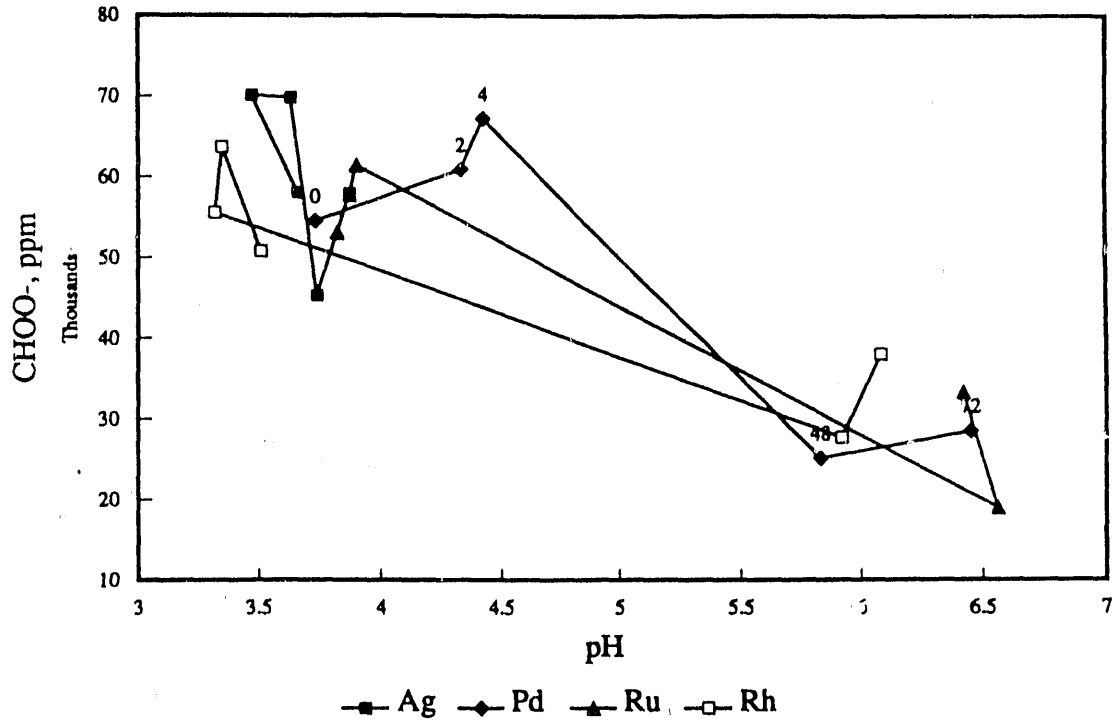
Lab Scale Tests: Labels indicate hours of Digestion.



Pd, Rh, and Ru were effective in destroying HCOOH, and NO<sub>3</sub><sup>-</sup>, resulting in a pH shift. The NO<sub>3</sub><sup>-</sup> destruction was by noble metal catalyzed denitration.

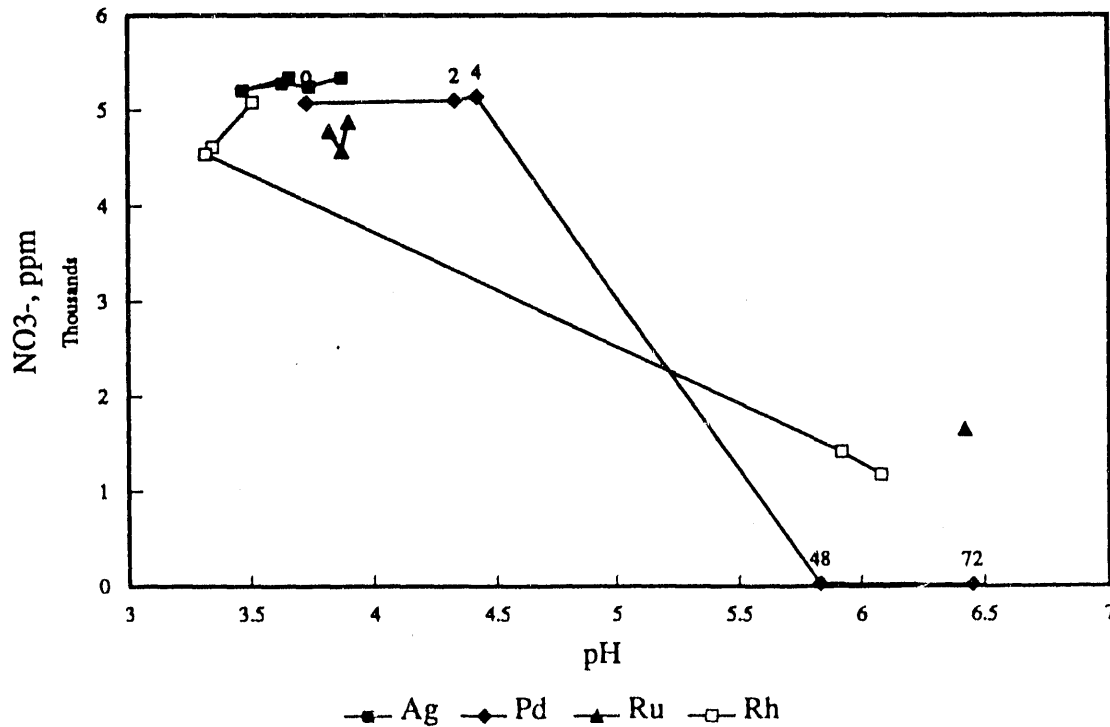
## Effect of Noble Metals on Formic Acid Decomposition

Lab Scale Tests: Labels indicate hours of Digestion.



## Effect of Noble Metals on Nitric Acid Concentration

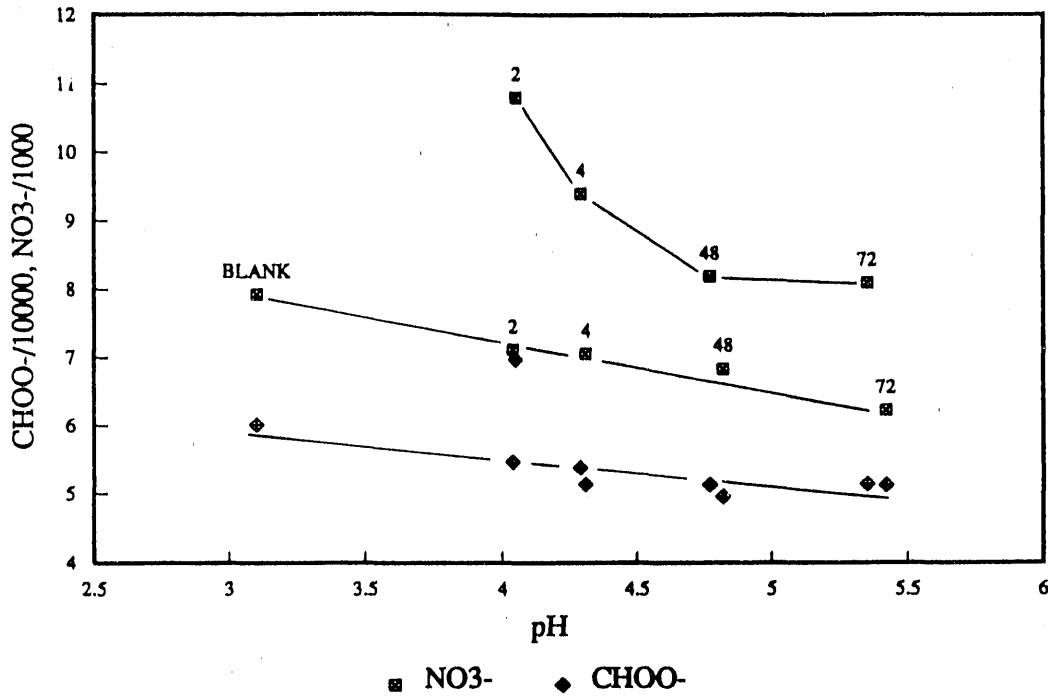
Lab Scale Tests: Labels indicate hours of Digestion.



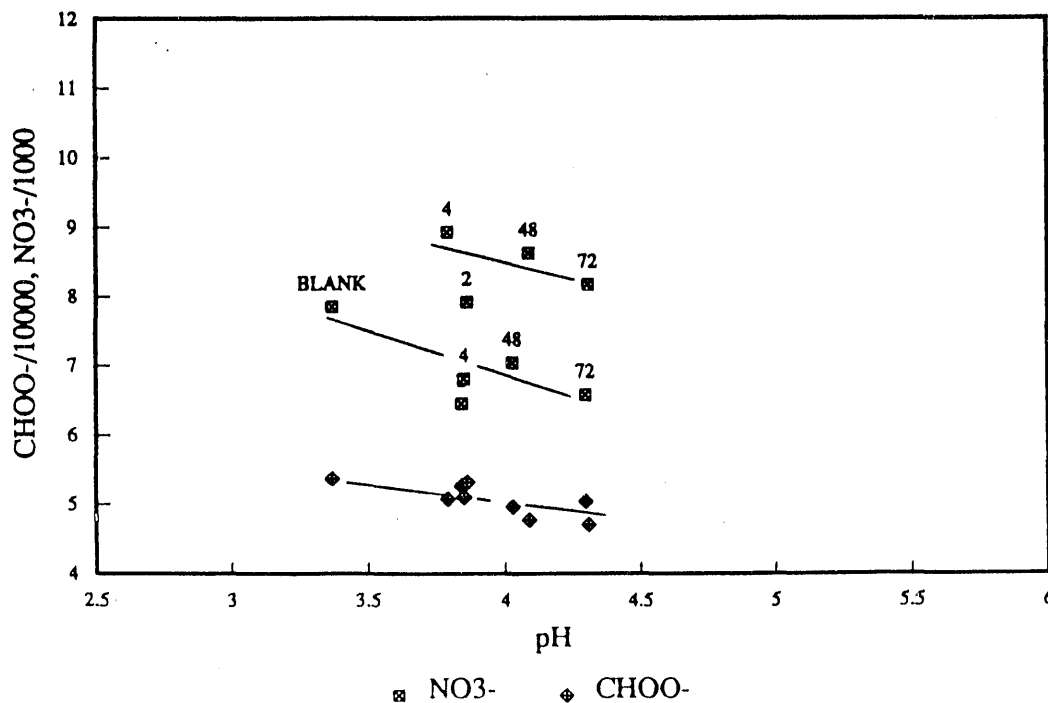


Further tests were conducted to determine the relative effects of the different noble metal species, with mercury, on the rate of decomposition. Only Pd and Ru showed significant shifts. The pH shift for Pd was one PH unit less that seen with no mercury present, indicating mercury poisoning of the catalyst. Rh and Ru were more effectively poisoned. Two levels of  $Hg(NO_3)_2$  were used equal to 2 and 4 wt% Hg on a sludge solids basis, resulting in different beginning nitrate concentrations.

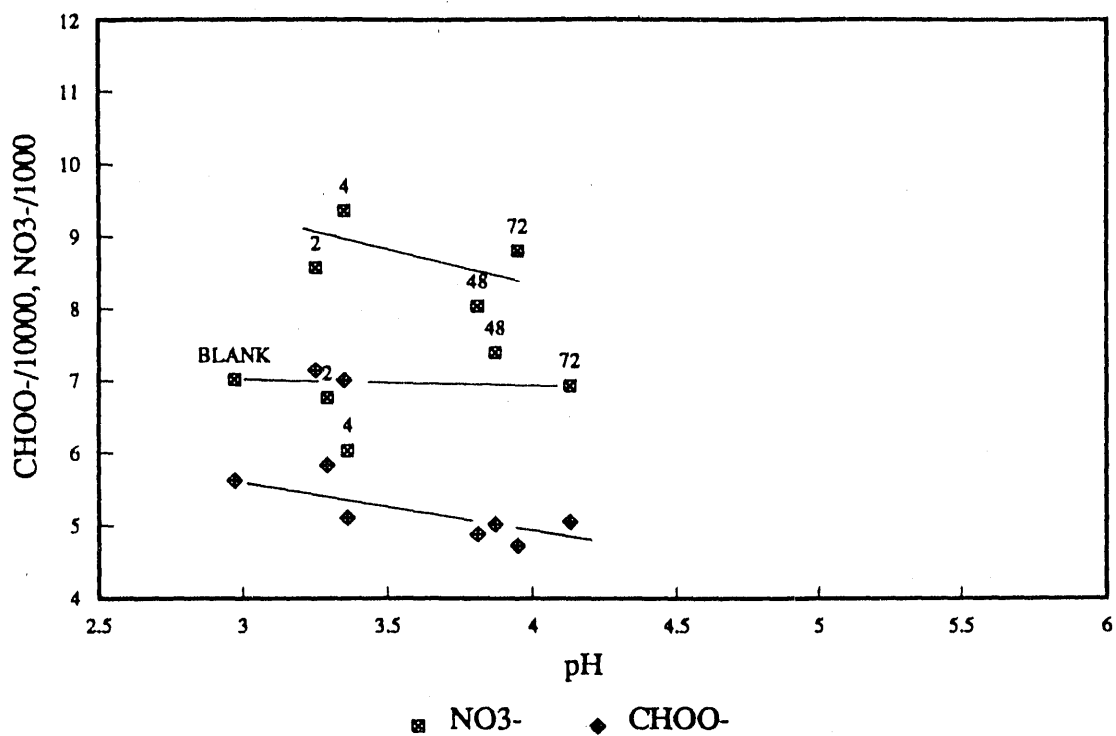
### Effect of Palladium with Mercury on Formic Acid Reactions Lab Scale Tests



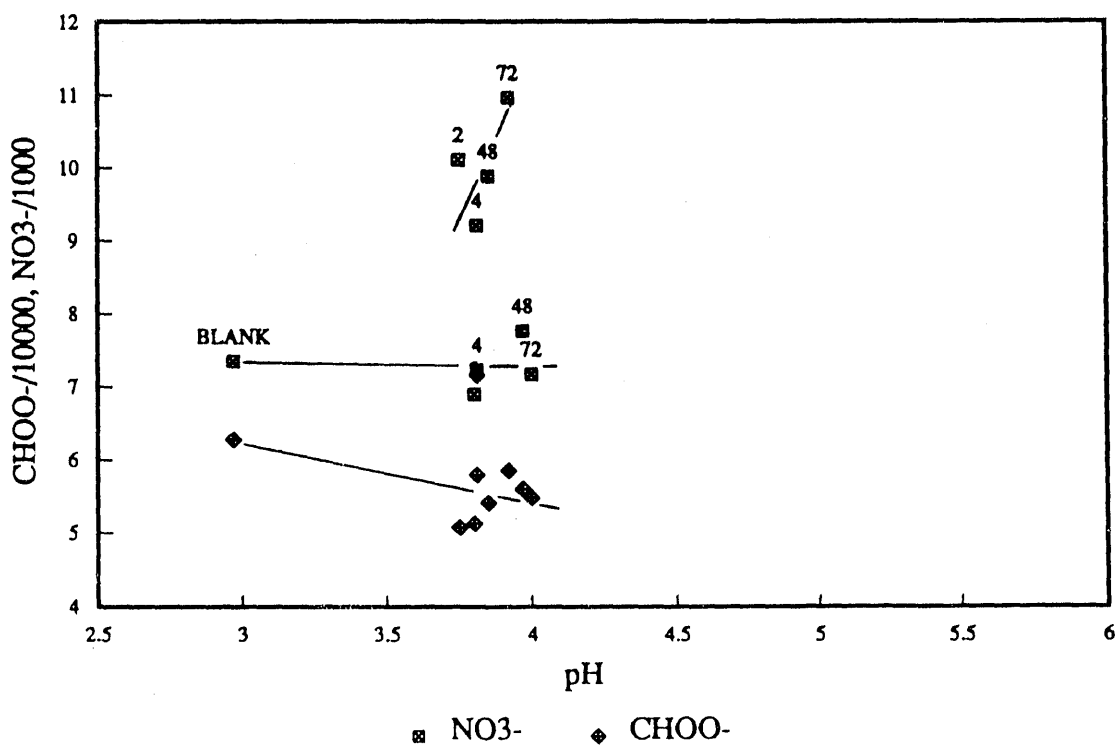
### Effect of Ruthenium with Mercury on Formic Acid Reactions Lab Scale Tests



### Effect of Rhodium with Mercury on Formic Acid Reactions Lab Scale Tests



### Effect of Silver with Mercury on Formic Acid Reactions Lab Scale Tests



**END**

**DATE  
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**4 / 22 / 92**

