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# TCAP Aluminum Dissolution Flowsheet Basis

**KEYWORDS:**
*TCAP*
*Aluminum*
*Palladium*
*Metal*
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*Nitric Acid*
*Fluoride*

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## OVERVIEW

The Actinide Technology Section has proposed the use of an nitric acid ($HNO_3$) and potassium fluoride (KF) flowsheet for stripping palladium (Pd) from palladium-coated kieselguhr (Pd/K) and removing aluminum (Al) metal foam from the TCAP coils. The basis for the $HNO_3$-KF flowsheet is drawn from many sources. A brief review of the sources will be presented.

The basic flowsheet involves three process steps, each with its own chemistry. In the first step, Pd metal is stripped from the Pd/K substrate in the coils using 8M $HNO_3$. The acid is continually circulated through the coil at or near ambient temperature. Successful completion of the first step will involve the dissolution of almost all Pd as soluble palladium nitrate ($Pd(NO_3)_2$). The kieselguhr substrate will remain in the coil. Following the Pd dissolution step, the coil will be rinsed thoroughly with water to remove residual Pd and much of the kieselguhr. Kieselguhr, which is a diatomaceous earth, does not dissolve readily in 8M $HNO_3$.

In the second step, 8M $HNO_3$/0.125M KF is circulated through the coil at 20-50$^{o}$C. The fluoride serves to remove the oxide coating from the surface of the Al foam. This removal allows the foam to dissolve in a gradual, controllable fashion. A byproduct of the dissolution reaction is the formation of NOx. As the aluminum dissolves, fluoride will be complexed and the reaction rate will diminish. At some point, it may be necessary to either replace the solution or add additional KF.

The third chemistry of the process is the absorption of NOx into 30% hydrogen peroxide ($H_2O_2$). As NOx is bubbled through $H_2O_2$, it dissolves readily to form $HNO_3$ up to high concentrations. The system configuration should have a primary vessel for bulk NOx absorption and a finishing vessel for scrubbing NOx because absorption efficiency in the primary vessel will diminish as the $H_2O_2$ is consumed.

## FLOWSHEET BASIS

<u>Palladium Metal Dissolution</u>: The dissolution of Pd metal from the Pd/K is based on the fact that Pd is soluble in $HNO_3$.[1] This reaction is consistent with the understanding that the precious metals industry will often use Pd nitrate solution for plating operations. Communications with others in the Savannah River Technology Center (SRTC) suggest that the solubility of Pd in $HNO_3$ is on the order of 0.5M. However, it is not clear what the effect of acid concentration will be on solubility. An average reaction for the dissolution was not immediately available. Flowsheet calculations assume the following reaction:

$$Pd + 4HNO_3 \rightarrow Pd(NO_3)_2 + 2NO_2 + 2H_2O \qquad (1)$$

<u>Aluminum Foam Dissolution</u>: Dissolution of Al in the processing of uranium (U) and plutonium (Pu) spent nuclear fuel is common as Al is frequently used as cladding with

either Pu or U. The dissolution chemistry for these systems has been studied at some length.[2,3] The average chemical reaction for 4-8M $HNO_3$ is:

$$Al + 6HNO_3 \rightarrow Al(NO_3)_3 + 3NO_2 + 3H_2O \quad (2)$$

However, the dissolution rate of Al in $HNO_3$ is greatly inhibited by the formation of an oxide coating on the surface of the metal. Therefore, a catalyst must be used to obtain significant rates. Mercuric nitrate is generally used.[2]

The use of $HNO_3$-HF acid mixtures has been used for the dissolution of Pu oxides for more than two decades.[4] Without the presence of $F^-$ (active as HF), typically added as either KF or calcium fluoride ($CaF_2$), the dissolution of $PuO_2$ is slow. Due to recent experimental work in SRTC, dilute concentrations of $F^-$ have been used as the catalyst to dissolve both U metal and a Pu-Al metal alloy.

Using a 4M $HNO_3$/0.3M HF (added as $CaF_2$), Pu-Al metal buttons, comprised primarily of Pu and Al metal, were dissolved completely with light, effervescent gas generation at the material surface with small trace amounts of NOx generation.[4] This flowsheet was extended for the dissolution of U metal which will be dissolved in an upcoming H-Canyon campaign. Uranium metal dissolution experiments have shown that acceptable dissolution rates could be achieved using either $HNO_3$ concentrations above 7M or low $HNO_3$ concentrations (1-4M) in the presence of fluoride. Increases in fluoride concentration produce visible changes in the amount of oxide coating on the surface of the uranium metal during dissolution. At low acid concentrations in the absence of fluoride, the reaction rates are unacceptably slow.[6]

Work with the use of a comparable flowsheet for the dissolution of $PuO_2$ tied up in sand, slag and crucible (SS&C) residues in F-Canyon showed that the dissolution is accomplished by free fluoride ions in solution. Chemicals such as boron, Pu and Al will form complexes with the fluoride and gradually diminish the free fluoride concentration in solution.[7] Because of equilibrium reactions, Al will not complex all of the fluoride. However, if enough fluoride is complexed, the reaction becomes extremely slow. As aluminum metal dissolves, it forms the $AlF^{2+}$ complex, which greatly decreases dissolution rate.[8]

The complexation of fluoride by Al is the basis for assurance that corrosion of stainless steel during the dissolution process is at an acceptably slow rate. Aluminum nitrate is used extensively in F- and H-Canyon to complex fluoride in dissolver solutions after Pu has been removed. The SS&C dissolution campaign showed that the presence of a complexant (boron) in a solution containing 0.35M total fluoride reduced the free fluoride concentration to less than 50 ppm.[7] This complexation was also evident in corrosion rate data collected on these solutions. The data are referenced in a recent communication from John Mickalonis who performed the studies. The communication refers to “data from a study supporting the dissolution of sand, slag and crucible tested 304L in 8-10 M nitric acid with 0.3-0.7 M KF and 2.0 g/L boron at 30 C. Boron also complexes fluoride. Corrosion rates were generally below 3 mil per year. These tests were conducted on both welded and non-welded samples."[9] Similarly, as free fluoride is consumed, the risk of HF exposure to the worker diminishes.

Gas generation from the dissolution of Al in $HNO_3$ has been well-characterized. An extensive discussion of this dissolution and how it relates to U metal dissolution is given in the literature.[6] The conclusion of the studies was that gas generation tests have demonstrated that hydrogen generation is not an issue at the conditions being proposed for plant operations. At $HNO_3$ concentrations above 2M, the hydrogen component of the offgas is less that 0.1% by volume. This conclusion applies to both U and Al metal dissolution.

Absorption of NOx: Absorption of NOx into 30% $H_2O_2$ has been demonstrated through a series of prior tests. For expediency, an excerpt from that work is below:[10]

*Discussion*: Several approaches exist for the recycle of $HNO_3$. Some options are proprietary technology of which little is known aside from vendor claims. The most attractive alternative for radioactive service is $H_2O_2$ absorption. Calculations of the maximum theoretical $HNO_3$ concentration expected for absorption of $NO_2$ using $H_2O_2$ indicates that high $HNO_3$ concentrations could be obtained using 30% $H_2O_2$. Using the equation

$$2\ NO_2 + H_2O_2 \longrightarrow 2\ HNO_3 \qquad (3)$$

it was determined that a maximum concentration of 61.3 wt% could be obtained with 30% $H_2O_2$. These calculations do not account for any acid formation that may occur due to $NO_2$ absorption by the balance of water in the $H_2O_2$ solution.

It is important to note that the presence of NO gas in the stream reduces the maximum theoretical concentration. The reaction of NO with $H_2O_2$ is as follows:

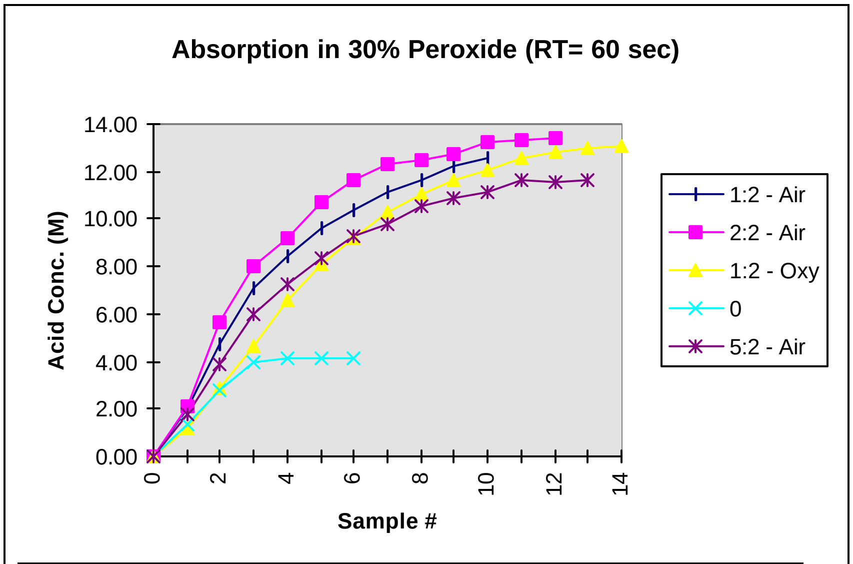
$$2\ NO + 3\ H_2O_2 \longrightarrow 2\ HNO_3 + 2\ H_2O \qquad (4)$$

Not only is peroxide use efficiency reduced, but there is also a dilution effect from the water in the reaction products. This yields theoretical maximum acid concentration of 47.0 wt% for 30% $H_2O_2$.

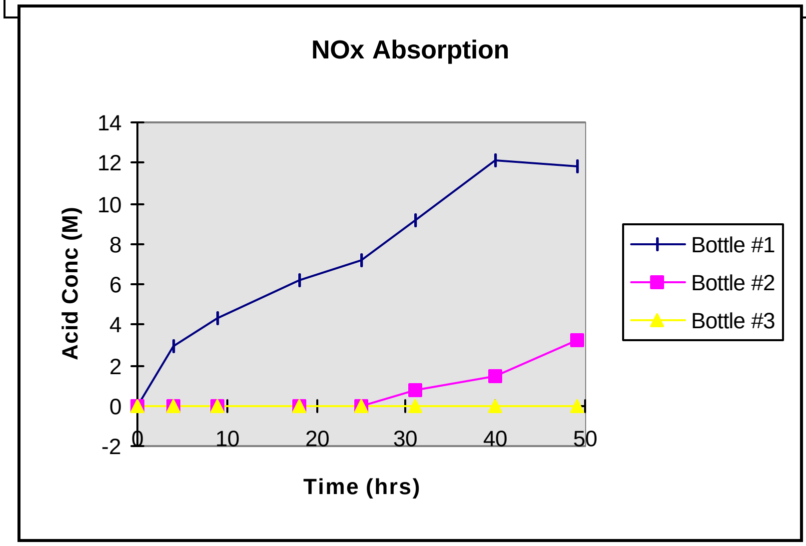
*Results*:

Experiments were conducted to study NOx absorption into $H_2O_2$ to confirm design parameters for the pilot-scale acid recycle unit. Four key parameters were evaluated: NO:$O_2$ ratio, residence time to convert NO to $NO_2$ prior to absorption, percent $H_2O_2$, and use of oxygen versus air to convert NO to $NO_2$. A series of twelve tests were run in which NO was generated, pumped at a constant rate, mixed with an oxygen source fed at a constant rate, through $H_2O_2$. The liquid was then titrated to determine acid concentrations.

The most important things to note from the data are as follows: 1) tests with pure NO yield a $HNO_3$ concentration of 4.1M compared to NO and air which yields approximately 13M; 2) controlled absorption conditions have consistently shown conversion of 30% $H_2O_2$ to above 13M which is well above the 11.5M measured under less controlled conditions in FY96; 3) oxygen does not seem to provide any significant benefit over air; 4) the optimum residence time prior to $NO_2$ absorption is on the order of 60 seconds; the optimum $NO:O_2$ ratio is 2:2 but ratios as low as 1:2 reduce NOx absorption less than 10%.



Experiments were also run using three $H_2O_2$ bottles in series and flowing a small amount of NOx through the system to show how the NOx distributes through the three bottles as a function of acid concentration in the peroxide. The test showed that the $H_2O_2$ in the first bottle will absorb NOx completely until it is about two-thirds consumed before allowing NOx to pass through to the second bottle. Also, throughout the test, continuous monitoring of NOx emissions from the third peroxide bottle always showed 30 ppm or less as compared to the clean air standard limit of 200 ppm. Absorption efficiency is a function of geometry, but is indicative of what can be expected during the proper use of hydrogen peroxide units in series to absorb NOx to recycle nitric acid.



## EXPERIMENTAL RESULTS

Batch Dissolution Tests: A series of batch tests was performed. Smaller pieces of the aluminum foam (1.0-1.3g) were placed in 150-mL beakers and contacted with 125 mL of varying concentrations of $HNO_3$ and KF. The five initial conditions included: 1) 8M $HNO_3$, 2) 8M $HNO_3$/0.025M KF, 3) 8M $HNO_3$/0.125M KF, 4) 4M $HNO_3$/0.125M KF, 5) 2M $HNO_3$/0.125M KF. The initial reaction rates for 8M $HNO_3$ and 2M $HNO_3$/0.125M KF were judged sufficiently slow to not warrant ongoing testing.

For the three remaining conditions, the effects of temperature, extended dissolution and stirring were evaluated as a function of dissolution rate. The data are presented in Table 1 in two manners. The top portion of the table shows dissolution data as percent of original sample dissolved per minute. The bottom portion presents the dissolution data as hours required for complete dissolution. It should be noted that the cumulative dissolution rate was re-normalized at 120 minutes for the unstirred tests. Data in bold italics are at 50$^o$C.

**Table 1.** Batch Dissolution Data

| | 8M $HNO_3$/0.025M KF | | 4M $HNO_3$/0.125M KF | | 8M $HNO_3$/0.125M KF | |
|---|---|---|---|---|---|---|
| Time (min) no stirring | Instant %/min | Cumul %/min | Instant %/min | Cumul %/min | Instant %/min | Cumul %/min |
| 30 | 0.096 | 0.096 | 0.333 | 0.333 | 0.291 | 0.292 |
| 60 | 0.042 | 0.069 | 0.133 | 0.233 | 0.133 | 0.212 |
| ***120*** | ***0.058*** | ***0.058*** | ***0.193*** | ***0.193*** | ***0.181*** | ***0.181*** |
| ***150*** | ***0.162*** | ***0.078*** | ***0.326*** | ***0.220*** | ***0.343*** | ***0.213*** |
| ***255*** | ***0.090*** | ***0.083*** | ***0.177*** | ***0.202*** | ***0.149*** | ***0.187*** |
| ***390*** | ***0.038*** | ***0.068*** | ***0.083*** | ***0.161*** | ***0.084*** | ***0.151*** |
| | | | | ***fell apart*** | | ***fell apart*** |
| Stirred | | | | | | |
| 35 | 0.094 | 0.094 | 0.323 | 0.323 | 0.289 | 0.289 |
| 85 | 0.060 | 0.073 | 0.106 | 0.195 | 0.077 | 0.164 |
| 120 | 0.051 | 0.067 | 0.127 | 0.175 | 0.113 | 0.149 |
| | | | | | | |
| | | | | | | |
| Time (min) no stirring | 8M $HNO_3$/0.025M KF | | 4M $HNO_3$/0.125M KF | | 8M $HNO_3$/0.125M KF | |
| | Instant hr to diss. | Cumul hr to diss. | Instant hr to diss. | Cumul hr to diss. | Instant hr to diss. | Cumul hr to diss. |
| 30 | 17.4 | 17.4 | 5.0 | 5.0 | 5.7 | 5.7 |
| 60 | 40.0 | 24.3 | 12.5 | 7.2 | 12.6 | 7.9 |
| ***120*** | ***28.9*** | ***28.9*** | ***8.6*** | ***8.6*** | ***9.2*** | ***9.2*** |
| ***150*** | ***10.3*** | ***21.2*** | ***5.1*** | ***7.6*** | ***4.9*** | ***7.8*** |
| ***255*** | ***18.6*** | ***20.1*** | ***9.4*** | ***8.2*** | ***11.1*** | ***8.9*** |
| ***390*** | ***43.5*** | ***24.7*** | ***20.0*** | ***10.3*** | ***19.8*** | ***11.0*** |
| Stirred | | | | | | |
| 35 | 17.6 | 17.6 | 5.2 | 5.2 | 5.8 | 5.8 |
| 85 | 28.0 | 22.5 | 15.8 | 8.5 | 21.7 | 10.1 |
| 120 | 32.6 | 24.8 | 13.1 | 9.5 | 14.7 | 11.2 |

Note: Black numbers are at ambient temperature, *bold, italics numbers are at 50°C*

The data show that 4M $HNO_3$/0.125M KF and 8M $HNO_3$/0.125M KF produce comparable dissolution rates for all conditions. The rate for 8M $HNO_3$/0.025M KF is considerably slower. As expected, dissolution at 50°C is quite a bit faster than at 20°C, especially when considering the data at 50°C represents a condition where much of the fluoride has been complexed by aluminum. One would expect the dissolution rate to follow typical Arrhenius-type behavior. Using the standard rule of thumb, a 30°C increase in reaction temperature should produce approximately an order of magnitude increase in dissolution rate. The data also suggest that stirring added very little to the batch dissolution rate. Due to concerns about acid depletion during dissolution, 8M $HNO_3$/0.125M KF was selected for use in the flowsheet.

A batch test was performed to get an idea of how much heat rise might be expected during processing. A piece of 1.3 grams of Al foam was placed in 125 mL of 8M $HNO_3$/0.125M KF without stirring. The beaker was insulated and a thermocouple was placed in the vessel. Over a 30-minute period, the temperature increase in the beaker was 5.8°C.

Batch dissolution tests were performed with Pd/K in 8M $HNO_3$. The Pd dissolves readily, although gradually, from the surface of the kieselguhr with a small amount of NOx gas generation. The dissolution leaves a tan-colored residue. The low amount of gas generation suggests that the average Pd dissolution equation used above overstates $HNO_3$ consumption. However, the presence of NOx generation affirms that Pd dissolution occurs according to a reaction similar to Eq. (1), hence no hydrogen production, instead of a reaction such as Eq. (5):

$$Pd + 2HNO_3 \rightarrow Pd(NO_3)_3 + H_2 \qquad (5)$$

When Pd/K and Al foam are present together, the Pd dissolves readily and then inhibits Al dissolution. It is expected that the Pd ties up the free fluoride, thus requiring additional fluoride. Batch testing has determined a Pd solubility of at least 50 g/L Pd in 8M $HNO_3$.

Flow-Through Dissolution Tests: Two test units were fabricated for flow-through testing. One unit was made of 316 stainless steel and the other of borosilicate glass. Both units had filters on the bottom end caps in order to retain Pd/K in the unit. Both were configured for flow-through operation using an FMI piston pump with 4 liter/hour flow capacity. Each unit was loaded with three aluminum pucks, each weighing about 13.3 grams. It should be noted that the aluminum foam does not fit as tightly into the glass unit as the stainless steel one.

*Palladium Dissolution*: The first test used the stainless steel unit. About 40 grams of Pd/K were place in the unit and attempts were made to pack the material in the bottom. Air was passed through the unit from top to bottom at the maximum capacity of SRTC building air in the lab while tapping the unit. When the unit was inverted, it was not evident that the material had been adequately packed. Nonetheless, the unit was repacked and set up for dissolution.

The feed vessel was filled with 500 mL of 8M $HNO_3$ which flowed through the unit at 2 liters/hour. Unlike the beaker tests that showed gradual dissolution of the Pd, the solution exiting the unit was immediate a very dark, brick red color indicating a high concentration of dissolved palladium nitrate. The solution was circulated for 2 hours and samples were pulled from the feed vessel at 15, 60 and 120 minutes.

The unit was then drained and the feed vessel was filled with 2 liters of 8M $HNO_3$/ 0.125M KF. The pump was again turned on and liquid flowed through the system for 4 hours. In the first thirty minutes of the test, the feed vessel temperature rose to $34^oC$ before it began to slowly decline. After about one hour of testing, it was noted that the gas generation was lower than expected and the solution color was indicative of soluble Pd. Subsequent analysis of samples from the Pd dissolution step discussed in the previous paragraph yielded 18 g/L at 15 minutes, 23 g/L at 60 minutes, and 24 g/L at 120 minutes. The final solution concentration indicates that only 57% of the Pd was dissolved in the first acid step. When the unit was opened up, it was noted that the solids were heavily packed kieselguhr at the bottom of the unit. This opens up the possibility that channeling had occurred at the low flow rates tested.

Total acid (TA) and free acid (FA) were measured for the solutions containing 18 g/L, 23 g/L and 24 g/L dissolved Pd. At 18 g/L Pd, TA = 7.64M and FA = 7.00M; at 23 g/L Pd, TA = 7.60M and FA = 6.32M; at 24 g/L Pd, TA = 7.59M and FA = 6.92. The difference between total acid and free acid indicates that Pd ties up approximately 3 moles of acid per mole of Pd. The difference between the starting total acid (8M) and the measured total acid values indicates the consumption of about 1.35 moles of $HNO_3$ per mole of Pd. It is reasonable to assume that this also represents the ratio of NOx production per mole of Pd.

The glass unit was set up in a similar fashion, but the powder was not packed into the unit. Flow through the unit was set up at about 400 mL/ hr to test a one-pass system. Once again, the Pd solution exited as a concentrated solution. However, after a period of time, it was clear that channeling was occurring because there were streaks of tan kieselguhr and areas of gray Pd/K. The flowrate was accelerated to 4 liter/hour and the solution was circulated. Channeling still occurred and the Pd concentration of the aggregate solution did not appear to increase (e.g. become darker). Inspection of the powder after dissolution showed that the Pd/K has become somewhat packed in the column and especially along the wall of the unit.

*Aluminum Dissolution*: The glass column was emptied and the three Al foam pucks were cleaned of nearly all Pd/K and kieselguhr. The pucks were returned to the apparatus. The total starting weight of the three pucks was 34.1 grams. The system feed reservoir was charged with 2 liters of 8M $HNO_3$/0.125M KF. The feed pump was turned on at about 2 liters per minute and the solution was circulated through the glass unit. Within the first 30 minutes, the feed solution temperature rose to $34^oC$. Gas generation was much lower than anticipated and the amount of NOx generation from solution was also small. As will be discussed later, $NO_2$ is not being released because it has a high solubility in 8M $HNO_3$. As the reaction progressed, the temperature gradually decreased to about 30°C. The feed solution developed a yellow tint.

After about 2 hours, due to the low gas generation rate, the KF concentration in the pot was doubled to 0.25M. Although some gas generation increase was observed, it was still less than anticipated. After 3 hours, the feed temperature was raised to 50°C and the solution was circulated about another 2.2 hours. Throughout the test, the vapor space of the feed vessel was purged through a $H_2O_2$ scrubber to quantify total NOx generation.

After about 5.2 hours of process time, the pump was shut down and the unit drained. When the unit was exposed to air, large concentrations of NOx gas were emitted from the surface of the Al foam. The three pucks were rinsed, dried and weighed. The bottom puck (where feed liquid enters) weighed 7.3 grams, the middle puck weighed 7.1 grams and the top puck weighed 7.3 grams (total weight = 21.7g). The three pucks showed uniform dissolution throughout. The amount of NOx captured in the $H_2O_2$ scrubber was negligible. A total acid and free acid analysis of the pot showed total acid = 7.60M and free acid = 6.32M.

The three pucks were returned to the glass unit. They were contacted continually at 50°C with the feed solution for 3 hours. After 3 hours, the unit was drained and NOx gas generation was once again noted at the surface. The samples were dried and weighed. The bottom puck weighed 4.2 grams, the middle puck weighed 4.2 grams and the top puck weighed 4.3 grams (total weight = 12.7 g). Because of pieces falling off of the main pucks, the actual total Al weight was estimated at 13.2 grams. The three pucks showed uniform dissolution throughout. Filter fines were being observed at the inlet side of the glass unit. The $H_2O_2$ solution was titrated and calculations show that 0.003 moles of NOx had been absorbed during this dissolution stage. This corresponds to a dissolved-Al-to-NOx-released mole ratio of 0.31/0.003 or about 100:1.

The pucks were returned to the glass unit and contacted with 50°C feed solution. However, during this test for the first hour of dissolution, the vapor space of the feed vessel was purged with $CO_2$ gas. After 55 minutes, the feed vessel was sealed from external gas sources and attached to a gas sample bag. Gas sample was collected for 30 minutes. After 30 minutes, not enough gas had been generated to expand the sample bag. A known amount of $CO_2$ was placed in the feed vessel to displace gas into the bag. The gas in the bag was analyzed to contain about 81% $CO_2$. The balance of gas analyzed was $N_2$ = 15.0%, $O_2$ = 3.5%, $H_2$ = 0.1% and NOx = 0.25%. Based on the total vapor space in the feed vessel and sample bag, it is estimated that a total of 8.5 mL of NOx and 3.4 mL of $H_2$ gases were generated during the 25 minute sample period. Nitrogen and oxygen are believed to be from dissolved air released from solution.

Once the gas sample had been taken, the pump was turned off and the system drained. No NOx was observed emanating from the Al foam surface. The pucks were disintegrating and began to resemble Spanish moss. The total weight of the Al foam fragments was 9.1

grams. The pro-rated weight of aluminum dissolved during gas sampling was 1.1 grams. Calculations for this test show a dissolved-Al-to-NOx-released mole ratio of 0.042/0.00035 or 120:1. An analysis of the feed total acid and feed acid showed total acid = 7.10 M and free acid = 5.49 M.

## SAFETY ISSUES

Much has been done to address safety concerns during accelerated flowsheet development. Based on data in the literature, prior experience with comparable systems, and Al puck dissolution data, there is good reason to believe the flowsheet will perform safely. Although there is some uncertainty with respect to scale-up – there always is – the concerns are minimized by the fact that the only dimension changing between lab test and flowsheet implementation is unit length. Below is a list of the more significant issues and their resolution.

Presence of Unstable Dissolved $NO_2$ Gas: One unexplained aspect of the flowsheet development is the lower-than-expect NOx generation rates. As a result, there is concern that $NO_2$ is dissolving into and building up in solution. This concern is further heightened by the fact that when the unit is drained much NOx production is observed at the surface of the Al foam. As such, the safety issue is whether or not $NO_2$ can build up in the feed vessel and then suddenly release large amounts of gas all at once and create a pressure-protection hazard.

Calculations were performed by J.E. Laurinat of ATS.[11] For the $NO_2$ gas, two questions were asked. These are 1) will the acid solution become saturated with $NO_2$ in one pass through the tube, and 2) will the acid solution become saturated with $NO_2$ with many passes through the tube, assuming the 55-gallon acid drum remains well mixed as the solution recirculates. These questions can be answered by comparing both the dissolved $NO_2$ concentrations at the end of one pass through the coil, and the $NO_2$ concentrations when the aluminum is completely dissolved, with the $NO_2$ solubility in 8 M $HNO_3$.

Each pass through the coil should produce approximately 0.07M $NO_2$ dissolved in solution. The total $NO_2$ concentration cannot ever exceed the equivalent solubility at $25^oC$. This means that no gas will be generated due to dissolution at this temperature. At $50^oC$, the total $NO_2$ concentration could be as much as 2.4 times the equivalent solubility if all the aluminum dissolved and all $NO_2$ remained in solution as dissolved gas. Actually, secondary reactions will take place to convert some of the $NO_2/N_2O_4$ back to $HNO_3$, so the dissolved gas concentration would be somewhat lower. However, if the solution were subsequently exposed to free air, the excess $NO_2/N_2O_4$ would bubble out of solution. Therefore, because the system is circulated and the feed vessel is exposed to free air, excess $NO_2/N_2O_4$ will not collect in the feed solution to be rapidly released by some other event.

Bounding Case Gas Generation Rate: Although gas generation rates have been lower than expected, attempts have been made to provide a bounding case for the worst-case gas generation rate. The bounding case occurs at the start of operations with aluminum-free feed solution. Experimental data shows an initial dissolution rate on the order of 0.291 wt% Al dissolution per minute (see Table 1). Assuming 2700 grams of Al foam and gas generation according to Eq. (2), a limiting gas generation rate of 19.5 liters/minute is calculated.

However, the calculations by J.E. Laurinat of ATS show that this amount of initial gas release is soluble in 8M $HNO_3$. Solubility limits for $NO_2$ in 8M $HNO_3$ were calculated at 3.29M at 25°C and 0.49M at 50°C. At 25°C, the solution never reaches its solubility limit. At 50°C, assuming no $NO_2$ conversion to $HNO_3$ or dimerization to $N_2O_4$, by the time $NO_2$ reaches its solubility limit, the dissolved aluminum will be at least 0.16M. Consequently, the free fluoride will be greatly reduced, as will the overall dissolution rate.

A more reasonable calculation can be made from the foam dissolution tests. Between 5.2 and 8.2 hours of dissolution time, 8.5 grams of aluminum dissolved from 3 pucks in three hours. For the full coil (204 pucks), this translates into 578 grams for three hours (3.21 grams per minute or 0.12 moles per minute). Assuming 3 moles $NO_2$ released per mole of aluminum dissolved, this yields 8.0 liters per minute. Because this calculation assumes no $NO_2$ conversion to $HNO_3$, no dimerization, and occurs at 50°C (versus 40-45°C recommended), this represents a good bounding case number.

Volatility of HF: The dissolution of KF into 8M $HNO_3$ effectively creates HF in solution. Because of its presence and concern for worker safety, it was requested that calculations be performed to estimate HF volatility. Calculations performed by J. E. Laurinat of ATS conclude the following: Before dissolution begins at 1 atm total pressure, the vapor pressure of HF for the dissolution solution is about 107 ppm at 50°C and 39 ppm at 25°C. After dissolution starts, the dissolved aluminum complexes virtually all of the fluoride as $AlF^{2+}$, so HF vapor pressures drop precipitously. When 0.125M aluminum is dissolved into solution, the HF vapor pressure is 259 *ppb* at 50°C and 96 *ppb* at 25°C. The HF vapor pressure after complete dissolution is 1.02 *ppb* at 50°C and 0.47 *ppb* at 25°C.[11] Therefore, the HF has a low volatility that will drop quickly once dissolution of Al foam has begun. Any HF vapors coming from the feed vessel will then pass through the scrubbers where they will be greatly reduced.

Reaction Mechanism: The aluminum foam dissolution reaction appears to be occurring, to some degree, according to Eq. (2) with 6 moles of $HNO_3$ consumed and 3 moles of $NO_2$ released per mole of aluminum dissolved. As the aluminum dissolves, $NO_2$ is generated and dissolves into solution. This is indicated by the yellow color of the solution. This may also explain why NOx emanates from the surface of the aluminum when the unit is drain – there is no liquid available to dissolve the gas. The total acid data for the first 5.2 hours of dissolution shows a measured free acid of 6.32M. At the end of the test, free acid is down to 5.49M. Since there are 2 liters of feed solution, calculated acid consumption values, based on the moles of Al dissolved (0.46 moles at 5.2 hours and 0.92 moles at the end), yield acid consumption ratios of 7.3 moles of $HNO_3$ per mole of Al at 5.2 hours and 5.4 moles $HNO_3$ per mole of Al at the end of the experiment. These match well with the Eq. (2) ratio of 6.

Hydrogen Generation: The presence of hydrogen in the gas sample has raised concerns about whether or not hydrogen generation is a credible safety hazard. If one considers the volume of $H_2$ generation that was measured, it is extremely small and can be easily removed by a feed vessel purge. The sample showed 3.4 mL of $H_2$ gas for 1.1 grams of Al dissolved. This translates into 8.3 liters of hydrogen over at least 10 hours of run time for the full-scale coil.

Acid consumption data show that the ratio of Eq. (2) describes the chemistry fairly accurately. However, because of the absorption of $NO_2$ into solution, the percentage of $H_2$ in the offgas is skewed high. For example, the calculation of 3.4 mL of $H_2$ gas for 1.1 grams of Al, assuming no $NO_2$ absorption, would be diluted by 2.7 liters of gas (0.12%). However, because almost all $NO_2$ dissolves into the acid, $H_2$ gas represent a much larger fraction of the gas emitted. Therefore, to continually remove hydrogen gas from the system, a purge will be applied to the headspace of the feed vessel.

## PROCESS OPERATIONS

Palladium Dissolution: Testing indicates that 8M $HNO_3$ dissolves Pd metal effectively but that 4M $HNO_3$ does not. Therefore, the dissolution should be performed with 8M $HNO_3$. Solubility of $Pd(NO_3)_2$ in $HNO_3$ is greater than 50 g/L. The upper limit is not readily available in the literature. The flowsheet for Pd dissolution should try to limit the Pd concentration to about 45 g/L. Although not much gas is observed during the dissolution, NOx gas is generated. Based on free acid calculations, it should be assumed that 1.35 moles of NOx will be generated per mole of Pd dissolved. However, as discussed above, it is likely that most of this NOx generated will be soluble in the feed solution.

Experimental data indicates that the Pd dissolves quite rapidly. However, some packed areas may be difficult to dissolve. Therefore, it is recommended that flow rates through the coil be at least 2 liter per minute, and up to 10 liters per minute, if possible. At elevated flow rates, dissolution should be complete after 2-3 hours. The column should be drained, rinsed with water, and drained again prior to Al foam dissolution.

Aluminum Dissolution: Available data indicates that a good starting solution for dissolution of aluminum foam is 8M $HNO_3$/0.125M KF. During the initial stages of dissolution, the maximum amount of reaction and subsequent heat generation will occur. Therefore, initial liquid flow to the coil ought to be at ambient temperature. Expectations are that the temperature of the feed solution will rise to 30-40$^oC$. After the initial rise, the feed solution temperature will gradually decrease unless maintained through external heating. Operations should be maintained between 25$^oC$ and 50$^oC$. Long-term dissolution ought to be maintained at about 40-45$^oC$. Lower temperatures can be used, but slower dissolution rates should be expected.

As the reaction proceeds, $HNO_3$ and free fluoride concentrations will decrease. Allowances ought to be made to analyze for $HNO_3$ and free fluoride concentrations every two hours. $HNO_3$ concentration ought to be maintained as a guideline for estimating total aluminum dissolution. After it is estimated that enough Al to form 0.125M has been dissolved, additional fluoride may be added up to 0.25M total fluoride. Based on the applicability of Eq. (2), the initial value of 175 liters of 8M $HNO_3$/0.125M KF seems to be a good estimate for total acid usage. Because of concerns about residual Pd/K and the intent to operate the Al dissolution process as a two-dayshift process, it may be a good practice to treat the coils with 2 smaller batches of acid.

Pumping rates for simulation tests ran at 2 liters per minute. Lower flow rates did not appear to decrease the rate of gas generation from the aluminum foam. However, due to the length of the column, it may be advisable to operate at slightly higher velocities such as 3-4 liters per minute. There is still some concern that slow flow rates will tend to produce higher reaction rates where the feed solution enters the coil and lower reaction rates toward the end of the coil.

Offgas Handling: Generation of gas, in general, and NOx, in particular, during aluminum foam dissolution has been much lower than anticipated. Very little NOx has been observed in the feed vessel vapor space. The amount captured in the $H_2O_2$ scrubber has also been small. Therefore, the amount of $H_2O_2$ needed for the flowsheet is smaller than initially predicted. The reason for the greatly reduced amount of NOx gas is attributable to $NO_2$ solubility in 8M $HNO_3$. An air sweep of the feed vessel headspace will remove and control the small volume of gases generated during the process. In order to control NOx emissions from the $H_2O_2$ scrubber, samples of the $H_2O_2$ ought to be titrated for acid every 2 hours. This will insure that the scrubber does not become exhausted. Based on experimental results, the gas generation rate during the first 30 minutes of dissolution ought to be less than 0.5 liters/minute. After the initial reaction, the gas generation rate should diminish and remain quite small until the solubility limit for $NO_2$ has been exceeded.

## Dissolution Testing of TCAP Demonstration Coil

### Summary

During the initial dissolution test of the TCAP demonstration coil, 8M acid at 32 C was pumped into the coil. A minimal temperature rise (2-5 C) and some gas generation were observed in the first 25 minutes. Shortly thereafter, temperature and gas generation increased dramatically, with a 50 C temperature rise observed in 30 seconds and enough gas generation to force liquid out of both ends of the coil. A boroscope showed that the aluminum foam at the inlet of the coil was in "pristine" condition, but at the outlet end, the aluminum was black, thin, packed with a sludge material, and in some places had begun to fall apart. Samples of this aluminum and black sludge (essentially Pd/k) material were removed. Laboratory tests demonstrated that the aluminum coil material was significantly more reactive than the virgin aluminum foam used to develop the initial dissolution flowsheet. The reactivity of the coil material has been attributed to its process history, which includes a brief temperature excursion to ~500 C. It is thought that less than 1/3 of the aluminum in the demonstration coil was altered by this event.

Significantly, the aluminum material dissolves in 8M nitric acid or in 7M acid + 48g Pd/L without a catalyst such as fluoride or mercury. The initial temperature rise is slow, but after an 'incubation period' of ~30 minutes or a temperature above 40 C, the reaction accelerates rapidly. The reaction of the aluminum/sludge material is minimal in 4, 6, 7, and even 7.5 M HNO3 with no added palladium. The demonstration coil tests and all current bench-scale beaker tests were done without cooling. The test done in a cooling bath demonstrated that 17.8 g Pd/L dissolved in 8M HNO3 at 3 C after 90 minutes with minimal stirring. The solubility at room temperature is well over 50 g/L. Also, a calculation showed that an ice bath removes more heat from the TCAP demonstration coil than is generated by the Pd and Al reactions if the solution temperature is between 0.8 and 40 C.[12]

Though acid levels below 8M will be used initially, a level below 4M is not expected. Tests showed that aluminum/sludge material from the demonstration coil along with additional Pd/k did not dissolve appreciably in 4M HNO3 at room temperature, and a gas sample of the headspace of the reaction test vessel indicated no hydrogen was present.

It is recommended that the dissolution of palladium from the Jacobs coil proceed using the current solution in the mixing tank, which is ~6 M free acid, and will be diluted by about 5% with the water present in the coil. A cooling water/ice bath installed around the demonstration coil will prevent the heat up of the solution within the coil, and protect against the self-accelerating dissolution of the altered aluminum within the coil. After the ~140 L of solution are cooled below 10 C, nitric acid will be added slowly to increase the concentration by 0.5 M. Pumping will continue to cool the solution and monitor visual changes. This step will be repeated until the solution reaches 8M HNO3. Pumping for 2 hours at 5-10 C should dissolve the palladium in the coil, yielding an estimated concentration of 10 g Pd/L (1660 g Pd in 170 L).

## Actual Demonstration Coil Test

The TCAP demonstration coil, or “Jacob’s” coil, was used for flowsheet testing on Feb. 11, 2004. The feed solution, 8M nitric acid at 32 C, was pumped into the coil. Flow into the coil was not steady, due to gas generation within the coil. After 12 minutes, the coil inlet temperature was 34 C (measured outside the coil inlet). This reading remained constant until t=25 minutes. After that, the temperature rose gradually at first and then very quickly, reaching 103 C at the coil outlet at t=35 minutes. Significant gas generation was observed and liquid was forced out of both ends of the coil. After the reaction subsided, water was pumped into the coil. A more detailed description of the test, provided by Adamson, is given below.[13,14]

“Chemical dissolution of the palladium started at 1405 on 2/11, starting with approximately 5 liters of DI water in the demo coil. Initially 8M nitric acid” at 32 C “was being pumped from the mixing tank through the coil. However, the flow of the acid into the coil was intermittent, due to the formation of significant greater quantities of gases than anticipated. The pump eventually pulled the gases out of the coil. This took approximately twice as long as observed during water runs (no gases are formed in the coil during water runs). At this time the pump established a full flow (2.5 L/min) of acid to the coil for approximately 30 seconds. Signs of a reaction began at 1417 with black solids and Pd fines flowing into the knockout pot. Reddish liquid was pulsing in and out of the inlet side of the coil at 1434. As the acid flowed into the coil, the pump became errant due to the pump struggling to keep up with gases (presumably NO2) forming in the coil. The gases caused a pulsing action of the liquid out of the coil and black fines were observed in the tubing flowing to Pump 1. At 1440, Pump 1 was turned off as temperature, T1 increased from 50 C to 103 C in approximately 30 seconds. Violent pulsating flows were observed out both ends of the coil at the same time. The pulsing continued for approximately five minutes after the pump was turned off. At 1443, violent back flow of reddish liquid was observed flowing from the coil inlet to the mixing tank. At 1545, the knockout pot had a black liquid in it that appeared to have solids fines.

At 1631, 19 liters of DI water was pumped through the coil to place the system in a safe standby mode. At 1632, the initial water flush gave a viscous brown liquid that was collected in the knockout pot. The following day, a sample of the liquid was observed to have solids that settled out.

On the morning of 2/12/04, the DI water supply container contained 2.8 liters of yellowish liquid. The container was emptied the evening before. Gas bubbles were observed flowing from the coil through the clear tube between the mixing tank and the coil inlet. Gas formation in the coil over night appeared to have driven the liquid out. At 1620, 20 liters of clean DI water was flushed through the coil to remove residual chemical. The initial flush (8.5 liters) was also a viscous brown liquid similar to that seen on the previous DI water flush.

At 1645, a boroscope was used to look at the inside of both the inlet and outlet of the coil. The aluminum foam did not appear to have dissolved, but a high temperature reaction with the foam had occurred on the outlet side of the coil. At 1706, a 1.5-inch hole saw was used to obtain samples of aluminum and contents from the straight end (outlet) of demo coil. Samples were bagged and labeled Puck #1 through Puck #5. After returning the system to normal, DI water was used to fill the coil, thus keeping the Pd/k wet while in a safe shut down mode."

## Analytical Results from Demonstration Coil Test

Analyses by ICP-ES are shown (in mg/L) in the Table below. Note, the mixing drum sample from 2/11 1720 has a free acid content of 6.04 M and total acid of 6.48 M.

| | Mixing Drum | Knockout Pot | Mixing Drum | Flush Water | Mixing Drum |
|---|---|---|---|---|---|
| | 2/11 1545 | 2/11 1645<br>(sample not filtered) | 2/11 1720 | 2/12 1742 | 2/13 0815 |
| LIMS#: | 206404 | 206405 | 206406 | 206407 | 206408 |
| Pd | 1120 | 4750 | 1080 | 132 | 1026 |
| | | | | | |
| LIMS#: | 206404 | 206405 | 206406 | 206407 | 206408 |
| Al | 130 | 12500 | 500 | 2980 | 484 |
| B | 0.44 | 3.48 | 2.69 | 0.36 | 1.06 |
| Ba | 0.23 | 1.05 | 0.24 | 0.18 | 0.27 |
| Ca | 0.37 | 13.6 | 1.19 | 1.34 | 0.69 |
| Cd | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| Co | <0.16 | <0.16 | <0.16 | <0.16 | <0.16 |
| Cr | 0.50 | 2.33 | 0.52 | 0.42 | 0.54 |
| Cu | 0.21 | 1.28 | 0.22 | 0.10 | 0.22 |
| Fe | 8.15 | 74.2 | 9.31 | 14.0 | 9.59 |
| Li | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 |
| Mg | 4.12 | 155 | 8.42 | 34.0 | 8.12 |
| Mn | 0.11 | 2.97 | 0.19 | 0.74 | 0.19 |
| Mo | <0.2 | 0.83 | <0.2 | 0.21 | <0.2 |
| Na | 3.59 | 66.3 | 9.38 | 13.8 | 6.96 |
| Ni | 0.68 | 4.98 | 0.73 | 1.14 | 0.71 |
| P | <1.6 | <1.6 | <1.6 | <1.6 | <1.6 |
| Pb | <1.6 | 19.1 | <1.6 | 4.56 | <1.6 |
| Si | 18.6 | 103 | 18.1 | 23.9 | 23.4 |
| Sn | <0.8 | <0.8 | <0.8 | <0.8 | <0.8 |
| Sr | 0.04 | 0.15 | 0.01 | 0.02 | 0.02 |
| Ti | 0.30 | 2.12 | 0.32 | 0.34 | 0.34 |
| V | <0.8 | <0.8 | <0.8 | <0.8 | <0.8 |
| Zn | 0.22 | 1.91 | 0.35 | 0.41 | 0.84 |

| | | | | | |
|---|---|---|---|---|---|
| Zr | <0.06 | <0.06 | <0.06 | <0.06 | <0.06 |
| Nb | <0.14 | <0.14 | <0.14 | <0.14 | <0.14 |
| La | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| K | <12 | 30.80 | <12 | <12 | <12 |
| Re | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| S | <2 | <2 | <2 | <2 | <2 |
| Ag | <0.6 | <0.6 | <0.6 | <0.6 | <0.6 |
| Ce | <1.4 | <1.4 | <1.4 | <1.4 | <1.4 |
| Nd | <1.8 | <1.8 | <1.8 | <1.8 | <1.8 |

## Small-scale Tests: Palladium Dissolution From Pd/k Fines

A series of experiments were performed to determine how much heat is released during treatment of Pd/k with increasing concentrations of $HNO_3$.[15]

All experiments were performed on fine material from a mixture of coils: Col C, NDA, Jacobs, Col D. The fines passed through a 50 mesh sieve, which has 300-micron openings. Each experiment was performed in a ~ 12 mL spherical glass flask surrounded by fiberglass insulation. After the fines were added to the flask, $HNO_3$ solutions were added with either a 1 or 5 mL pipet. Certain solutions were stirred at 300 rpm with a magnetic stirrer. The temperature was measured with a thermocouple and the results were manually recorded at specific intervals.

**Table 1: Summary of Experimental Parameters for Pd/K Dissolution Experiments**

| Acid (M) | Volume (mL) | Sample Mass (g) | Initial T (C) | Highest T (C) Achieved | Δ Temp. (C) | Δ Time for Δ Temp. |
|---|---|---|---|---|---|---|
| 8 M $HNO_3$ | 5 | 1.5205 | 24.4 | 35.0 | 10.6 | 14 minutes |
| 8 M $HNO_3$ | 10 | 1.5351 | 24.5 | 29.2 | 4.7 | 15 minutes |
| 8 M $HNO_3$ | 10* | 0.4902 | 25.5 | 27.7 | 2.2 | 14.5 minutes |
| 4 M $HNO_3$ | 10* | 1.5090 | 24.3 | NC | NC | NC |
| 8 M $HNO_3$ | 5 | 5.0007 | 26.6 | 53.6 | 26 | 8 minutes |
| 8 M $HNO_3$ | 5 | 10.0072 | 25.9 | 60.2 | 34.3 | 10 minutes |
| 6 M $HNO_3$ | 10* | 1.5023 | 25.1 | NC | NC | NC |

NC = No change greater than ± 0.2 C in the temperature
* Sample was stirred at 300 rpm.

Observations

At the end of the first two experiments, the supernate was very dark reddish-brown and, after removing the supernate from the flask, the solids were still dark colored. When a smaller amount of Pd/K was used in 10 mL, less heat was released. However, the solution was still dark reddish-brown and, after removing the supernate, the solids in the reaction flask were more tan in color.

When 4 or 6 M $HNO_3$ was used, the supernate remained light gray in color and the Pd/K is still very dark. The lack of color change and no change in temperature correspond to no dissolution of Pd under those conditions.

Summary

For the maximum case (i.e., 10.0072 g Pd/K + 5 mL of 8 M $HNO_3$) in which the acid wetted all solids but gave no excess, the temperature rise was 34.3 C. A calculation performed by James Laurinat predicted 35.5 C but included both Pd/K and aluminum foam. Without aluminum foam, the theoretical amount would be even higher than experimental, which would be expected due to heat losses.

## Small-scale Tests: Aluminum/sludge Dissolution Tests

Material from the Jacob's coil was removed using a 1 ½-inch hole saw. The five pucks removed were embedded with a black sludge and appeared thinner than virgin pucks.

Bench-scale tests[16] demonstrated that portions of aluminum + sludge removed from the Jacob's coil are much more reactive in 8M nitric acid than virgin aluminum foam. This confirms observations during Jacob's coil startup.

Laboratory tests were carried out on the 5th aluminum puck with sludge material which was pulled out of the (current) exit end of the Jacob's coil.

| Material | Solution | Observations |
|---|---|---|
| Al + sludge | 7M HNO3 in 48 g Pd/L | Temp. rose steadily to ~45 C with fizzing, then rose sharply with much gas evolution, reaching ~90 C. Beaker filled with foam until reaction subsided. |
| Virgin Al + Virgin Pd/k | 7M HNO3 with 48 g Pd/L | No temperature rise or visual changes. |
| Virgin Al + Virgin Pd/k | 7M HNO3 with 48 g Pd/L | Heat added gradually via hot plate to 80 C. No visual changes and no self-heating observed. |
| Al + sludge | 8M HNO3 | Self-heating to 43 C in 40 minutes with light fizzing. After 72 minutes, temperature rose from 56 to 66 C in 8 minutes, with moderate fizzing. Water added.<br>Temperature decreased steadily. |

The 4th puck from the demonstration coil was divided into 3 parts and placed in solutions of 4, 6, and 8 M HNO3. Beakers were insulated unless reaction became vigorous. Tests involved nominally 5 g of solids and 20 mL solution.

4M HNO3  Temperature increased from 24.2 C initially to 25.1 after 44 minutes and continued to a maximum of 28.4 C after 157 minutes.

6M HNO3  Temperature dropped from 25 to 24 in first 12 minutes. Insulation added. Temperature rose to 27.3 after 57 more minutes. Temperature remained near 27 for 2 hours. Concentration was increased to 7M HNO3. Temperature rose 6 C in 45 minutes, then started to decline.

8M HNO3  Temperature jumped to 28.8 C initially with some fizzing. Temperature rose to 41 C after 35 minutes, then began to increase rapidly, reaching 84 with excessive foaming after 45 minutes. Solution began to boil (101 C) and 25 mL of water was added. Reaction subsided after 3-4 minutes.

The 3rd puck from the Jacob's coil was cut in half and placed in separate beakers. Nitric acid was placed in the beakers -- 8M in one and 7.5 M in the other. Test size was nominally 6 g Al/sludge in 20 mL acid.

8M HNO3  The beaker temperature rose gradually and was 47 C after 40 minutes. At 50 minutes, the solution was at 77 C and fuming reddish brown. At 53 minutes, it reached 107 C, but by 59 minutes it was calm and 93 C. Cooling continued steadily.

7.5M HNO3  The solution temperature rose from room temp to 27 C in the first minute, then reduced slightly over the next 20 minutes. Temperature increased slowly to a maximum of 30.1 C at 97 minutes. The solution was left uncovered. Eventually, enough evaporation occurred to concentrate the acid that a vigorous reaction did occur, as evidenced by the foam residue on the walls of the beaker. So, the solid material was not significantly different from that in the 8M test.

Observations:
1. The 3rd puck had a ~40 minute "incubation" time before a vigorous reaction occurred. This is about the same as the incubation time for the 4th puck in plain 8M HNO3, but longer than the 30 minutes of incubation for the 5th puck in 7 M HNO3 with 48g Pd/L.

2. Since the Al/sludge material was from the same puck, this test demonstrated that the reactive portion of aluminum/sludge in the Jacob's coil is quite sensitive to nitric acid concentration.

These tests confirm the value of having cooling capability, and of starting with a reduced acid concentration for palladium dissolution in the Jacob's coil.

## Solids Analyses

SEM photos and elemental scans as well as XRD analysis were taken of demonstration coil aluminum and sludge material. As expected, Pd, SiO2, and Al oxide/hydroxide compounds were observed. A Pd/Al alloy was not detected by XRD, but SEM photos show Pd particles enmeshed with aluminum, even though the sample was well-rinsed. SEM photos also revealed spots with aluminum and very little oxygen, though most aluminum portions had significant oxygen present. A complete understanding of the nature of the demonstration coil aluminum is not available at this time.

## Gas Analysis

To test for hydrogen generation, 5.03 g of demonstration coil aluminum/sludge material and 1.787 g of Pd/k fines were placed in 46 mL of 4M HNO3 to cover the solids and kept at room temperature. The reaction vessel (355 mL) was closed. Very light gas generation was observed. After 2 hours, gas samples (2 x 5 mL) were taken of the headspace. Five hours later, a Gas Chromatography analysis detected <0.1 % hydrogen. Because of the lag time between sampling and analysis, up to 1/3 of any hydrogen present in the sample could have diffused into the Teflon in the sampling syringe. The reaction vessel was left sealed overnight. Though very light bubbling was observed, no pressure rise (i.e., <0.1 psig) was observed. Most likely, NOx gas was slowly produced but was also dissolving into the solution. No visual changes in the Pd/k particles or the Al/sludge material were observed after the test, indicating minimal dissolution at 4M HNO3 at room temperature.

## Process Demonstration

To simulate recommended conditions, 3.8757 g from the 1st demonstration coil puck, 7.8939 g of Al/sludge from the 5th demo coil puck, and 1.1834 g of Pd/k fines were placed in a 355 mL glass reaction vessel. The vessel was cooled in an ice bath to about 7 C. Then, 20 mL of 8M HNO3 at room temperature was added. The vessel was sealed. The temperature decreased steadily and the solution started to darken, indicating dissolution of palladium. No pressure increase was observed while the bath remained below 10 C. However, when the bath and reaction vessel were raised to room temperature, a pressure increase was observed (attributed to temperature rise). Then, bubbling increased somewhat and pressure rise became measurable. The test confirms low reactivity of demonstration coil material at low temperature in the presence of 8M HNO3.

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