CHARACTERIZATION OF INDIVIDUAL CHEMICAL REACTIONS CONSUMING ACID DURING NUCLEAR WASTE PROCESSING AT THE SAVANNAH RIVER SITE – 136b

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ABSTRACT

Conversion of legacy radioactive high-level waste at the Savannah River Site into a stable glass waste form involves a chemical pretreatment process to prepare the waste for vitrification. Waste slurry is treated with nitric and formic acids to achieve certain goals. The total quantity of acid added to a batch of waste slurry is constrained by the catalytic activity of trace noble metal fission products in the waste that can convert formic acid into hydrogen gas at many hundreds of times the radiolytic hydrogen generation rate. A large block of experimental process simulations were performed to characterize the chemical reactions that consume acid prior to hydrogen generation. The analysis led to a new equation for predicting the quantity of acid required to process a given volume of waste slurry.

INTRODUCTION

Legacy radioactive high-level waste (HLW) generated at the U. S. Department of Energy - Savannah River Site (SRS) during production of enriched uranium and plutonium during the Cold War is currently being processed in the Defense Waste Processing Facility (DWPF) into a stable borosilicate glass waste form for long term storage. The majority of the legacy HLW is stored either as mixtures of hydroxides and hydrous oxide insoluble solids or as precipitated salt cakes in large cylindrical storage tanks at SRS. These 3.5-4.9 thousand cubic meter (900,000-1,300,000 gallon) carbon steel storage tanks also contain 5-7M sodium solutions rich in hydroxide, nitrate, and nitrite anions. Batch feed preparation for processing in the DWPF involves washing the aqueous phase of slurries obtained from one or two individual waste tanks to about a 1M sodium concentration.

The DWPF brings approximately 25 cubic meters of fresh washed sludge slurry into the Sludge Receipt and Adjustment Tank (SRAT) at a time. The SRAT is the primary vessel for chemical pretreatment of the HLW prior to vitrification. The DWPF primarily employs batch processing, although the waste glass melter is fed semi-continuously. Nitric and formic acids are added during the SRAT cycle to adjust the rheology, dissolve some of the alkaline earth and transition metal compounds, convert HgO to elemental mercury for steam stripping, destroy some of the existing anions such as carbonate and nitrite, and chemically reduce a portion of the MnO_2 to Mn^{2+}. (Thermal reduction of Mn in the DWPF melter leads to reduced melter throughput and can also lead to foam formation.) Optimal performance of the DWPF waste glass melter requires a balance of chemical oxidizers and reductants in the feed in order to avoid foam formation and metal precipitation. The balance is achieved by dividing the SRAT acid demand between nitric acid (oxidizer) and formic acid (reductant).

The original concept for the DWPF involved a dual feed capability that would process insoluble radioactive waste solids in parallel with soluble radioactive salt waste cake material. The DWPF flowsheet was subsequently modified to substitute 90 wt% formic acid for the dilute formic acid stream coming from salt waste processing. A stoichiometric acid requirement equation was derived based on what was known at the time about the process chemistry, equation [1]:

$$\frac{\text{moles acid}}{\text{L slurry}} = \text{base equivalents} + 2 * \text{TIC} + 0.75 * \text{nitrite} + 1.2 * \text{Mn} + \text{Hg}$$

Equation 1, current estimating equation for the stoichiometric acid requirement.

All right-hand-side quantities in eqn. [1] are measured for the slurry (aqueous phase plus insoluble solids) and converted to moles per liter slurry units. Each term is measured independently (five different analytical instruments). The DWPF uses averages over four independent samples for each analysis. The base equivalents term represents the equivalent hydroxide molarity of the slurry determined by a strong acid titration to pH 7. The total inorganic carbon (TIC) term represents the total carbonate content of the slurry.

This approach to predicting total acid requirements was initially seen as an interim measure that would not be needed once “short-term” issues with salt waste processing were resolved. The DWPF, however, continues to operate in the interim mode fourteen years later. Supporting experimental work done during that time has shown that the above equation predicts the acid demand 20-30% lower than the observed demand. An empirical multiplier has been used as a correction factor for each new large batch of feed. Each large sludge batch typically is used to provide feed for 70-100 SRAT cycles during which the multiplier is typically held constant.

Changes in the preparation strategy of the legacy waste sludges over the past decade have been made to reduce the volume of decanted wash water, since tank farm storage space and evaporator capacity are limited. The resulting DWPF feed sludge compositions require proportionally more acid to process (increased hydroxide, carbonate, and nitrite ion concentrations in the DWPF feed). This doctrinal evolution has constrained the quantity of acid that can be added relative to the minimum required to accomplish various processing goals that constituted the original design concept.

Tightened constraints have renewed interest in understanding the nature and timing of the chemical reactions that consume acid. Predicting and controlling the quantity of acid added in the SRAT is an essential part of the DWPF operational strategy for minimizing noble metal catalyzed hydrogen generation from excess formic acid. Alternative salt processing has started at SRS. Streams concentrated in radionuclides from salt separations are now being incorporated into the DWPF flowsheet. These streams are typically either acidic or basic, and consequently they impact the actual acid requirement. The quantity of salt processing streams in a given SRAT cycle varies considerably. This causes increased variability in the acid requirement. The variability in actual acid demand raises the issue of whether or not a single multiplicative correction factor is adequate to handle a wide range of feeds.

Another issue with the acid equation (despite the fact the equation predicted low) was the potential for double counting certain species. For example, since measurement of hydroxide ion concentration was problematic in the system, a slurry titration to pH 7 was substituted. A total inorganic carbon measurement was used to get the carbonate concentration of the slurry. Soluble carbonate, however, was partially titrated to bicarbonate during the titration measurement and was being counted twice for acid demand. Experiments showed that it was only soluble carbonate, and not insoluble carbonate, that was being titrated and counted twice in the current equation. There was also a concern that HgO might be dissolved during titration. Experiments indicate that mercury was not appreciably dissolved during pH 7 titrations, although titrations to pH 5.5 were being impacted.

Two other findings emerged from preliminary experiments. Different titration techniques produced different equivalent base molarities for the slurry. The DWPF used 20:1 to 25:1 diluted slurry in their automatic titrator, while some work within the Savannah River National Laboratory used direct titrations. Results by the two methods were typically within 5-15%. This has been deemed tolerable, although this term is often the largest contributor to the total in eqn. [1]. Obtaining a reliable measurement for slurry total inorganic carbon, however, has been a bigger issue. Uncertainties of reported quantities have been high. Therefore, finding methods to predict the stoichiometric acid requirement that did not require the measurement of slurry TIC or the titration to pH 7 were promoted over a strategy that only sought to refine some of the coefficients in the existing acid equation.

TEST PROGRAM

A matrix of large lab-scale tests were completed in duplicate with an integrated sampling plan that permitted the chemistry of the SRAT during acid addition to be elucidated and better quantified. Batches of simulated waste were processed 15 dm^3 (15-L) at a time. Data from these tests filled gaps in the historical database. Reactions were identified that were actively consuming acid. The dissolutions of $Mg(OH)_2$ and $CaCO_3$ were successfully tracked as functions of pH during processing. These reactions were found to occur below pH 7 and at rates comparable to half of the acid addition rate (not unexpected, since Mg^{2+} and Ca^{2+} need two H^+ to neutralize their anions). They also were contributing significantly to the total demand for acid.

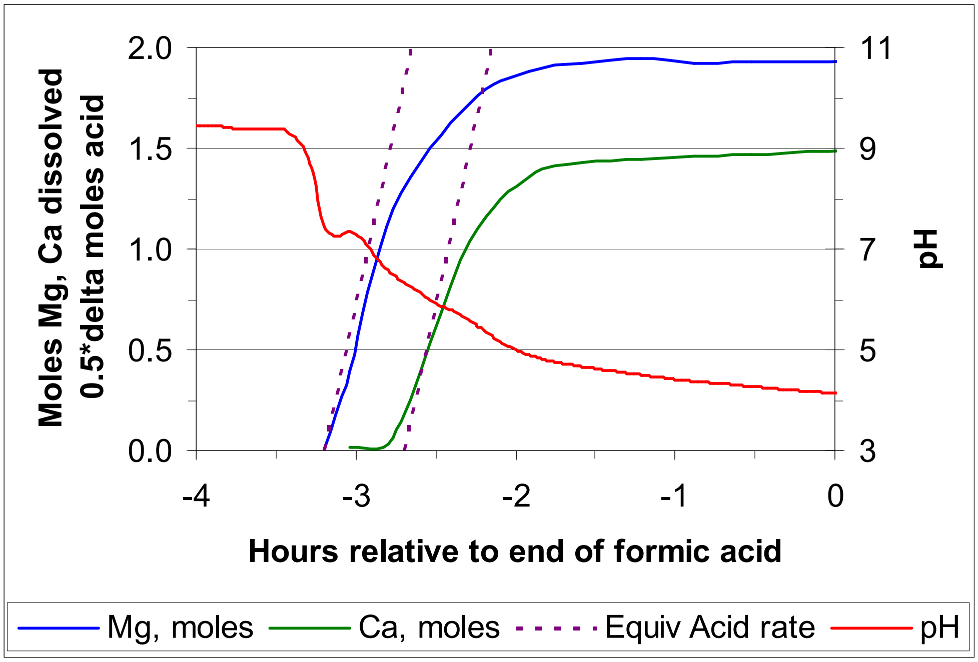

Figure 1. Dissolution rates of insoluble Mg and Ca during acid addition

The dissolution rate of Mg was initially nearly identical to the equivalent addition rate of acid protons. Mg is suspected to be present as $Mg(OH)_2$ with perhaps a small fraction of $MgCO_3$. The onset of $CaCO_3$ dissolution about two-thirds of the way through Mg dissolution occurred with a reduction in the rate of Mg dissolution. The combined Ca plus Mg dissolution rate was also essentially equal to the equivalent addition rate of acid protons. It is believed that some of the acid protons are reacting with soluble bicarbonate from the Na_2CO_3 in the starting aqueous phase during this same period. Total slurry TIC versus time data indicate that all carbonate was destroyed by the end of Ca dissolution. Integration of the carbon dioxide production rate through the end of Ca dissolution gave a value essentially identical to the moles of starting carbonate in the slurry feed.

The period following Ca and Mg dissolution was dominated by two main reactions. These were the reduction of Mn(IV) as insoluble MnO_2 to soluble Mn(II) and the destruction of nitrite ions, NO_2^-. Nitrite ions are destroyed by several parallel chemical pathways. Rh and Pd, present at 10-100 ppm in the waste from thermal neutron fission of ^{235}U, catalyze two of these pathways. The main by-products are nitrate ion, NO, and N_2O. Since the SRAT is air-purged, most of the NO is converted to NO_2 (along with N_2O_4). Brown colored gas formation is observed during nitrite destruction. Gas chromatograph data indicate formation of NO and N_2O, and depletion of O_2. Ion chromatography tracks formation of nitrate ion during this period. The sequence of these reactions relative to Ca dissolution is shown in Figure 2.

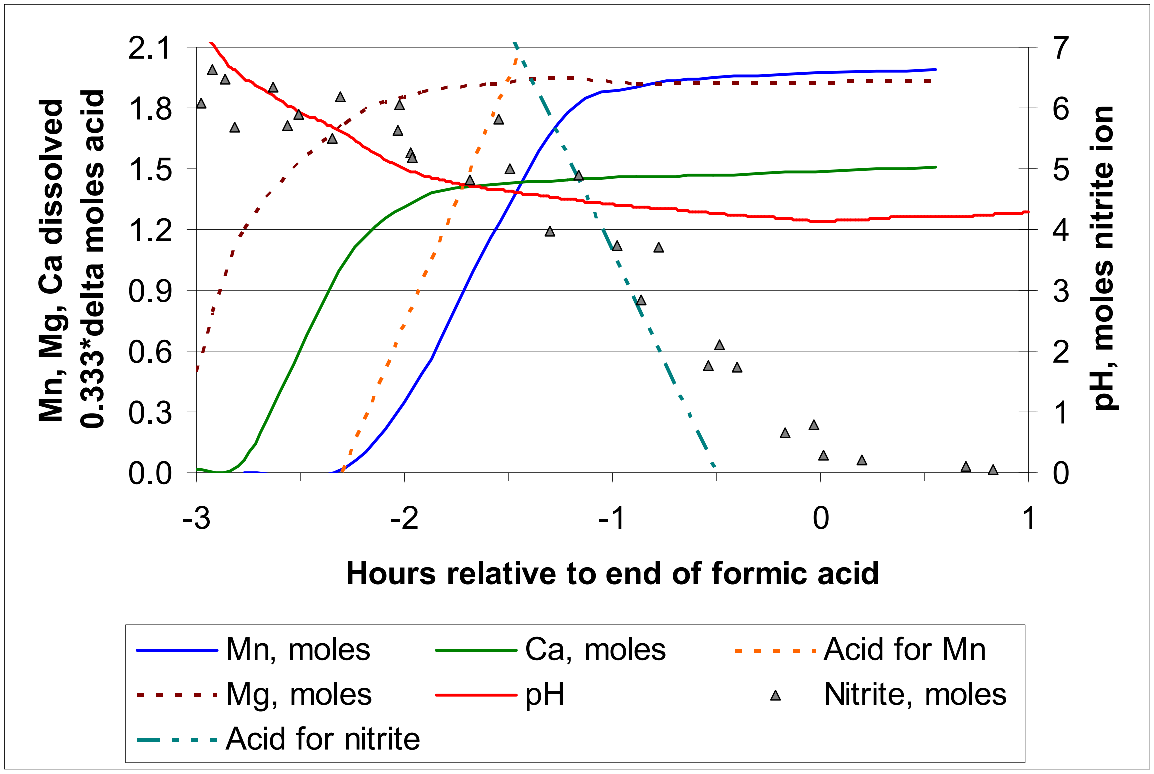

Figure 2. Mn reduction-dissolution and nitrite destruction after Ca dissolution.

MnO_2 reduction by formic acid requires consumption of three moles of acid per mole of Mn reduced.

$$MnO_2 + 3HCO_2H \rightarrow Mn(HCO_2)_2 + 2H_2O + CO_2$$

Figure 2 indicates that the rate of Mn dissolution is slower than one-third the rate of acid addition. This is partly due to the end of Ca dissolution and partly due to the onset of nitrite destruction. About half of the nitrite was destroyed during Mn reduction and the other half after Mn reduction. The reductive destruction of nitrite by formic acid also produces carbon dioxide. Consequently CO_2 formation is not directly useful for discriminating between the timing of Mn reduction and nitrite destruction. The mean consumption of acid by nitrite ion destruction is in the range of 0.9-1.5 moles acid per mole nitrite depending on catalytic activity. The amount of acid consumed increases with increasing noble metal concentrations. Typical HLW noble metal concentrations, however, generally result in about 1.0-1.1 mole acid per mole of nitrite destroyed.

Other reactions were found to consume acid during acid addition, but the initial concentrations and/or extent of reaction achieved were too small to have a significant impact on the calculated acid consumption. Some of these reactions included the partial dissolution of $Ni(OH)_2$, ZnO, and CuO. These reactions started once the pH was about five.

The following second generation stoichiometric acid equation was proposed to explain the data:

$$\frac{\text{moles acid}}{\text{L slurry}} = \text{base equivalents} + \text{soluble TIC} + \text{nitrite} + 1.5 * \text{Mn} + 1.5 * (\text{Ca} + \text{Mg}) + \text{Hg}$$

Equation 2, second generation equation for predicting the stoichiometric acid requirement in the DWPF SRAT cycle.

Soluble carbonate was given one mole acid per mole, since titration accounts for the second mole needed to convert carbonate to carbon dioxide. Calcium and magnesium were brought in at 75% of the stoichiometric requirement for $Mg(OH)_2$ and $CaCO_3$, since there exists a certain fraction of non-acid reacting compounds, such as oxalate, phosphate, sulfate, etc. associated especially with calcium and perhaps magnesium. These two terms are appear to account for the insoluble carbonate contribution so no measurement of slurry TIC is required. Elimination of the problematic analysis is considered a positive feature of the proposed equation.

Although the case shown in Figure 2 has Mn reduction essentially 100% complete prior to nitrite destruction, other simulations have produced contradictory results. The data in Figure 2 are from tests with low catalytic activity. Nitrite is often sufficiently destroyed prior to complete Mn reduction under other test compositions. The second generation stoichiometric acid equation has treated Mn as 50% reduced by complete nitrite ion destruction as a temporary compromise pending a more detailed evaluation of the available kinetic data.

Preliminary validation experiments show that the second generation equation fits the historical database much better than the original equation, while still retaining the first-principles premise that the chemistry can be understood in detail as a sum of individual reactions. Experimentally determined minimum acid requirements for nitrite destruction have been collected over the years and put into a statistical database for analysis using JMP statistical software. A simple comparison of the second generation equation to the minimum acid data is given in Figure 3.

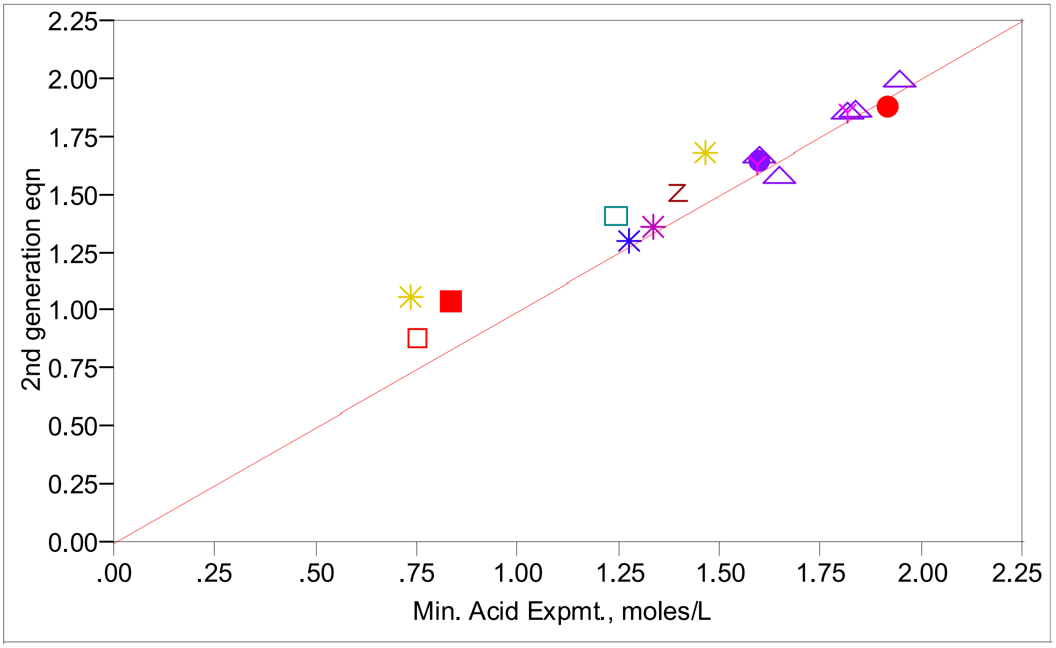

Figure 3. Validation of second generation stoichiometric acid equation predictions against experimentally determined minimum acid requirements.

The second generation acid equation shows a slight bias toward higher than measured values for acid demand but it generally matches the observed trend. Comparable agreement with successful plant operational data was obtained. Further studies are planned to investigate certain individual coefficients in the second generation equation and their impact on the fit of the equation to the existing data.

A second approach was taken toward evaluating the stoichiometric acid demand during SRAT processing. This approach led to an equation that contained neither titration nor TIC measurements. Consequently, it is not simply another evolution of the original equation (which is primarily driven by slurry anions). The premise was that a sum could be made over the soluble cations present after acid addition/consumption that would represent the cations that had had a basic anion neutralized by H^+. It was recognized immediately that this sum would overstate the acid demand, since not all of the associated anions were bases. Therefore, a credit for non-acid reacting anions was taken to reduce the result obtained by summing the soluble cations. The resulting equation is given as eqn. [3].

$$\frac{moles\ acid}{L\ slurry} = Na + K + Hg + 2*(Ca + Mg) + 1.5*Mn - NO_3^- - 2*SO_4^{2-} - HCO_2^- -$$
$$2*C_2O_4^{2-} - 3*PO_4^{3-} - Cl^- - F^- - NO_2^-*(\mathit{fraction}\ NO_2^-\ \mathit{converted\ to}\ NO_3^-)$$

Equation 3, cation-based prediction of the stoichiometric acid requirement.

The cation-based equation, like the two equations preceding it, has all terms expressed in terms of moles species per liter (dm^3) of waste slurry charged to the SRAT. The cation equation and the second generation equation track each other more closely than the original equation [1]. Both new equations seem to respond more appropriately to compositional changes than the original stoichiometric acid equation.

The cation-based stoichiometric acid equation appears to be conceptually sound. It would also eliminate two of the more difficult measurements in the original equation: base equivalents of the slurry and total slurry inorganic carbon. The main issues with the cation equation appear to be the large number of terms (14), the accumulation of measurement uncertainty (random error propagation), and the presence of both positive and negative terms. For example, the sodium term can be comparable to the entire stoichiometric acid requirement but is only accurate to about +/-10% when measured by inductively coupled plasma-atomic emission spectroscopy.

The new data on the chemistry of the major species present during SRAT processing have led to a greatly improved understanding of the sequence of reactions occurring and their impact on acid consumption. This has led to the development of two new equations for predicting the stoichiometric acid requirement for SRAT processing. The two new equations have already been implemented for lab-scale testing in parallel with the original equation. The plan is to attempt to implement a change in DWPF at the time of the next major sludge batch (within six months). At present, it will be the second generation stoichiometric acid equation that is implemented, since it has shown less random variability during validation tests than the cation equation.