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Mathematically Determined Scavenger Impacts during Ozonolysis of Oxalic Acid Waste Slurries – 15600

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ABSTRACT

A basic oxidant balance, including the primary chemical reactions associated with ozone, hydroxyl radical generation, scavengers and oxalate decomposition reactions was constructed and used to develop mathematical models to represent both steady state and time dependent changes in ozone concentrations, hydroxyl radical concentrations, scavenger concentrations and oxalate concentrations.

Using the results from previous spent 1 wt% oxalic acid decomposition testing, a plot of 1/(oxalate reaction rate) vs. 1/[$C_2O_4^{2-}$]) was used to estimate the initial hydroxyl radical generation values (i.e., g values) at time = 0. These g values are then compared for the different slurries to determine if the changes in g values are consistent with the scavenger dilution between the sequentially created slurries.

Also considered as a potential scavenger is the CO_2 arising from the oxalate decomposition. In this case the scavenger concentration and the carbon dioxide concentrations would be the same, and $k_{s2} = k_{sc}$. Since the CO_2 is created from the decomposition of oxalate, a standard equation can be used to compensate for time dependence of [$C_2O_4^{2-}$]. Using the results from previous spent 1 wt% oxalic acid decomposition testing, plots of oxalate concentration over time were used to determine time specific g values. The g values are then compared to determine how the values change throughput the oxalate decomposition. Using the results from previous spent 1 wt% oxalic acid decomposition testing, time dependent values are developed for *"*k_g/k_a*"* to show the relative significance of hydroxyl radical reacting with the scavenger vs decomposition of the oxalate.

INTRODUCTION

Decontamination of nuclear facilities is essential for reducing occupational exposures, limiting potential releases, and facilitating closure. For decontaminating of large processes, chemical decontamination methods are often applied. During the last twenty years, several key advances have occurred in decontamination chemistry associated with the commercial nuclear power industry. These advances include the use of tailored cocktails to optimize decontamination. In stark contrast, oxalic acid remains the primary acid used for decontaminating the carbon steel walls of the Savanah River Site's radioactive liquid waste tanks. Although oxalic acid was the paramount decontamination agent investigated during the early 1950s, the commonality of carbon steel, versus the use of Stainless Steel within the legacy cold war United States Department of Energy nuclear complex ensures its continued use. Similar to other common organic acids, oxalic acid acts as a complexing agent with metal ions released during the dissolution. In addition, the corrosion of carbon steel has been studied, such that general corrosion from oxalic acid is considered controllable. More importantly however, when oxidized, oxalic acid will decompose directly into carbon dioxide, with no intermediate or potential flammable organics produced. Therefore, using oxalic acid as a decontamination solution, tied to catalytic ozonalysis using the transition metals already contained within the slurry as catalysts (i.e., adding only oxalic acid and ozone) results in a net green process. Alternately stated, the net combined effect is no net chemical additions to the waste contents.

Previously performed process testing (including 1/10-scale process testing) using a myriad of simulant slurries created from the dissolution of representative sludge simulants using 1wt% oxalic acid confirmed the overall robustness of the oxalate decomposition process (Ref. 1, 2). With the decomposition tests being overwhelming successful, the overall effect of the scavengers on the oxalate decomposition rates, was previously deemed to be minor/acceptable, without any further attempt to analytically quantify or estimate the impact. With a need to advance the technology readiness level/technical maturation of the process, there is a current desire to better understand and quantify the negative effects of the scavengers on the oxalate decomposition rate.

Using ozone to decompose spent oxalic acid has been well studied, however, for high-risk type applications in the nuclear industry various technical questions still exist. Although the various catalytic reactions have been studied for creating the necessary hydroxyl radicals to decompose the oxalate, and the technical readiness level for using combined ozone-oxalate systems in the nuclear industry has significantly advanced, understanding the impact of ozone and oxalate scavengers related to High Level Waste tank cleaning/sludge dissolution has largely been treated as a black box. From literature, common anion type hydroxyl radicals and or ozone scavengers of potential concern include carbon monoxide, carbon dioxide, and nitrites.

Various SRS test data currently exists on spent oxalic acid decomposition rates, sadly however, at no direct analytical testing was performed during the testing to quantify the scavengers. Since the bulk of the SRS testing was completed about 1.5 years ago, (Ref. 1) but questions on the scavenger significance is now being asked to ensure a fair assessment of the robustness of the oxalate decomposition process, and an accurate understanding of the chemistry, understanding what the scavengers are, as well as their impact would be beneficial.

METHODS

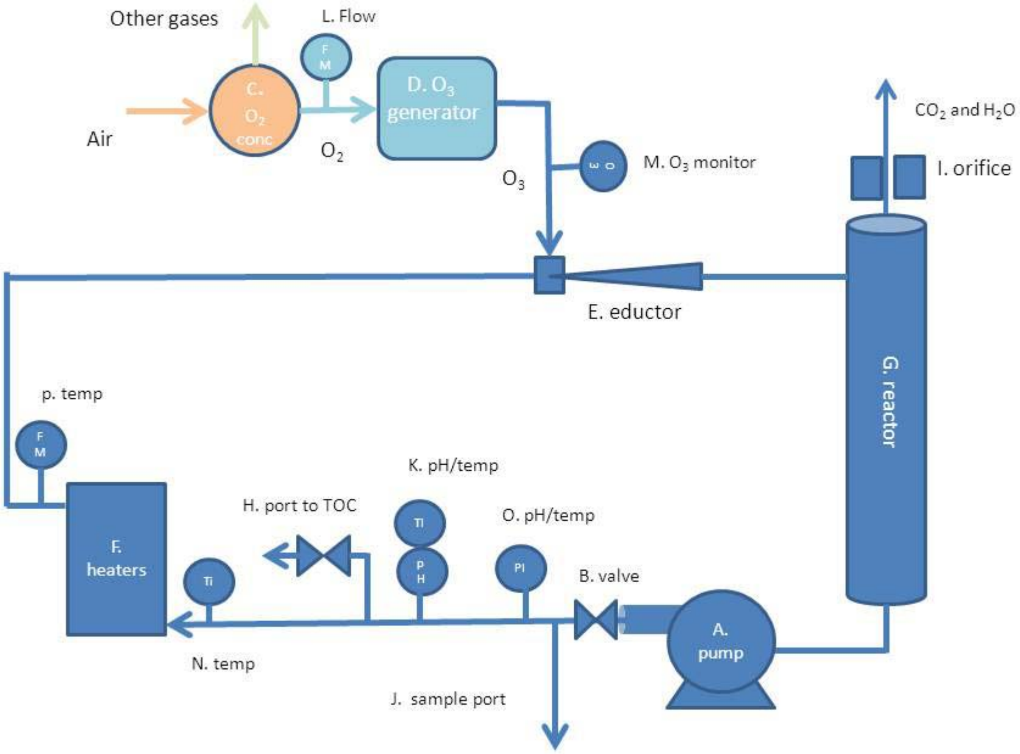
Previously Performed Oxalate Decomposition Testing

The decompositions created from 1 wt% oxalic acid were previously presented in (Ref 1). As an overview of the oxalate decomposition results the pH and oxalate concentrations for the slurries created with 1 wt% OA are shown as a function of time in Table 1.

Table 1. Results from Previous Performed Oxalate Decomposition Testing

Slurry Name	time (hrs)	pH	Oxalate (mol/L)	Slurry Name	time (hrs)	pH	Oxalate (mol/L)
Fe-NL-1	0	1.7	9.3E-2	Al/Mn-NL-1	0	2.5	6.8E-2
	1	3.2	7.8E-2		1	5.4	5.1E-2
	2	3.8	7.0E-2		2	6.6	3.1E-2
	4.0	5.5	3.1E-3		4	5.5	3.8E-3
	6.0	7.4	3.1E-3		5.6	7.0	1.1E-3
	7.3	8.2	1.1E-3		6.1	7.4	3.1E-4
	9.4	8.8	1.6E-4		6.4	8.5	1.6E-4
Fe-NL-2	0	1.8	1.1E-1	Al/Mn-NL-2	0	1.7	1.1E-1
	1	2.0	1.1E-1		1	2.3	7.6E-2
	2	2.3	9.8E-2		2	4.9	4.6E-2
	3.9	3.5	5.5E-2		4	6.5	1.9E-2
	6.0	5.2	2.5E-2		6.0	8.2	1.1E-3
	7.2	6.3	7.6E-3		6.1	8.3	2.0E-4
	8.5	7.6	2.2E-4		6.4	8.4	2.0E-4
Fe-NL-3	0	1.9	1.1E-1	Al/Mn-NL-3	0	1.5	1.1E-1
	1	1.9	9.7E-2		1	1.9	7.1E-2
	2	2.1	8.2E-2		2	4.5	5.9E-2
	4.0	3.5	4.0E-2		4	5.5	1.2E-2
	6.0	5.6	1.2E-2		5.9	8.0	1.1E-3
	7.7	6.7	1.1E-3		6.0	8.2	3.1E-4
	8.1	7.6	1.0E-4		6.3	8.5	1.6E-4
Fe-CL-1	0	2.0	7.7E-2	Al/Mn-CL-1	0	2.4	7.5E-2
	1	4.7	5.1E-2		1	5.7	3.4E-2
	2	5.4	3.2E-2		2	6.8	1.1E-2
	4	7.2	2.7E-3		4.1	8.2	3.6E-3
	5.0	8.3	2.7E-3		4.8	8.4	1.1E-3
	5.5	8.7	2.6E-4		5.4	8.6	2.0E-4
Fe-CL-2	0	1.8	9.0E-2	Al/Mn -CL-2	0	2.2	8.2E-2
	1	2.4	6.7E-2		1	5.3	6.8E-2
	2	4.3	4.4E-2		2	5.7	4.5E-2
	4.0	6.0	1.9E-2		5	8.0	1.1E-3
	5.5	7.9	4.1E-4		6	8.4	1.6E-4
Fe-CL-3	0	1.5	1.0E-1	Al/Mn -CL-3	0	2.0	8.6E-2
	1	2.0	6.2E-2		1	5.1	4.5E-2
	2	4.1	3.5E-2		2	5.5	4.0E-2
	4.0	5.3	4.2E-3		4	7.3	1.1E-2
	6.0	7.2	2.0E-4		5.0	7.9	5.7E-4
	6.2	7.3	1.5E-4		5.3	8.2	2.0E-4
Fe-DL-1	0	1.7	1.0E-1	Al/Mn -DL-1	0	2.2	7.7E-2
	1	1.6	9.7E-2		1	5.5	5.7E-2
	2	2.0	6.8E-2		2	6.6	3.4E-2
	3	4.7	3.4E-2		4	8.2	7.8E-3
	4.0	6.6	2.3E-3		4.9	8.4	1.1E-3
	6.3	8.5	2.6E-4		5.4	8.2	1.9E-4
Fe-DL-2	0	1.7	1.0E-1	Al/Mn -DL-2	0	1.9	9.2E-2
	1	2.1	6.8E-2		1	5.0	6.8E-2
	2	4.4	3.4E-2		2	5.4	2.3E-2
	4.0	6.1	2.3E-3		4	7.4	9.2E-3
	5.5	7.7	2.6E-4		5.0	8.0	1.1E-3
	6.0	8.1	2.0E-4		5.4	8.2	2.0E-4
Fe-DL-3	0	1.7	1.0E-1	Al/Mn -DL-3	0	2.7	8.2E-2
	1	1.8	9.1E-2		1	5.0	5.7E-2
	2	4.1	6.8E-2		2	5.4	4.5E-2
	4.8	6.7	1.1E-3		5.1	8.0	2.5E-3
	5.5	7.7	2.6E-4		5.8	8.1	2.0E-4

In Table 1, the Fe and Al/Mn in the Slurry Names refers a slurry created from digesting an Fe-rich or an Al/Mn-rich sludge simulant (Ref. 3) using 1wt% oxalic acid. The NL, CL and DL refer to type of UV applied, with NL referring to no UV; CL referring to a maintained clean UV-light; and DL referring to a UV-light where film was allowed to build up during testing. The -1, -2, and-3 refers to the sequential digestion of the sludge which created the slurry (i.e., -1 refers to first digestion of the sludge with the oxalic acid, etc.). During decomposition testing, the amount of oxalate (remaining in the slurry) was determined recorded periodically using an inline automated Total Organic Carbon (TOC) Analyzer. A simplification of the ozonation process is shown in Figure 1.



Process Conditions during Testing

- Slurry volume in simulant process was approximately 60 liters, while for actual waste and hematite was
- Band heaters located at "F" maintains temperature ~70±5°C during simulant testing testing.
- Recirculation pump located at "A" recirculates the slurry in loop at 40 L/min during testing.
- Ozone fed to the test loop at 60 kg/h), with solubility of ~30 ppm calculated based on Henry's Law.
- Orifice maintaining ~10-psig backpressure in reactor.

Figure 1. Schematic diagram of the experimental test setup

Current Effort

The primary chemical reactions associated with ozone and hydroxyl radical generation reaction including the decomposition of oxalates were identified, with associated mathematical models generated. Equations were then modified to enable the models to be validated and determine the following properties associated with the scavengers:

- Quantify the negative effect of the scavengers on the oxalate decomposition rate
- Determine the source of the scavenger, specifically:
    - Is the scavenger primarily something in the sludge?
      or
    - Is the scavenger CO_2 generated as the result of oxalate decomposition?

Steady State - Ozone Analysis

Based on the reactions, a simple mathematical model of the ozone balance is constructed. Based on the ozone balance, a general mathematical equation for calculating hydroxyl radical generation rates based on the concentration of aqueous ozone is developed.

Steady State - Oxalate Analysis

Based on the developed chemical reactions identified as being associated with the ozone and hydroxyl radical reactions, an equation for oxalate decomposition rate based on both ozone concentration and the hydroxyl radical concentration is developed (Ref. 4, 5, 6). Since the decomposition of oxalate under acid conditions is driven by the concentration of hydroxyl radicals, and the direct reaction of oxalate with ozone is slow in comparison, the associated rate constant decomposition rate can be determined using the calculated hydroxyl radical concentration and the measured oxalate concentration.

Steady State - Hydroxyl Radical Analysis

The hydroxyl radical generation rate, g, is set equal to the hydroxyl radicals reacting with oxalate, plus the hydroxyl radicals reacting with scavenger. Then, the first possibility, that the scavenger is associated with a component of the sludge is evaluated. By assuming a short time has occurred, the scavenger is considered to be non-depleted and effectively a constant. Using the results from the previously performed oxalate decomposition testing, a plot of $1/(r_{oxalate})$ vs. $1/[C_2O_4^{2-}]$) is used to estimate the hydroxyl radical generation rates (i.e., the g values represent the intercept at t = 0, ie, $g_{t=0}$) . The $g_{t=0}$ values are then contrasted to determining how the values vary between the slurries and as the result of ozonolysis.

The possibility that the scavenger is CO_2 arising from the oxalate decomposition is also evaluated. Since the CO_2 is created from the decomposition of oxalate, a standard equation for time dependence of $[C_2O_4^{2-}]$ can be used. Using the data from the previously determined oxalate decomposition testing, plots of each slurries oxalate decomposition as a function of time (slope) are used to determine the time dependent hydroxyl radical generation rates, g values. With time dependent g values determined, the relative significance of the scavenger is determined by solving for k_γ/k_a, where k_γ represents the rate constant for the hydroxyl radicals reacting with the scavenger, while k_a represents the rate constant for O_3 being converted to hydroxyl radicals .

DISCUSSION

The primary reaction schemes for ozone reactions, including the generation of hydroxyl radicals from ozone can be shown by Reactions 1 through 3.

$$O_3 + M \overset{k_c}{\rightarrow} M + {}^\circ OH^- \quad \text{(Reaction 1)}$$

$$O_3 + \ scav1 \overset{k_{s1}}{\longrightarrow} \text{"}product1\text{"} \quad \text{(Reaction 2)}$$

$$O_3 + C_2O_4{}^{2-} \overset{k_o}{\rightarrow} CO_2 \quad \text{(Reaction 3)}$$

<u>Where:</u>

O_3 = ozone concentration maintained in the waste slurry

$^\circ OH-$ = concentration of hydroxyl radicals in solution

$[M]$ = combined concentration of iron, manganese and nickel
$scav_1$ = concentration of ozone scavengers
$product_1$= product created from reacting ozone with scav1
$C_2O_4^{2-}$ = oxalate concentration
CO_2 = concentration of carbon dioxide generated
k_c = rate constant for generating hydroxyl radicals from catalytic reactions with ozone
ks_1 = rate constant for ozone reactions with oxalate

The hydroxyl radical reactions are shown as Reactions 4 through 6.

$$°OH^- + {C_2O_4}^{2-} \xrightarrow{k_I} CO_2$$

(Reaction 4)

$$°OH^- + scav2 \xrightarrow{k_{s2}} \text{"}product\ 2\text{"}$$

(Reaction 5)

$$°OH^- + CO_2 \xrightarrow{k_{s3}} \text{"}product\ 3\text{"}$$

(Reaction 6)

Where:
k_1 = rate constant for hydroxyl radicals reacting with oxalate, $C_2O_4^{2-}$
ks_2 = rate constant for hydroxyl radical reacting with $Scav_2$ to create unwanted *product 2*
ks_3 = rate constant for hydroxyl radical reacting with carbon dioxide creating *product 3*

From Reaction 1, the hydroxyl radical generation rate can be expressed as Equation 1.

$$g = k_c[O_3][M] \qquad \text{(Equation 1)}$$

Steady State Analysis

Solving for the oxalate concentration - $d[C_2O_4^{2-}]/dt$, which is also referred to as oxalate reaction rate, $r_{oxlate,}$ results in Equation 2

$$-\frac{d[C_2O_4]}{dt} = k_o[O_3][{C_2O_4}^{2-}] + k_1[{C_2O_4}^{2-}][°OH^-]$$

(Equation 2)

Since the reaction of the hydroxyl radical with oxalate is significantly faster than that for the rate of ozone reacting with oxalate under acid conditions (Ref. 4), Equation 2 is simplified as Equation 3.

$$-\frac{d[C_2O_4]}{dt} = k_1\left[C_2{O_4}^{2-}\right][°OH^-]$$

(Equation 3)

Solving for the hydroxyl radical concentration using Equation 1, results in Equation 4

$$g - \ k_1\left[C_2{O_4}^{2-}\right][°OH^-] - k_{s2}[scav2][°OH^-]$$

(Equation 4)

Rearranging

$$[°OH^-] = \frac{g}{k_1\left[C_2{O_4}^{2-}\right] + k_{s2}\,[scav2]}$$

(Equation 5)

Combining Equations 3 and 5, results in Equation 6

$$-\frac{d[C_2O_4]}{dt} = r_{oxalate} = g\,\frac{k_1\left[C_2{O_4}^{2-}\right]}{k_1\left[C_2{O_4}^{2-}\right] + k_{s2}\,[scav2]}$$

(Equation 6)

For Equation 6, there are two common possibilities associated with the scavenger. The first considered is that the scavenger, $scav_2$ is form some component associated with the sludge. It can be represented using Equation 7.

$$\frac{1}{r_{oxalate}} = \frac{1}{g}\left[1 + \frac{k_{s2}\,[scav2]}{k_1\left[C_2{O_4}^{2-}\right]}\right]$$

(Equation 7)

If we assume we are at some short time, the scavenger has not yet been depleted, and therefore is effectively constant. Using the previously performed oxalate decomposition testing, specifically the determined oxalate decomposition rates, at the corresponding oxalate concentrations, enables the $slope = (k_{s2}[scav_2]/(k_{Ig})$ to be calculated, with initial g values easily determined from the $1/g$ intercept at the origin. Table 2 is provided as an example showing the determination of the $1/g$ value using the plots of $1/r_{oxalate}$ vs. the oxalate concentration

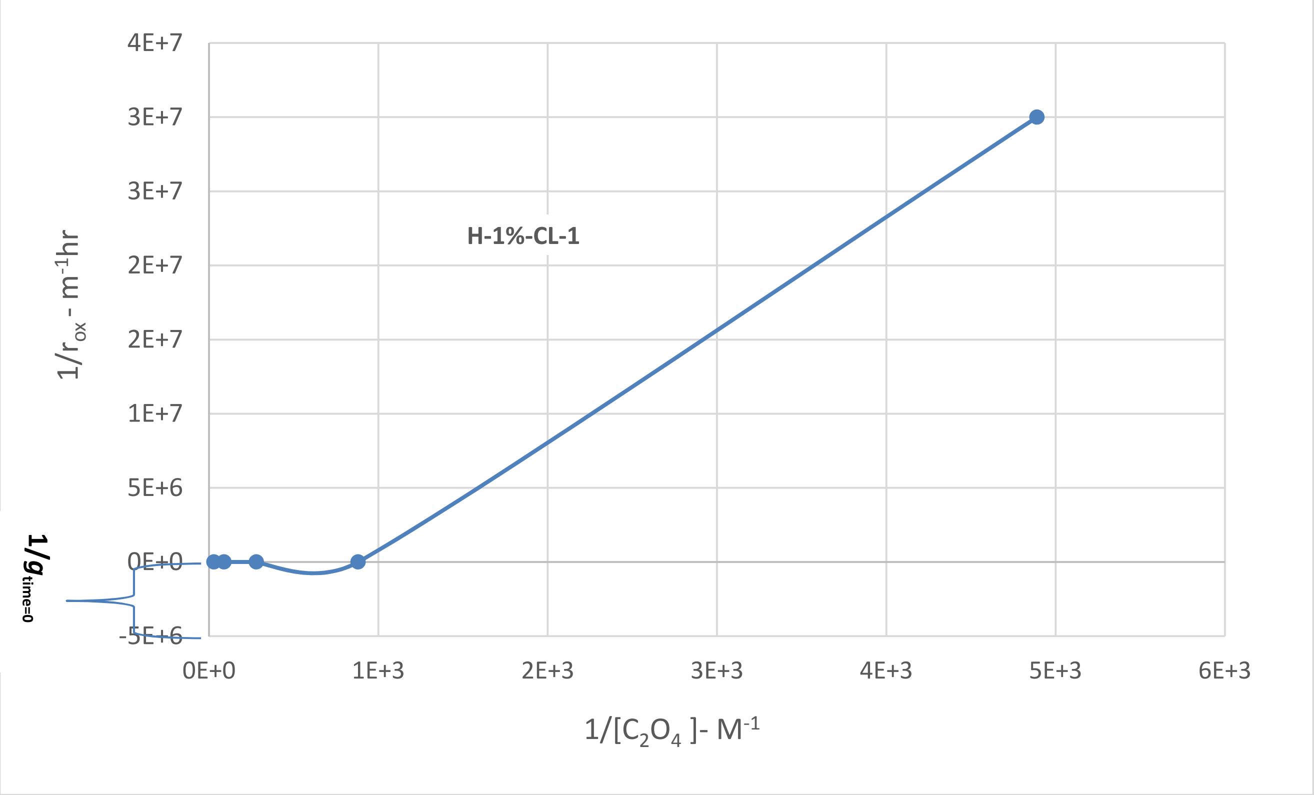


Figure 2. Example Determination of g Values Using $1/r_{oxalate}$ and $1/[C_2O_4^{2-}]$

As shown in Table 3, the g values at time= 0 for slurries, including those created from the subsequent treatment of the same simulant using 1 wt% oxalic acid are similar, but show no general pattern consistent with dilution (i.e., such as would be caused by the decrease of anion concentration in each new slurry created after additional treatment of the sludge with 1 wt%

oxalic acid).

Table 3. *g* Values Derived from Test Data at Time=0

Slurry	***g* values mol/L per hr**
Fe-NL-1	1.48E-02
Fe-NL-2	1.55E-02
Fe-NL-3	1.16E-02
Fe-Cl-1	2.59E-02
Fe-Cl-2	2.28E-02
Fe-Cl-3	3.93E-02
Fe-DL-1	2.91E-02
Fe-DLl-2	3.10E-02
Fe-DL-3	2.27E-02
Al/Mn-NL-1	1.54E-02
Al/Mn-NL-2	2.96E-02
Al/Mn-NL-3	4.34E-02
Al/Mn-CL-1	3.71E-02
Al/Mn-CL-2	1.43E-02
Al/Mn-CL-3	1.42E-02
Al/Mn-DL-1	2.27E-02
Al/Mn-DL-2	2.13E-02
Al/Mn-DL-3	2.33E-02

The second possibility is that $scav_2$ is actually CO_2 arising from the oxalate decomposition, then $scav_2 = CO_2$ and $k_{s2} = k_{sc}$. Since the CO_2 is created from the decomposition of oxalate, it can be shown in Equation 8

Rate Based Analysis

For time dependence of oxalate as a function of time, where $y = [C_2O_4{}^{2-}]$

$$-\frac{dy}{dt} = g\,\frac{k_a\,y}{k_b\,y + k_\gamma} \qquad \text{(Equation 8)}$$

Where $y = [C_2O_4{}^{2-}]$

$$\int_{yo}^{y} \frac{k_B y + k_\gamma}{k_a y}\,dy = -\,g\int_{t=0}^{t} dt \qquad \text{(Equation 9)}$$

$$\frac{k_B}{k_a}(y - y_o) + \frac{k_\gamma}{k_a}\,ln\left(\frac{y}{y_o}\right) = -\,g\,t \qquad \text{(Equation 10)}$$

Where Z can be defined as Equation 11

:

$$Z = \frac{y}{y_o} = \frac{[C_2O_4{}^{2-}]_t}{[C_2O_4{}^{2-}]_{t=0}} \qquad \text{(Equation 11)}$$

Then, re-arranging results in at Equation 12

$$k_b y_o\,(Z - 1) + k_\gamma[\ln Z\,] = -g k_a\,t \qquad \text{(Equation 12)}$$

Dividing the right hand side of the Equation 12 by “$-g\ k_a$” results in Equation 13.

$$\frac{(k_b y_o\,(Z-1))}{g k_a} - \frac{k_\gamma[\ln Z\,]}{g k_a} = t \qquad \text{(Equation 13)}$$

Based on comparing Equation 9 with Equation 6, k_a and k_b can be considered equal to each other. Then recognizing that k_γ/k_a, compares the rate constant of the scavenger to be compared to that the oxalate, we re-arrange the terms into Equation 14, below, and solve using available test data.

$$\frac{k_{\gamma}}{k_a} = -\frac{1}{\ln\ z}(gt - zy_o + y_o) \qquad \text{(Equation 14)}$$

Table 4, shows the calculated values for $k_g/k_{a,}$ as a function of decomposition time for each of the slurries.

Table 4. Calculated Time Dependent $\underline{k_g/k_a}$ Values Based on Previous Testing

Slurry	Fe-NL-1	Fe-NL-2	Fe-NL-3	Fe-CL-1	Fe-CL-2	Fe-CL-3	Fe-DL-1	Fe-DL-2	Fe-DL-3
Treatment time=hr	k_g/k_a								
1	NR	5.5E-1	3.6E-1	8.4E-18	5.9E-18	3.5E-18	6.1E-1	6.1E-1	4.3E-3
2	2.6E-2	9.8E-2	9.6E-3	4.3E-3	4.2E-4	1.0E-2	6.3E-2	6.3E-2	1.5E-3
3	NR	NR	NR	NR	NR	NR	1.8E-2	1.8E-2	9.6E-3
4	9.0E-3	1.4E-2	2.9E-4	5.2E-3	9.3E-3	7.5E-3	4.6E-3	4.6E-3	1.6E-2
5	NR	NR	NR	9.8E-3	5.5E-3	NR	7.9E-3	7.9E-3	1.9E-2
6	3.0E-4	1.1E-2	1.1E-4	6.9E-3	4.5E-3	1.0E-2	1.4E-2	1.4E-2	TC
7	3.7E-3	7.6E-3	NR	TC	TC	TC	TC	TC	TC
8	4.0E-3	7.1E-3	4.3E-5	TC	TC	TC	TC	TC	TC
9	7.5E-3	5.5E-3	TC	TC	TC	TC	TC	TC	TC

Slurry	Al/Mn-NL-1	Al/Mn-NL-2	Al/Mn-NL-3	Al/Mn-CL-1	Al/Mn-CL-2	Al/Mn-CL-3	Al/Mn-DL-1	Al/Mn-DL-2	Al/Mn-DL-3
Treatment time=hr	k_g/k_a								
1	NR	2.5E-3	6.9E-18	1.1E-17	8.7E-17	4.1E-2	4.5E-3	NR	NR
2	5.9E-3	1.1E-3	3.3E-2	7.4E-3	3.1E-2	1.9E-2	1.7E-3	1.7E-2	1.8E-2
3	NR	NR	NR	NR	NR	NR	NR	NR	NR
4	4.6E-4	1.8E-2	2.2E-2	2.6E-2	1.8E-2	1.4E-2	5.8E-3	2.2E-3	1.2E-2
5	NR	NR	NR	1.9E-2	3.2E-3	2.2E-3	5.1E-3	3.7E-3	9.5E-3
6	4.7E-3	1.3E-2	1.7E-2	4.1E-3	1.0E-3	TC	TC	TC	8.1E-3

Note: NR refers to not recorded and TC refers to test complete

With some of the first initial readings (1st hour) values having values a slow of $10^{-17\text{ and}}$ 10^{-18} some gas like CO_2 could likely be the scavenger. As can be seen in Table 4, however, the ratio of scavenger rate constant vs. the hydroxyl radical reaction rate varies, but is on a general order of 10^{-2} or 10^{-3}, confirming a very low, almost negligible, impact from the scavengers

CONCLUSIONS

To better quantify the impact from scavengers; a simple mathematical model based on an oxidant balance was constructed. Using steady state analyses, an equation for the hydroxyl radical generation rate was constructed. Since at time t=0, any hydroxyl radical scavenger has not been depleted and is constant, inserting the measured changes of oxalate as a function of time, and oxalate concentration enabled the initial hydroxyl radical generation rates to be estimated. Comparison of the hydroxyl radical generation rates for different slurries even with varying concentrations of metals and oxalate as discussed in Ref. 1, shows a negligible impact on the hydroxyl radical generation rate, supporting the position that there is an initial overabundance of catalysts vs. ozone in all of the slurries (i.e., and time t=0 the ozone is controlling the reaction).

Revising the model to include a time dependent term for scavengers, and combining rate terms, results in a value for relative scavenger impact, k_{scav}/k_a, where k_{scav} represents the effect of scavengers per unit time, and k_a represents the generation rate of hydroxyl radicals. Again using data from laboratory testing, the relative impacts from scavengers on the oxalate decomposition in each of the slurries were estimated. The results showed that the combined effect of scavengers represented a minor loss in efficiency at the initiation of ozonolysis on each of the slurries. In addition, based on little difference between the values for slurries with significant levels of dilution and only very small changes over time, it could be concluded that the scavenger effect most likely was not from the soluble anions. With some of the first initial readings (1st hour) values having values a slow of $10^{-17 \text{ and}}$ 10^{-18} some gas like CO_2 could likely be the scavenger. As can be seen in Table 4, however, the ratio of scavenger rate constant vs. the hydroxyl radical reaction rate varies, but is on a general order of 10^{-2} or 10^{-3}, confirming a very low, almost negligible, impact from the scavengers.

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