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Removal of Chloride from Acidic Solutions Using NO_2

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ABSTRACT

Chloride (Cl^-) salt processing in strong acids is used to recycle plutonium (Pu) from pyrochemical residues. The Savannah River National Laboratory (SRNL) is studying the potential application of nitrogen dioxide (NO_2) gas to effectively convert dissolved pyrochemical salt solutions to chloride-free solutions and improve recovery operations. An NO_2 sparge has been shown to effectively remove Cl^- from solutions containing 6-8 M acid (H^+) and up to 5 M Cl^-. Chloride removal occurs as a result of the competition of at least two reactions, one which is acid-dependent. Below 4 M H^+, NO_2 reacts with Cl^- to produce nitrosyl chloride (ClNO). Between 6 M and 8 M H^+, the reaction of hydrochloric acid (HCl) with nitric acid (HNO_3), facilitated by the presence of NO_2, strongly affects the rate of Cl^- removal. The effect of heating the acidic Cl^- salt solution without pre-heating the NO_2 gas has minimal effect on Cl^- removal rates when the contact times between NO_2 and the salt solution are on the order of seconds.

Keywords: Nitrogen dioxide, chloride removal, plutonium

INTRODUCTION

The Los Alamos National Laboratory (LANL) flowsheet for plutonium (Pu) metal production involves pyrochemistry to recover and purify Pu metal. The pyrochemical processes generate chloride salts with entrained Pu. The salts can contain a mixture of the following: plutonium oxide (PuO_2), plutonium chloride ($PuCl_3$), plutonium oxychloride (PuOCl), americium chloride ($AmCl_3$), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), sodium chloride (NaCl), and potassium chloride (KCl). Aqueous chloride processing is typically used to recover Pu from pyrochemical residues. Aqueous nitrate processing is used to recover Pu from non-chloride containing residues such as metal turnings.

At LANL, parallel glovebox systems handle the chloride-bearing streams separately from the nitrate-bearing streams. The current flowsheet incorporates dissolution of the chloride-bearing salts in hydrochloric acid (HCl), followed by chloride ion exchange and chloride solvent extraction to recover Pu. Process operations can be simplified and waste volumes reduced if chloride-bearing salts can be readily converted to chloride-free nitrate salts and Pu recovered using only aqueous nitrate processing. The Savannah River National Laboratory (SRNL) performed an initial evaluation of a process for stripping chloride from dissolved pyrochemical salt solutions using nitrogen dioxide (NO_2) gas and converting the solutions to nitrate-based solutions.

One method is available for performing the chloride conversion on solids. Whitaker et al[1] report a 93% conversion using NO_2 in the reaction with damp potassium chloride (KCl) to produce solid potassium nitrate (KNO_3) and nitrosyl chloride (ClNO) according to the following reaction:

$$KCl_{(s)} + 2\,NO_{2(g)} \rightarrow KNO_{3(s)} + ClNO_{(g)} \qquad (1)$$

Similar reactions occur when liquid dinitrogen tetroxide (N_2O_4) mixes with zinc chloride ($ZnCl_2$)[2] and uranium tetrachloride (UCl_4).[3] Because of the role of moisture in the conversion of KCl solid, it was expected that chloride conversion using NO_2 could be performed in aqueous solutions.

$$Cl^-_{(aq)} + 2\,NO_{2(g)} \rightarrow ClNO_{(g)} + NO_3^-{}_{(aq)} \qquad (2)$$

It has been shown that chlorides are removed from solutions of KCl in *aqua regia* (a 3:1 mixture of HCl and HNO_3).[4] When HNO_3 is mixed with NaCl, a solution of $NaNO_3$ is formed and Cl_2 and ClNO gases evolve.[5] Similarly, in excess of certain limiting conditions, HNO_3 and HCl react with each other to form chlorine and ClNO according to the reaction:

$$3\,HCl + HNO_3 \rightarrow ClNO + Cl_2 + 2\,H_2O \qquad (3)$$

Interpolation of the data from Mehring et al.[4] suggests that the limiting concentration for Reaction 3 to occur is about 6.5 M H^+. Herein we report the initial results for removing chloride from simulated pyrochemical salt solutions by sparging the solution with NO_2.

EXPERIMENTAL

Chloride solutions were prepared by adding weighed amounts of chloride salts into solutions containing specific concentrations of HCl and HNO_3. The salts added included NaCl, $CaCl_2$, $MgCl_2{\cdot}6H_2O$, and neodymium chloride ($NdCl_3$). For tests containing plutonium (Pu), solutions containing dissolved Pu were used in conjunction with HCl, HNO_3, and other chloride salts to produce the desired starting mixtures. All metal salts and acid solutions were at least reagent grade and used as received from Fisher Scientific or Aldrich. For non-radioactive tests, $NdCl_3$ was used as a surrogate for $PuCl_3$. In some tests, there were undissolved salts present at the start

of the experiment which dissolved shortly after the experiment was initiated. Liquid N_2O_4 [99.5%, b.p. = 21 ^oC] was used as received in a cylinder from Matheson Tri-Gas. At its boiling point, N_2O_4 is approximately 20% dissociated into NO_2.[6]

The setup for the chloride removal experiments is shown in Figure 1. As much as possible, NO_2 was evaporated from the cylinder at a constant rate. For the non-radioactive experiments performed in a chemical hood, the N_2O_4 cylinder was submerged in hot water to boil the liquid N_2O_4 and release NO_2 gas. For radioactive experiments performed in a glovebox, a hot-air blower was used to boil the liquid N_2O_4.

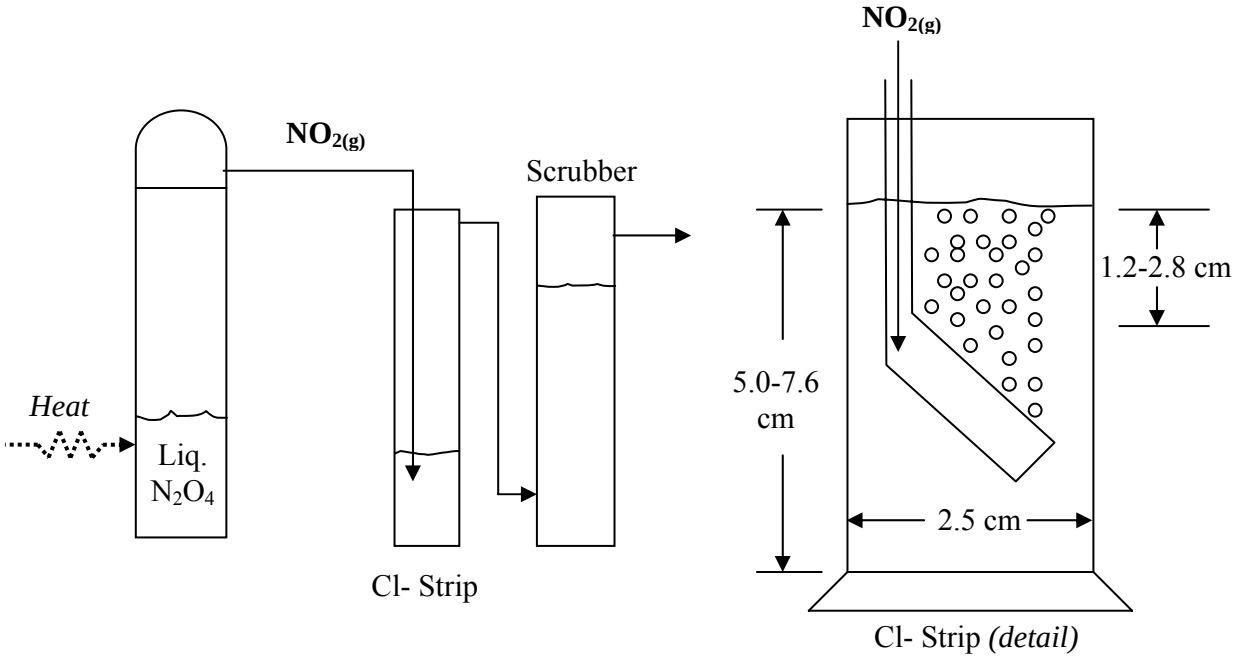

Figure 1. Experimental Setup

Nitrogen dioxide was bubbled into a glass gas washing bottle with a 2.5-cm diameter frit (40-60 μm pore size). Calculations estimate that NO_2 bubbles coming from a 40-60 μm frit are 1.9-2.3 mm in diameter.[7] The gas washing bottle contained 75 - 100 mL (the solution depth was 5.0 - 7.6 cm in the 2.5-cm wide bottle) of chloride-containing solution, which submerged the top of

the frit by 1.2 - 2.8 cm. The off-gas from the gas washing bottle was passed into another gas washing bottle containing 5 M NaOH as a scrub solution to retain the chloride.

A list of the test conditions is contained in Table 1. Prior to beginning most experiments, the N_2O_4 cylinder was weighed. Nitrogen dioxide gas was bubbled through the solution for a measured amount of time. At various intervals, the flow of gas was stopped and an aliquot of solution was removed from the acidic chloride solution. In later experiments, the weight of the N_2O_4 cylinder was also measured at each interval. The acidity of the chloride solution was determined by titrating a 100 μL aliquot with 0.05 M NaOH and phenolphthalein indicator. All analyses for anion content were performed by ion chromatography (IC). The IC analyses were performed on a Dionex DX-500 instrument with 1mM HCO_3^-/3.5mM CO_3^{2-} as the eluent on an AS-14 column with an AG-14 guard column and auto-suppressed conductivity detection.

Some experiments were performed with the chloride solution at greater than ambient temperature. For those tests, the gas washing bottle was wrapped with heating tape and the temperature controlled to ±2 ^oC using a Variac variable voltage controller.

Table 1. Experimental Test Matrix

Test #	Chloride Solution Temperature (^{o}C)	Initial HNO_3, M	Initial HCl, M	Calculated Total Initial Cl^-, M	Measured Total Initial Cl^-, M	Average NO_2 Feed (g/min)	Initial Liquid Volume (mL)	Other Chloride Salts in Solution (nominal)
1	20	6.0	2.0	5.0	3.9	0.45	75	0.125M $NdCl_3$, 1.3M $CaCl_2$
2	20	4.0	2.0	5.0	4.4	0.39	75	0.125M $NdCl_3$, 1.3M $CaCl_2$
3	20	6.0	2.0	5.0	3.3	2.0	75	0.125M $NdCl_3$, 1.3M$CaCl_2$
4	20	0	0	5.0	4.9	0.19	100	0.125M $NdCl_3$, 2.3M $CaCl_2$
5	20	2.0	2.0	5.0	4.9	0.19	100	0.125M $NdCl_3$, 1.3M $CaCl_2$
6	20	6.4	1.6	5.0	4.9	0.41	100	0.125M $NdCl_3$, 0.5M $CaCl_2$, 0.5M $MgCl_2$, 1M NaCl
7	40	6.4	1.6	5.0	4.9	0.47	100	0.125M $NdCl_3$, 0.5M $CaCl_2$, 0.5M $MgCl_2$, 1M NaCl
8	70	6.4	1.6	5.0	4.9	0.49	100	0.125M $NdCl_3$, 0.5M $CaCl_2$, 0.5M $MgCl_2$, 1M NaCl
9	75	3.5	0.5	2.4	2.4	0.38	100	0.125M $NdCl_3$, 0.25M $CaCl_2$, 0.25M $MgCl_2$, 0.5M NaCl
10	20	8.0	0	2.8	2.8	0.53	85	0.082M $PuCl_3$, 0.5M $CaCl_2$, 0.4M $MgCl_2$, 1M NaCl

RESULTS AND DISCUSSIONS

Reaction Kinetics

Whittaker et al.[1] showed that the solid-phase reaction between NO_2 and KCl was fast and probably limited by mass transfer. The same study also demonstrated that NO_2 gas without any moisture present was not effective at stripping chloride from solid KCl. As a result, it was expected that NO_2 would be effective at stripping chloride from an aqueous solution because water would be present and the reaction would not be limited by mass transfer into a solid phase. It was not known a priori what fraction of NO_2 would react with the water since NO_2 absorbs sparingly into water and undergoes the following reaction[8] to acidify the water:

$$3\ NO_2\ +\ H_2O\ \rightarrow\ 2\ HNO_3\ +\ NO \qquad (4)$$

The released NO can react with Cl_2 to form ClNO[9] according to the following reaction:

$$2\ NO\ +\ Cl_2\ \rightarrow\ 2\ ClNO \qquad (5)$$

The stripping of chloride from Tests 1-3 (Figure 2) confirms that aqueous chloride can be effectively removed from 6-8 M H^+ using NO_2. The speed of the reaction is underscored by two observations: 1) the residence time of bubbles in solution is less than 1 second; and 2) in the early stages of the tests at 6-8 M H^+, when the chloride concentration is still high, there is little visible NO_2 in the reaction vessel headspace.

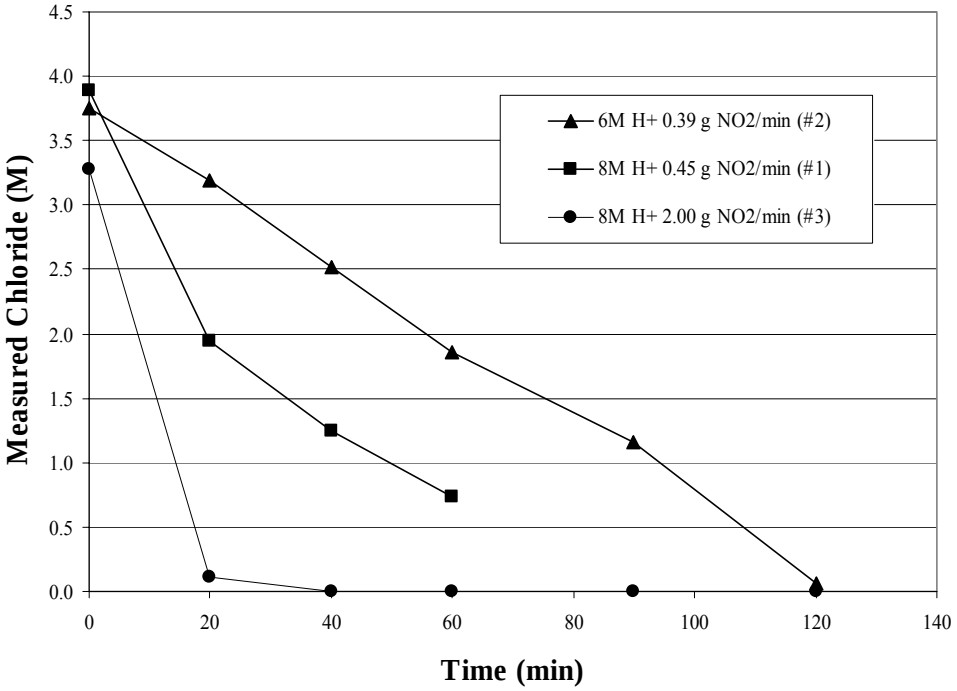

Figure 2: Measured Chloride Content as a Function of Reaction Time at 20 ^{o}C

Acid Dependence

The removal of chloride as a function of initial acid concentration is depicted in Figure 3. The figure also includes a line representing the stoichiometry of Reaction 2. Table 2 contains acid concentration data for the acid-chloride solutions as NO_2 is added and Cl^- removed. The data in Figure 3 and Table 2 provide several insights into the reaction mechanism and a starting point for future work.

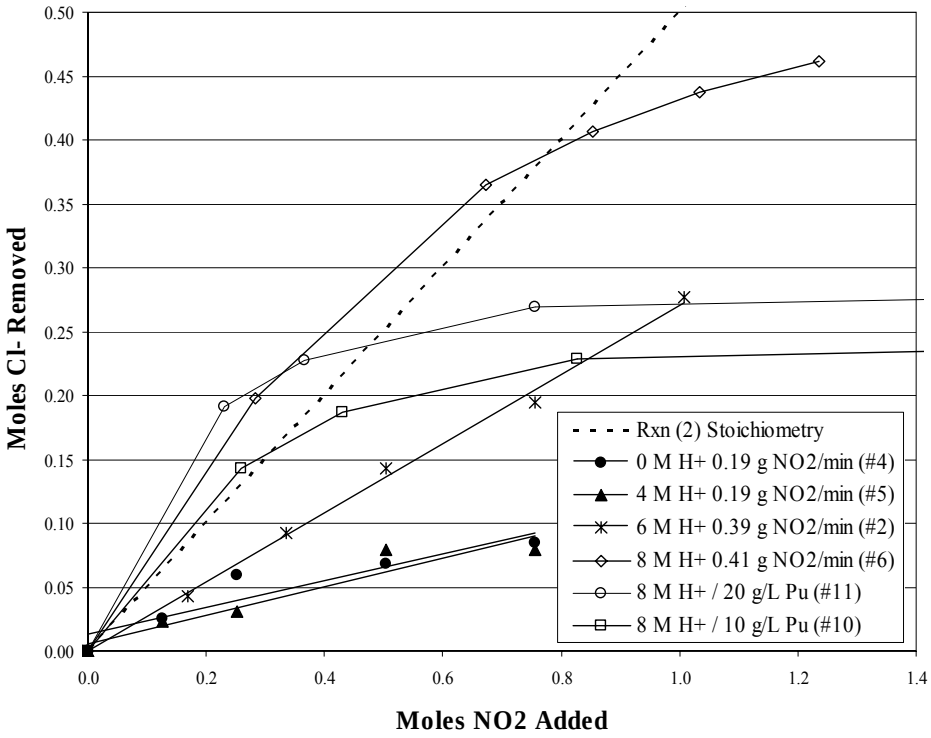

Figure 3: Effect of Initial Solution Acidity on Chloride Removal at 20 ^{o}C

The tests in 8 M H^+ indicate that Reaction 3 is occurring based on the fact that the number of moles of Cl^- removed per mole of NO_2 is greater than predicted by the Reaction 2 stoichiometry (see Figure 3), and acid depletion occurs during the first part of the tests (see Table 2). The conclusion is further supported by the data in Table 2 for Test #2 (6 M H^+). During the first part of Test #2, the acid concentration and chloride removal rates are relatively constant. Near the end of Test #2, the chloride concentration is reduced sufficiently that NO_2 absorption via Reaction 4 occurs and increases the H^+ concentration. Even though the chloride concentration is low at this point in the experiment, the increase in H^+ from 6.1 M to 7.9 M produces the highest chloride removal rate for the experiment. The shift in chloride removal rates between 6.1 M and

7.9 M H^+ is consistent with the estimated minimum acid concentration of 6.5 M required for the initiation of Reaction 3.[3]

The test data show that the reaction mechanism for less acidic solutions differs from the reaction mechanism for 8 M H^+. In Test #4, the chloride removal rate is much less than predicted by the Reaction 2 stoichiometry, while the overall acid concentration increases due to Reaction 4. The chloride removal data for Test #5 follow a trend similar to that for Test #4, suggesting that the chloride removal mechanism is comparable. However, unlike Test #4, there is no significant increase in H^+ in Test #5.

Although there is some scatter in the data, linear regressions of the data for Tests #4, #5 and #9 (4 M H^+, 75 ^oC) indicate that the chloride removal responses are linear as chloride concentration decreases. The data for Test #2 (6 M H^+) is strongly linear, based on both Table 2 and Figure 3, even when the chloride concentration is nearly depleted. If the principle reaction mechanism for Test #2, #4, #5, and #9 is Reaction 2, then a linear response is expected. However, if the mechanism in 6 M H^+ is the same as that for 0 M and 4 M H^+, it raises the question about why the slopes for Test #2, #4, and #5 in Figure 3 are not the same. The slopes for Tests #2, #4, #5 and #9 are 0.27, 0.10, 0.11 and 0.15 mole Cl^- per mole NO_2, respectively. The slope of Reaction 2 is 0.50 moles Cl^- per mole NO_2. The answer may be that there is an equilibrium shift between NO_2 and N_2O_4 or that the NO_2/N_2O_4 absorption mechanism changes. While it is assumed that NO_2 reacts with chloride, it is not yet understood if N_2O_4 enters into the reaction and, if so, whether by direct reaction with chloride or by dissociation to form NO_2 as NO_2 is consumed. Experiments with uranium chloride and N_2O_4 by Addison and Hodge[3] and zinc metal and N_2O_4 by Addison et al[2] suggest that the reaction may be dependent upon the dissociation of N_2O_4 to

NO_2. If N_2O_4 does not react with chloride in the acid solution, it should be detected in the off gas. Analyses have not yet been performed for detection of N_2O_4 in the off gas.

Table 2. Effect of Acid and Chloride Concentration on NO_2 Absorption

Test #4 (0 M H^+, 20 °C)				**Test #5 (4 M H^+, 20 °C)**				**Test #9 (4 M H^+, 75 °C)**			
NO_2 added (mol)	H^+ (M)	Cl^- (mol)	Increment Cl^-/NO_2 Usage	NO_2 added (mol)	H^+ (M)	Cl^- (mol)	Increment Cl^-/NO_2 Usage	NO_2 added (mol)	H^+ (M)	Cl^- (M)	Increment Cl^-/NO_2 Usage
0	0	0.485	---	0	4.0	0.485	---	0	4.0	0.238	---
0.126	0.24	0.460	0.198	0.126	4.1	0.463	0.174	0.130	4.2	0.198	0.308
0.252	0.62	0.426	0.270	0.252	4.0	0.454	0.071	0.317	4.4	0.197	0.005
0.503	1.10	0.417	0.036	0.503	4.2	0.406	0.191	0.776	5.2	0.111	0.187
0.755	1.46	0.401	0.063	0.755	4.2	0.406	0.000				

Test #2 (6 M H^+, 20 °C)				**Test #6 (8 M H^+, 20 °C)**				**Test #8 (8 M H^+, 70 °C)**			
NO_2 added (mol)	H^+ (M)	Cl^- (mol)	Increment Cl^-/NO_2 Usage	NO_2 added (mol)	H^+ (M)	Cl^- (mol)	Increment Cl^-/NO_2 Usage	NO_2 Added (mol)	H^+ (M)	Cl^- (mol)	Increment Cl^-/NO_2 Usage
0.00	5.9	0.281	---	0	8.0	0.485	---	0	8.0	0.485	---
0.168	5.7	0.239	0.250	0.283	6.6	0.288	0.696	0.178	6.5	0.293	1.077
0.336	5.6	0.189	0.298	0.672	6.2	0.120	0.432	0.443	6.4	0.163	0.49
0.504	5.9	0.139	0.298	0.854	6.7	0.078	0.231	0.911	6.8	0.027	0.290
0.757	6.1	0.087	0.206	1.035	7.3	0.047	0.171	1.289	7.9	0.010	0.045
1.009	7.9	0.005	0.325	1.237	7.0	0.024	0.114	1.493	9.0	0.007	0.015

Whereas the chloride removal rates at 0-6 M H^+ appear to yield linear responses, the same is not necessarily true for tests conducted at 8 M H^+. This lack of linearity is shown in both Table 2 and Figure 3. Assuming that Reaction 3 competes with Reaction 2, non-linearity is expected because the prominence of each reaction changes as acid and chloride concentrations change. While the data seem to support the occurrence of Reactions 2 and 3, they do not exclude the possibility that there are other prominent chloride removal reactions occurring.

Temperature Dependence

Several experiments were performed to determine whether increasing the temperature of the chloride-containing solution would increase the rate of chloride removal. Figure 4 shows the data for chloride removal from solutions containing 4 M HNO_3 at 20 ^oC or 75 ^oC and 8 M HNO_3 at 20 ^oC, 40 ^oC, or 70 ^oC. The data in Figures 4 indicate that heating the solution to 75 ^oC may have a minor impact on the rate of chloride removal from 4 M HNO_3. The data for chloride removal from 8 M HNO_3 show a similar response with a small increase in chloride removal rates due to heating of the acid chloride solution. Although the data for the 40 ^oC test in 8 M H^+ appear to have a negligible result from heating, the data in Table 2 demonstrate that the differences between 20 ^oC and 70 ^oC show a consistent positive impact from temperature for first three data points until chloride becomes depleted.

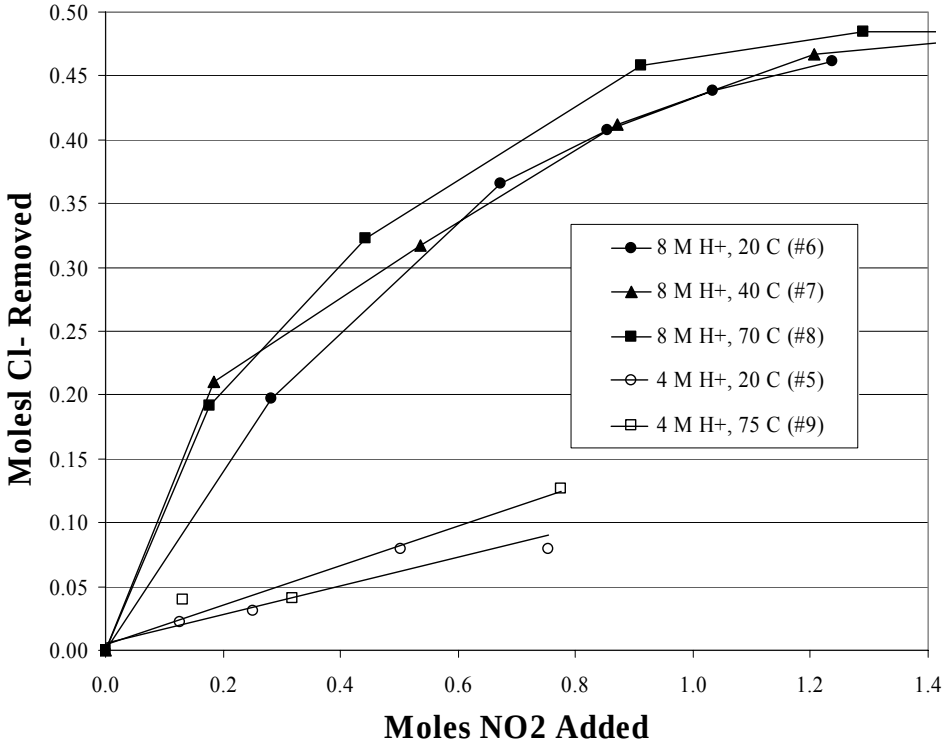

Figure 4: Chloride Removal with NO_2 at Various Temperatures

In the liquid state, NO_2 exists in a strongly temperature-dependent equilibrium with N_2O_4. At 21.15 ^oC, the liquid contains 0.1% NO_2.[8] At its boiling point of 21.3 ^oC, N_2O_4 is about 20% dissociated to NO_2 and 99% dissociated at 135 ^oC.[10] Since many reaction rates increase with increasing temperature, it was expected that chloride removal would increase, particularly at lower acid concentrations and later in the test when the chloride concentration had decreased significantly and NO_2 use efficiency with it. Since the observed reaction rates are fast at room temperature, almost all of the NO_2 reacts or leaves the liquid before it changes temperature significantly. Consequently, little increase in chloride removal should be expected due to an increase in solution temperature alone. To see a more pronounced effect from temperature, the NO_2/N_2O_4 gas needs to be preheated.

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