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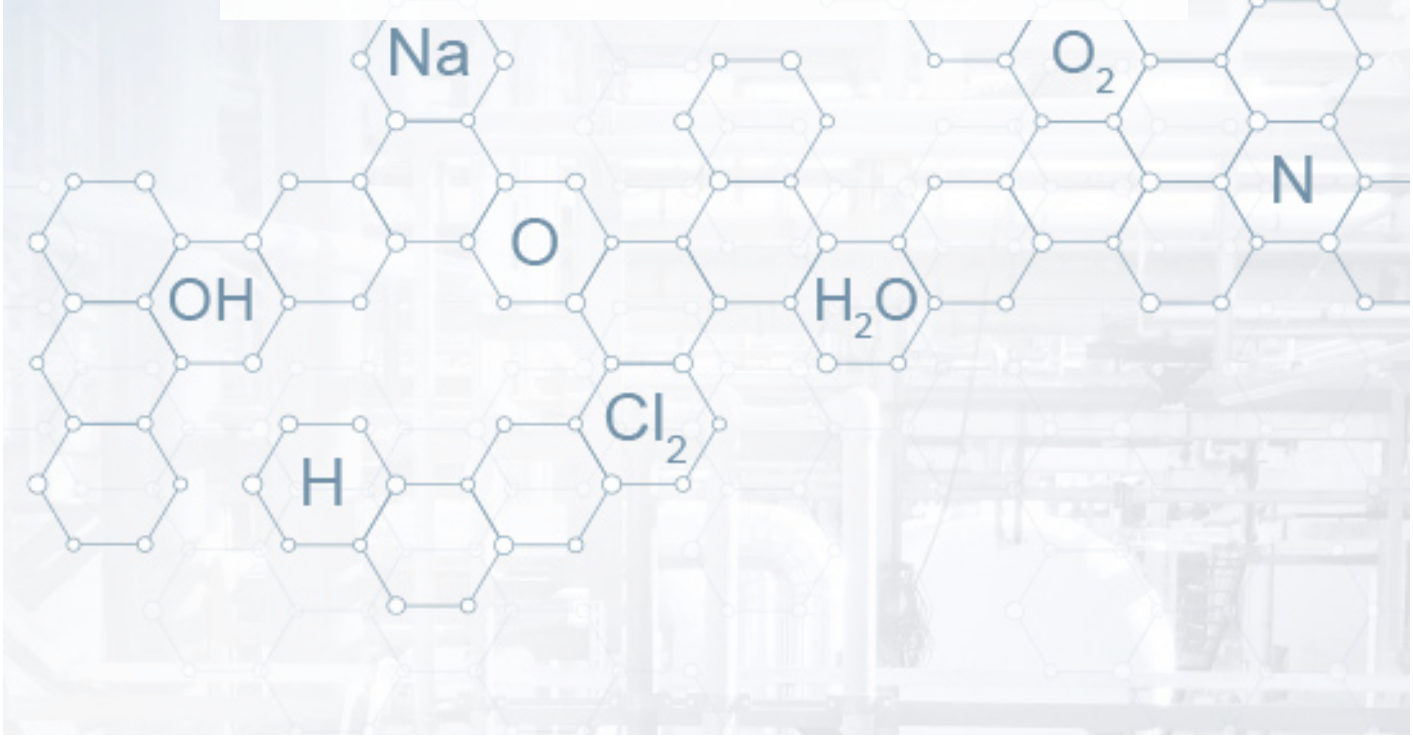

BLEACH STABILITY & FILTRATION

AWWA WATER QUALITY TECHNOLOGY CONFERENCE

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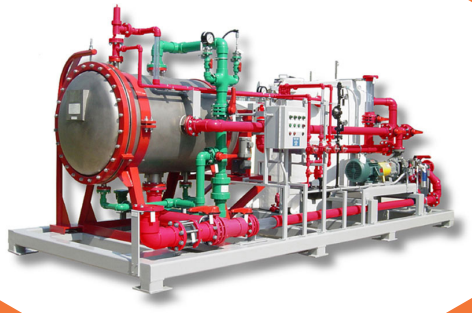

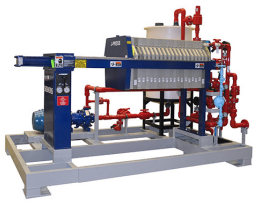

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Abstract

Liquid bleach is an alternative to gaseous chlorine for water disinfection. Commercially produced liquid bleach typically contains excess caustic and possibly dissolved transition metal ions. In basic solution, bleach (OCl^-) decomposition to form chlorate ion has been shown to be a second-order process (Rate = k_2 $[OCl^-]^2$). The formation of oxygen from decomposing OCl^- is a slow side reaction in solutions of very pure OCl^-. However, in the presence of transition metal ions the rate of bleach decomposition by the oxygen pathway is increased.

$$OCl^- + OCl^- \rightarrow O_2 + 2Cl^-$$

The chemistry of the catalytic decomposition of bleach is complex. In general, nickel ion appears to effectively catalyze decomposition either alone or in combination with other transition ions (Ni > Co > Cu > Fe > Mn > Hg). The addition of Mn^{2+} and Ni^{2+} together produced the highest rate of decomposition when compared to other transition metal ion combinations. The initial rate of decomposition with 10.3 mg/L Cu^{2+} is increased by a factor of 11 relative to NaOCl containing 1.03 mg/L Cu^{2+}. This indicates that the decomposition of NaOCl is roughly first-order in Cu^{2+}.

Bleach manufacturers recognize that transition metal ions cause oxygen formation and many have started to eliminate transition metal ion sources (e.g. in their raw materials) and/or carefully filter the finished product. High quality bleach can be produced when prudent selections are made to control starting chemicals, and the construction materials used for piping and storage tanks. An alternative is to filter the bleach prior to delivery to the utility.

Introduction

Chemical Modeling

Predictive mathematical models for chemical systems can be based either on a chemical understanding of the system or on an empirical analysis of the available data. It is therefore important to differentiate between the two.

The more accurate chemical model requires detailed kinetic data and a full mechanistic understanding of the important variables and molecular interactions that affect the chemical system.

In contrast empirical models provide approximate mathematical descriptions of chemical systems and are not based on a full understanding of the chemical details. This treatment does not provide an accurate chemical description of the process and the resulting mathematical representation has no chemical implication, is not totally predictive, and may not be applicable in situations where the conditions differ from used to develop the empirical regression.

Gordan/Adam Bleach Decomposition Model

The Gordan/Adam computer based model[1] was developed to predict ClO_3^- formation and OCl^- decomposition in stored liquid bleach. This chemical model helps utilities using liquid bleach answer important questions regarding bleach storage and usage. It also predicts the build-up of oxygen due to the presence of transition metal ions.

Field data indicates that the program can be used to predict bleach concentration to better than ± 10 percent. A sample printout as generated by the program showing input bleach information, predicted bleach decomposition, chlorate ion formation, oxygen formation, the residual chlorate ion concentration in the distribution system, and whether the predicted distribution concentration exceeds the user defined maximum contaminant level goal (MCLG) is show in the table below.

Results for the Gordan/Adam Predictive Model

Concentration of NaOCl	=	15.890 wt% FAC	Applied
Specific Gravity	=	1.239 g/mL	FAC Dose
Temperature	=	20.0°C	1.0mg/L
pH	=	13.000	
Chlorate Concentration	=	0.003 g/L	ClO_3^- MCLG
Chloride Concentration	=	2.777 mol/L	0.2mg/L

Half-Life 61.7 Days

Time (days)	NaOCl (Wt% NaOCl)	Chlorate (g/L)	Oxygen (L gas/L OCl^-)	Residual Chlorate (mg/L) ClO_3^-	Below 0.2 mg/L
0	15.890	0.003	0.000	0.00	ok
1	15.637	1.145	0.037	0.01	ok
7	14.271	7.298	0.235	0.04	ok
14	12.952	13.244	0.426	0.08	ok
28	10.931	22.352	0.719	0.17	ok
35	10.139	25.917	0.834	0.21	High
42	9.455	29.001	0.933	0.25	High
56	8.330	34.069	1.096	0.33	High

Bleach Decomposition

Hypochlorous Acid (HOCl), pH 5-8 Region when dissolved in water chlorine hydrolyzes rapidly to form hypochlorous acid (HOCl):

$Cl_2 + H_2O = HOCl + H^+ + Cl^-$ $\qquad$ Kg = 4 x 10$^-$ (25°C)

The position of equilibrium is highly depended upon pH. Hypochlorous acid also undergoes a pH dependent dissociation to form hypochlorite ion (OCl^-):

$HOCl = OCl^- + H^+$ $\qquad$ $pK_a = 7.54$ (25°C)

HOCl is a widely use oxidant. In near neutral solutions, HOCl decomposes slowly and the rate of decomposition is dependent on pH, temperature, and typical water impurities such as chloride ion. The literature[2] clearly suggests that the major decomposition pathway changes as the pH changes. The mechanistic detail presented below is proposed:

$2HOCl = Cl_2O + H_2O$ $\qquad$ $k_1 = 0.124\ M^{-1}\ sec^{-1}$, $k_{-1} = 10.8\ sec^{-1}$

$OCl^- + Cl_2O \rightarrow ClO_2^- + Cl_2$ $\qquad$ $k_2 = 7.9\ M^{-1}\ sec^{-1}$

$HOCl + Cl_2O \rightarrow ClO_2^- + Cl_2 + H^+$ $\qquad$ $k_3 = 0.1_0\ M^{-1}\ sec^{-1}$

$ClO_2^- + Cl_2O \rightarrow ClO_3^- + Cl_2$ $\qquad$ $k_4 = 6 \times 10^4\ M^{-1}\ sec^{-1}$

$Cl_2 + H_2O = HOCl = Cl^- + H^+$ $\qquad$ $k_5 = 11.0\ sec^{-1}$, $k_{-5} = 2.0 \times 10^4\ M^{-2}\ sec^{-1}$

$HOCl = OCl^- + H^+$ $\qquad$ $k_6 = 1.2 \times 10^3\ sec^{-1}$, $k_{-6} = 2 \times 10^{10}\ M^{-1}\ sec^{-1}$

The equilibrium between HOCl and chlorine monoxide (Cl_2)) in aqueous solution has been known to exist for many years. The rate data and the proposed mechanism suggest that decomposition involves either HOCl or OCl^- reacting with Cl_2O to form ClO_2^- and Cl_2. The ClO_2^- produced then reacts rapidly with Cl_2O to form ClO_3^- as the final product. Additional evidence for the mechanism is the fact that FAC decomposition in alkaline solution has two maxima (pH 13 and pH 8). At pH 10 or above there is essentially no HOCl present and for this reason very little, if any, Cl_2O can form. Thus, it is not surprising that in very alkaline solution OCl^- decomposes by a different mechanism. As the pH decreases below 9, HOCl is formed and the rate of decomposition again increases due to the pathway available involving Cl_2O.

Thus, HOCl decomposition in the pH 5-8 region has the following stoichiometry:

$$3HOCl \rightarrow ClO_3^- + 2Cl^- + 3H^+$$

and the following rate law:

$$d[ClO_3^-]/dt = k_{obs}\ [HOCl]^2\ [OCl^-]$$

The decomposition results in the formation of ClO_3^-. No oxygen is formed and there is no apparent effect of transition metal ions on the decomposition.

Liquid Bleach

Commercially produced liquid bleach typically contains excess caustic. In basic solution, OCl^- decomposition to form chlorate ion has been shown to be a second-order process[1,3]

$$Rate = k_2\ [OCl^-]^2$$

with the following stoichiometry: $3OCl^- \rightarrow ClO_3^- + 2Cl^-$

The decomposition of OCl^- involves chlorite ion (ClO_2^-) as an intermediate in the following generally accepted mechanism[1,3].

$$OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-$$

$$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$$

The observed OCl^-/ClO_3^- stoichiometry is determined by plotting the loss of NaOCl as a function of the ClO_3^- formed. In very pure laboratory prepared bleach and in the absence of transition metal ions, the data reveal a stoichiometry of 3 as described above. In the presence of transition metal ions, the observed OCl^-/ClO_3^- stoichiometry changes with temperature and NaOCl concentration studied. The stoichiometry ranges between 3.18 and 3.32. The average of all the ratios is 3.25.

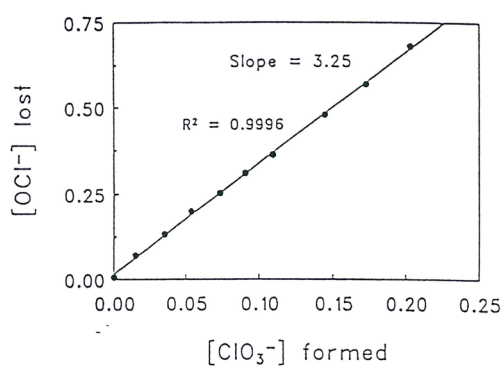

Figure 1 Observed decomposition stoichiometry in the presence of transition metal ions. Reference 1.

Because the decomposition stoichiometry is greater than 3, a second minor decomposition pathway becomes relatively more important. Further studies have shown that transition metal ions are responsible for this minor pathway and for oxygen build-up during bleach storage.

Oxygen Formation

The formation of oxygen from decomposing OCl^- is a very slow side reaction in solutions of pure OCl^-. However, in the presence of transition metal ions the rate of bleach decomposition by the oxygen pathway is increased.

$$OCl^- + OCl^- \rightarrow O_2 + 2Cl^-$$

The effect of various metal ions (Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) on the catalyzed decomposition of OCl^- in basic solution was investigated initially by Lister[4] and Ayres and Booth[5] and more recently by Gordon, Adam and Bubnis[1,3]. Nickel ion appears to strongly catalyze bleach decomposition either alone or in combination with other transition metal ions. Thus, bleach strength will be reduced[6] in the presence of transition metal ions (Ni > Co > Cu > Fe > Mn > Hg).

The manufacturers of liquid bleach recognize that transition metal ions cause oxygen formation and many have started to eliminate transition metal ion sources (e.g. in their raw materials) and/or filter the finished product. Filtering liquid bleach is the surest way to minimize metal ions.

Sources of Transition Metal Ions in Commercial Bleach

The electrolytic cells used to manufacture caustic are categorized into three classes: diaphragm, mercury, and membrane cells. Many bleach manufacturers use caustic produced by diaphragm cells because of its lower cost. Rayon grade diaphragm cell caustic is more expensive and membrane or mercury cell caustic is the most expensive. The primary quality issue with the respect to caustic type is the product impurities. In caustic, the transition metal ions (Fe, Cu, and Ni) are soluble and most likely present as the sodium salts of various anionic complexes. However, if the caustic is diluted precipitates of virtually unknown composition will slowly appear.

Bleach is regarded of poor quality when it is turbid. Bleach quality is directly related to the caustic used in manufacturing. The metal ions contained in bleach can originate from numerous sources. A few are listed below[7]:

Nickel

The origin of nickel in 50% caustic is from the nickel evaporators used to concentrate dilute caustic from the electrolytic cells. It can also come from nickel containing Na_2CO_3 and NaCl sediments from the bottom of the caustic storage tanks. In terms of quality, nickel in excess of 0.3 ppm results in black residues.

Iron

15% NaOH from cell liquor generally contains 0.6 ppm iron that is concentrated to about 3 ppm in 50% caustic. Iron also will concentrate in the sludge at the bottom of storage tanks resulting in more than 5 ppm Fe in 50% caustic. Caustic is generally transported in lined steel tanks and dilution and storage operations are generally carried our in unlined steel tanks. During these operations, the tank will corrode resulting in iron buildup. Iron in excess of 3 ppm in 50% caustic leads to off colored, brownish bleach.

Calcium and Magnesium

The levels of calcium and magnesium in caustic is low. However, if hard water is used for diluting the caustic, the calcium and magnesium levels will undoubtedly increase. Excessive levels can also result from the sludge at the bottom of storage tanks that are low in caustic. Calcium and magnesium in excess of 6 and 9 ppm respectively cause turbidity and sediment.

Transition Metal Ion Catalysis

The role of transition metal ion catalysis in liquid bleach is complex. In general, nickel ion appears to effectively catalyze decomposition either alone or in combination with other transition metal ions. The maximum concentration of transition metal ions that will not significantly affect the decomposition of bleach is ~0.1 mg/L Ni^{2+} and ~1 mg/L Cu^{2+}. Ferric ion (Fe^{3+}) and Mn^{2+} when present alone, are not considered to be effective catalysts for bleach decomposition and readily precipitate.

Prior to 1950, commercial bleach was known to contain transition metal ions including rhodium, iridium and cobalt that were demonstrated to be very strong catalysts from the decomposition of bleach[4,5]. Under the pH conditions of stored bleach, our understanding of the chemical form of transition metal ions is limited and it becomes very difficult to describe and even more difficult to measure the species present in solution and in the sediment.

For example, soluble transition metals are generally present as M^{11+} - hydroxide complexes or as anionic complexes such as phosphates, chlorides, or hypochlorites. The metal complexes also may be present as dimeric (or oligomeric)

M^{11+} -hydroxide complexes which eventually may or may not precipitate. Frequently, the precipitates formed are of unknown (and continuously changing) composition. This complicates our understanding of the species present in solution because the chemical form of these complexes can change over time, are frequently difficult to characterize, and are in general undefined.

Bleach solutions typically contain hypochlorite ion (OCl^-), chlorite ion (ClO_2^-), chlorate ion (ClO_3^-), hydroxide ion (OH^-), chloride ion (Cl^-), phosphate ion (PO_4^{3-}), sulfate ion (SO_4^{2-}), and carbonate ion (CO_3^{2-}). Each of these anions is present in relatively high concentrations and thus available as potential ligands for transition metal ion in solution.

At the high pH conditions maintained in bleach (pH>11), it is readily seen that metal hydroxides ($Fe(OH)_3$, $Ni(OH)_2$, $Cu(OH)_2$, and $Cu(OH)_4^{2-}$) can be easily formed and dissolved in the bleach. It is also easy to envision that these transition metals can be further oxidized in the bleach media to form complexes that can be "settled" or filtered (Fe_2O_3, NiO, CuO). Because the identification of the many transitions metal ion complexes has not been a priority, the presence and catalytic potential of numerous transition metal complexes has not been studied. However, because the concentrations of the various anions are high, it is conceivable that the transition metal ions exist in bleach as the chloride salts ($FeCl_3$, $NiCl_2$, $CuCl_2$), complexes that contain hypochlorite ion as a ligand (e.g. $Fe(OCl)(OH)_2$), species that contain sulfate ion (e.g. $CuSO_4$, $Fe_2(SO_4)_3$ or $KFe(SO_4)_2$), or numerous other mixed metal and mixed ligand complexes as neutral species, as shown above or as the appropriate (and complimentary) anionic and/or cationic species.

These examples illustrate that the individual species of the transition metal ions present in bleach are varied and complex. Heretofore, researchers have been satisfied to report oxygen formation resulting from transition metal ion catalysis as a general discussion without defining the species that are responsible for promoting the catalysis. For example, why in Figure 2 does the OCl^- decomposition curve bend for Ni^{2+}? Clearly a different decomposition pathway is operating. Is this the result of the formation of a second nickel metal ion complex? And, why do the mixed metal ion studies show a faster bleach decomposition than that of a single metal ion? Is this a result of a mixed metal ion complex that is a better catalyst for the decomposition of bleach? Do the ClO_3^- formation and O_2 formation pathways have the same intermediate and activated complex? These are chemical questions that need to be answered if our objective is to fully understand the complex, underlying chemistry.

Figure 2 is a second-order plot of NaOCl decomposition for the addition 1 mg/L of four different transition metal ions[3]. The blank experiment contained no added transition metal ions. The addition of 1 mg/L of Fe^{3+} of Mn^{2+} resulted in no increase in the rate of decomposition relative to the absence of any added transition metal. The addition of 1 mg/L Cu^{2+} accelerates the decomposition by a factor of 1.4 relative to its absence. The addition of 1 mg/L Ni^{2+} greatly enhances the rate of decomposition. Also, in contrast to the other transition metal containing solutions of NaOCl, after approximately 10 days of reaction time there is significant deviation in linearity of the second-order plot for Ni^{2+}. This strongly suggests that a different NaOCl decomposition pathway is operating when 1 mg/L Ni^{2+} is present.

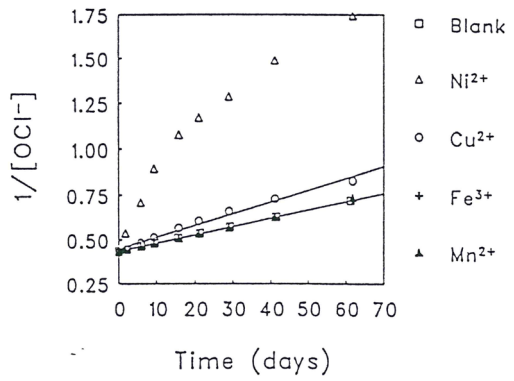

Figure 2 Second-order plot of NaOCl decomposition with 1 mg/L of transition metal ions added. Solutions containing Fe^{3+}, Mn^{2+}, and Ni^{2+} formed precipitates. $[NaOCl]_o$ = 13.5 percent measured as Cl_2. Reference 1.

Figure 3 illustrates the effect of two different concentrations of Cu^{2+} on NaOCl decomposition[3]. The initial rate of decomposition of 10.3 mg/L Cu^{2+} is increased by a factor of 11 relative to NaOCl containing 1.03 mg/L Cu^{2+}. This indicates that the decomposition of NaOCl is roughly first-order in Cu^{2+}. In other words, more copper gives more decomposition.

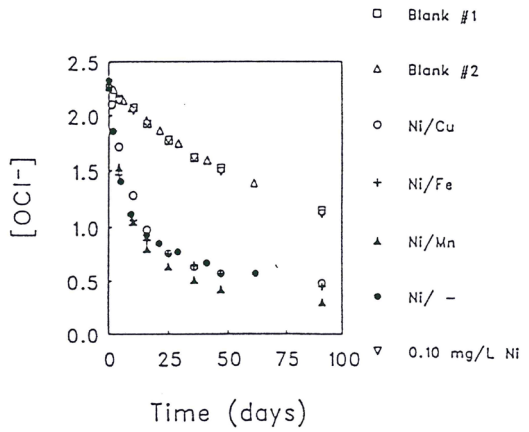

Figure 3 NaOCl concentration plotted as a function of time in the presence of Cu^{2+}, [NaOCl] = 13.5 percent measured as Cl_2. Reference 1.

Theoretical Considerations

In bleach in the pH 9-12 region the formation of ClO_3^- and O_2 can be described as

$$d(ClO_3^-)/dt = k_2 [OCl^-]^2 \qquad d(O_2)/dt = k_2 [OCl^-]^2$$

Thus, the disappearance of OCl^- can be described by

$$-d[OCl^-]/dt = (3k_{Cl} + 2k_{Ox}) [OCl^-]^2$$

where k_{Cl} is $OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-$

and k_{Ox} is $OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$

Theses rate equations suggest the activated complex for these reactions might be the same species. However, they provide no information about the role of the transition metal ion.

Additional observations show that the activation parameters derived from Eyring plots ($\Delta H^{\pm}$ and $\Delta S^{\pm}$) are constant from 15 to 55°C over the pH 11-14 region. Often, Eyring plots (ln(kT) vs 1/T) are non-linear because temperature may affect each rate constant differently[8]. Possible reasons that might explain the absence of curvature are:

- The temperature range studies may be too small to observe the curvature
- The oxygen forming pathway may only have a small contribution to the bulk $\Delta H^{\pm}$ and $\Delta S^{\pm}$ values
- The independent pathways could have similar values for $\Delta H^{\pm}$ and $\Delta S^{\pm}$
- Both pathways may involve the formation of ClO_2^- as a common intermediate

For the commercial bleach sample tested, the OCl^-/ClO_3^- stoichiometry is independent of temperature and NaOCl concentration. Thus, by using the average stoichiometry of 3.25, the ratio of the rate constants for the two decomposition pathways (k_{Cl}/k_{Ox}) was determined to be 8.3 ± 0.9. For commercial bleach the OCl^-/ClO_3^- stoichiometry is independent of temperature and NaOCl concentration. The temperature independence of k_{Cl}/k_{Ox} is expected if k_{Cl} is much larger than k_{Ox} (i.e. temperature sensitivity of the slower O_2 forming step is unobservable). However, k_{Cl} is less than 9 times larger than k_{Ox}. Thus, the activation parameters for O_2 formation should produce an observable curvature in the plot of ln(k/T) vs 1/T. This curvature is not observed.

Small changes in $\Delta H^{\pm}$ and/or $\Delta S^{\pm}$ can significantly change the calculated rate constants. Small variations in the bulk values of $\Delta H^{\pm}$ and/or $\Delta S^{\pm}$ would produce a significant variation in the ratio of k_{Cl} to k_{Ox} at different temperatures. With changes in temperature, even small differences in $\Delta H^{\pm}$ and/or $\Delta S^{\pm}$ for each pathway should produce an observable variation in the ratio of k_{Cl} to k_{Ox}, but this does not occur. Because the Eyring plots are linear and the ratio of k_{Cl} to k_{Ox} is independent of temperature, the pathways for ClO_3^- and O_2 formation may have the same rate determining step producing ClO_2^- as a common intermediate. Thus, the activation parameters would describe a single rate limiting step and would not be bulk values.

Oxygen formation is slow in the absence of measurable transition metal ions (≤0.01 mg/L). Possible causes for O_2 formation could be

- an intrinsic property of OCl^-
- through the involvement of chlorine species less abundant than OCl^-
- through the involvement of ClO_2^- as an intermediate as in ClO_3^- formation
- as a result of µg/L transition metal ion catalysis

The possibility of a single activated complex being the cause of ClO_2^- or O_2 forming is proposed because of the negatively charged oxygen atom of one of the OCl^- molecules might have an electrostatic attraction for the partial positive charge of chlorine atom of another OCl^- molecule of the activated complex. However, it can be argued that the activated complex for chlorate ion formation can not lead to oxygen formation[9] because direct formation of O_2 from OCl^- is a spin forbidden transition. Thus, oxygen formation probably occurs after ClO_2^- is formed as an intermediate.

In the pH 11-14 region, the amount of O_2 formed is constant. Below pH 9, O_2 formation is not observed. This observation is not expected if HOCl, $HOCl_2^-$, or Cl_2O are directly involved in O_2 formation. The calculation of second order rate constants for those species are more than 5 orders of magnitude larger than the experimental k_{Ox}.

The transition metal ion pathway can be describer by the general stoichiometric equation

$$OCl^- + OCl^- + M^{n+} \rightarrow O_2 + 2Cl^-$$

where M^{n+} refers to any catalytic transition metal ion in association with complexing ligands such as OCl^-. In laboratory prepared bleach solutions that contain ≤0.01 mg/L transition metal ions, small amounts of O_2 can be produced without significantly increasing the observed rate of OCl^- decomposition. If ≥0.1 mg/L of Ni(II) is added to 2M OCl^-, the measured ClO_2^- concentration decrease and is not detectable. Thus, experimentally it appears that ClO_2^- is involved in O_2 formation.

This argument requires that either a $ClO^- - M^{n+}$ or a $ClO_2^- - M^{n+}$ complex form and then react with OCl^- or ClO_2^- to form O_2. In 2M bleach the OCl^- concentration is more than 200 times greater than ClO_2^- and assuming similar formation constants, more $ClO^- - M^{n+}$ complex should be formed. Thus, a preliminary mechanism can be proposed

$$ClO^- + M^{n+} = [ClO - M]^{n-1} \qquad K_f$$

$$[ClO - M]^{n-1} + ClO_2^- \rightarrow [Cl_2O_3^-M^+]^{\pm} \rightarrow O_2 + Cl^- + [ClO - M]^{n-1}$$

The $ClO^- - M^{n+}$ complex is conserved and oxygen exchange has occurred between the complex and ClO_2^-. The formation of a $ClO^- - M^{n+}$ complex should be a fast equilibrium process. In 2M OCl^- containing 0.01M ClO_2^- and 10^{-7}M transition metal ion and using a K_f value of 1, the rate constant observed for oxygen formation is 7 x 10^{-10} M^{-1} sec^{-1}. The resulting $k_{oxygen\ formation}$ is 0.7 M^{-1} sec^{-1}. In acid the rate constant for the complexation reaction for Ni(II) with HOCl is 0.5 M^{-1} sec^{-1}. Thus, the calculated rate constant seems to support the proposed mechanism involving a $ClO^- - M^{n+}$ complex.

Bleach Filtration

A number of options are available to bleach manufacturers to reduce or eliminate the problems caused by metal ions. High quality bleach can made when careful selections are made for control of raw materials, and construction materials for piping and storage tanks. The use of dilution water containing low levels of calcium and magnesium also helps to control precipitation during storage. Chemical techniques to complex the metal ions have been successful as well as letting the bleach "settle".

An alternative is to filter the bleach. A presentation[7] given at the Chlorine Institute Seminar described recent laboratory findings and concluded that:

"The best option to produce stable and quality bleach is by implying a bleach filtration step, prior to storage, as this would not only allow the use of diaphragm grade caustic, but also act as a self-correcting step to eliminate the adverse effect from the potential pick-up of harmful cations during bleach production."

"Filtration essentially removes the 5 to 10 micron size particles of the various species of Fe, Ni, and Cu formed by reaction with OCl^- that catalyze the formation of oxygen thereby minimizing the potential pressure build-up of bleach containers. In addition, the inert sediments such as iron oxides, and Ca or Mg hydroxides which impart off-color and turbidity to the bleach are also removed during this operation."

Iron and nickel removal from 15% bleach by filtration[6,10]

Metal	Initial Concentration (mg/L)	Final Product (mg/L)
Fe	2 -3	0.15
Ni	2 - 3	0.05

Conclusions

Bleach loses its strength by two decomposition pathways. Typically, the more dominant pathway leads to the formation of chlorate ion. Chlorate ion formation can be controlled by maintaining the bleach at a pH between 11 and 13; by storing the bleach at lower concentrations (i.e. dilution); or by maintaining a low storage temperature.

The second bleach decomposition pathway leads to oxygen formation. This catalytic decomposition pathway is promoted by the presence of transition metal ions in the bleach. Clearly, the use of raw materials (for example caustic) that contain low amounts of transition metal ions will help to reduce oxygen formation and thus improve the bleach stability. However, the costs involved with purchasing high quality caustic can be substantial.

It is costly to purchase high quality raw materials that consistently meet the quality needs of bleach manufacture. A simpler approach is to filter the bleach after manufacture and prior to storage. The use of various filter-aids makes it possible to remove the majority of transition metal ions as precipitates in the final stage of the bleach making process. This allows the use of less expensive raw materials (especially caustic) and removes the need for large settling tanks both of which add to the cost of manufacture.

Finally, bleach filtration after manufacture and before delivery is a simpler way to improve the quality of concentrated bleach. Color and turbidity are easily removed using in-line filtration, and the product will have a longer storage lifetime. In the near future, the quality and storage issues will become more important as utilities begin to purchase bleach and test the delivered product to make sure that the bleach specifications are being met. Thus, it will be an advantage to have “filtered” bleach available.

References

1. Gordan, G., Adam L., Bubnis, B., 1995 “Minimizing Chlorate Ion Formation in Drinking Water When Hypochlorite Ion is the Chlorinating Agent”, ISBN 0-89867-871-5, American Water Works Association Research Foundation, Denver CO.
2. Adam, L., Fabian, I., Suzuki, K., and Gordon, G. 1992 “Hypochlorous Acid Decomposition in the pH 5 to 8 Region”, *Inorg. Chem.,* 31:3534-3541.
3. Gordon, G., Adam, L., Bubnis, B., 1995 “Minimizing Chlorate Ion Formation”, Journal of the American Water Work Association, 87:6:97-106
4. Lister, M.W. 1952 “Decomposition of Sodium Hypochlorite”, Canadian Journal of Chemistry, 30:879-889.
5. Ayres, G.H., and Booth, M.H. 1955 “Catalytic Decomposition of Hypochlorite Solution by Iridium Compounds - I. The pH-Time Relationship”, Journal of the American Chemical Society, 77:825-827.
6. Redemann, C.E. “The Chemistry of Hypochlorous Acid and the Hypochlorites with Applications to Bleaching and Bleach-making” Second Edition, October 1970, Purex.
7. Bommaraju, T.V. “Sodium Hypochlorite: It’s Chemistry and Stability”, August, 1994, Occidental Chemical Corporation.
8. Gordon, G. and Katakis, D., 1987 Mechanisms of Inorganic Reactions, New York: Wiley-Interscience.
9. Adam, L.C., Ph.D. Dissertation, 1994 “An Investigation of the Factors Involved in the Decomposition of Sodium Hypochlorite”, Miami University, Oxford, OH.
10. Personal Communication 1995. Powell Fabrication and Manufacturing, Inc.