

Factors Affecting Hydrogen Peroxide Stability in the
Brightening of Mechanical and Chemimechanical Pulps

by

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To my parents, Amelio and Mafalda,
and my sister and brothers, Natalia,
Jose, Antonio, Sergio, and Agostinho.
In Particular, to my great friend
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support encouraged me to strive for
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INTRODUCTION

One of the main properties of hydrogen peroxide in aqueous alkaline media is its tendency to decompose into water and oxygen with concomitant loss of oxidation capacity. Although the peroxide decomposition reaction appears to be very simple, the mechanism by which decomposition occurs in alkaline media is not clear. A careful review of the literature reveals that there is an abundance of conflicting information on this subject which stands in need of clarification. Most of the controversy arises from the indiscriminate use of concepts that are suitable for peroxide decomposition under acid conditions but not necessarily applicable for decomposition in alkaline media.

In technical pulp brightening processes, peroxide decomposition is commonly controlled by the addition of materials such as sodium silicate, magnesium sulfate, and various chelating agents. The beneficial effect of chelating agents is generally accepted as being attributable to their ability to deactivate transition metals which otherwise catalyze peroxide decomposition. On the other hand, in the case of sodium silicate and magnesium sulfate there is often a divergence of opinion as to the manner by which these chemicals function in reducing peroxide decomposition.

When peroxide is used in technical brightening processes, additional complications with respect to understanding peroxide decomposition as well as its stabilization arise because of the

fact that pulp is present. The introduction of a pulp surface creates a two-phase heterogeneous system whose effects on peroxide decomposition and stabilization are not known. In addition, the presence of pulp introduces a second variable, perhaps the most important, which is the effect of bound transition metals. Metals such as iron, copper, and manganese are allegedly the principal cause of peroxide decomposition especially during the brightening of mechanical and chemimechanical pulps. It is not clear, however, whether or not all of the metals present in the pulp catalyze peroxide decomposition. Those metals that can be removed from the pulp by a chelation treatment certainly play a role on peroxide decomposition, but the effect of the large fraction of non-chelatable metals in the pulp on peroxide stability needs clarification.

A full understanding of the mechanism of peroxide decomposition in alkaline media as well as of the mechanisms of peroxide stabilization by sodium silicate and magnesium is of fundamental importance in order to design conditions that assure optimum hydrogen peroxide stability during pulp brightening. With respect to silicate an additional impetus to gaining an understanding of the mechanism by which it stabilizes peroxide is to find a chemical or chemicals which will not cause equipment scaling and hardening of pulp fibers as silicate reportedly does.

The objectives of this investigation were to clarify the mechanisms of hydrogen peroxide decomposition and of hydrogen

peroxide stabilization by sodium silicate and magnesium sulfate in weakly alkaline solutions, the effect of sodium silicate, magnesium sulfate, Na_5DTPA , and their combinations on hydrogen peroxide stability in the presence of transition metals, and the effect of the non-chelatable transition metals in TMP on hydrogen peroxide stability.

**FACTORS AFFECTING HYDROGEN PEROXIDE STABILITY IN THE BRIGHTENING
OF MECHANICAL AND CHEMIMECHANICAL PULPS**

CHAPTER I - A REVIEW OF THE LITERATURE

1. The Stability of Hydrogen Peroxide in the Absence of Sodium Silicate

Hydrogen peroxide decomposition in dilute aqueous alkaline solutions has been studied by several investigators, especially with regard to the use of these solutions for bleaching wood pulp and textile materials. The mechanism of peroxide decomposition is very complex and is governed by several different variables including alkalinity, temperature, concentration and composition of transition metal impurities, and others. The decomposition reportedly takes place spontaneously, i.e., through catalysis by hydroxyl anions¹, but it is accelerated in the presence of catalysts such as certain transition metals^{2,3}, metal oxides^{4,5}, transition metal chelates, e.g. iron-EDTA⁶⁻⁸, enzymes such as peroxidase and catalase^{9,10}, and CO₂^{11,12}.

1.1. Effect of Hydroxyl Ion Concentration

The effect of hydroxyl ion concentration on the rate of hydrogen peroxide decomposition is a very controversial issue. Pure solutions of hydrogen peroxide have been reported to be fairly stable at pH values between 6 and 8 but to decrease in stability with increasing alkalinity^{13,14}. A similar effect of increasing pH on peroxide decomposition in the 9.5 to 13.0 range has been reported by other authors¹⁵⁻¹⁷. Nicoll and Smith¹⁸ have, however, contradicted this finding pointing out that hydrogen peroxide decomposition in deionized water is only slightly

affected by changes in the concentration of hydroxyl ions in the pH range 10.0 to 12.5. According to these authors, the increase in catalytic activity resulting from the presence of certain transition metals is the reason for the enhanced peroxide decomposition at higher pH levels. To complicate matters even more, Oki and Kaneko¹⁹ have reported that the maximum rate of hydrogen peroxide decomposition takes place at pH 13.4 and the minimum rate at pH 14.0.

It has been claimed that hydrogen peroxide decomposition is maximum at a pH equivalent to its pK_a ^{1,20}. This concept has been advanced by Koubek *et al.*²¹ who found that the rate of decomposition of 0.1 M hydrogen peroxide solutions in deionized water appears to pass through a maximum at a pH equivalent to its pK_a . However, when the initial concentration of hydrogen peroxide is 1 M, the decomposition rate simply decreases as pH is increased from 10.7 to 12.7 at 35° C.

According to Burki and Shaaf²² and Spalek *et al.*², decomposition of hydrogen peroxide in dilute alkaline solutions is a first order reaction with respect to hydrogen peroxide, the decomposition rate increasing with hydroxyl ion concentration²². Other workers^{20,21} found, however, that the reaction order with respect to total hydrogen peroxide depends on pH, and attains a maximum value of ca. 2.0 at pH 12.0, where approximately one half of the hydrogen peroxide is dissociated.

1.1.1. The Base-Catalyzed Ionic Mechanism of Peroxide

Decomposition

The $[H_2O_2]_0/[HO_2^-]$ ratio corresponding to the maximum rate of hydrogen peroxide decomposition was found to be $2.0^{20,23}$. Based on this value, which corresponds to 50.0 % dissociation of the hydrogen peroxide, Abel²³ proposed that hydrogen peroxide decomposition proceeds via reaction of perhydroxyl anions with undissociated hydrogen peroxide molecules:



This reaction, when occurring in pure alkaline solutions, was considered to be an uncatalyzed one resulting from the oxidizing properties of the undissociated hydrogen peroxide and the reducing properties of the perhydroxyl anions²³. Similar dependence of the decomposition rate on the total alkalinity was also found in the presence of colloidal catalysts²³.

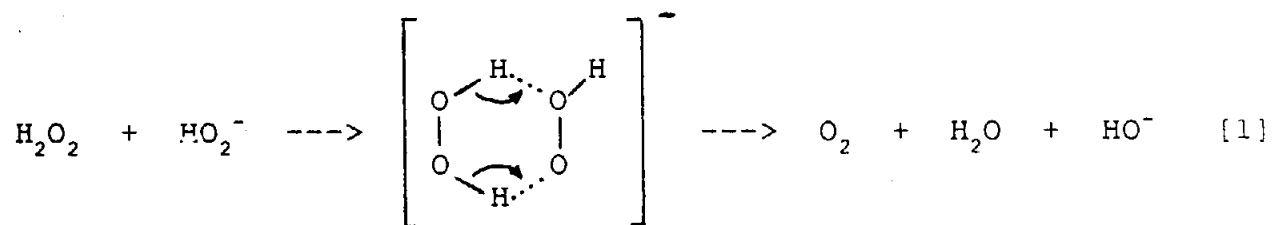
Duke and Haas¹ found that the dependence of hydrogen peroxide decomposition rate on total alkalinity at a constant total hydrogen peroxide content is analogous to the dependence of the product $[H_2O_2].[HO_2^-]$ on total alkalinity. The authors concluded that hydrogen peroxide decomposition obeys the equation

$$\frac{-da}{dt} = k [H_2O_2] [HO_2^-],$$

where a is the total hydrogen peroxide content in the solution and $[H_2O_2]$ and $[HO_2^-]$ are the concentrations of undissociated

hydrogen peroxide and perhydroxyl ions, respectively. Again, the hypothesis of metal catalyzed decomposition was discarded since further purification of the solutions by complexation and co-precipitation of transition metals had no effect on the decomposition rate¹.

Using isotopic measurements, Erdey and Inczedy²⁰ concluded that the peroxide bond in the hydrogen peroxide molecule is never dissociated in the reactions of hydrogen peroxide with oxidants containing oxygen. Based on this finding, these authors proposed a mechanism involving interaction between hydrogen peroxide and perhydroxyl anion according to the following reaction:



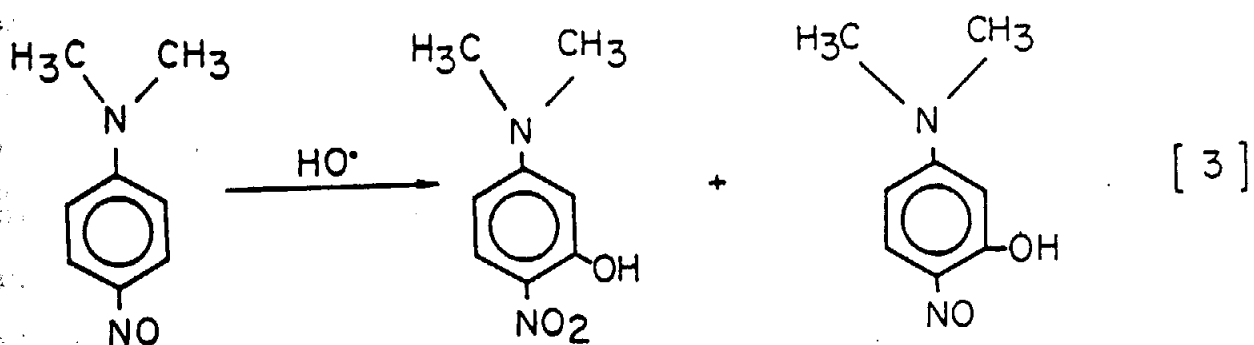
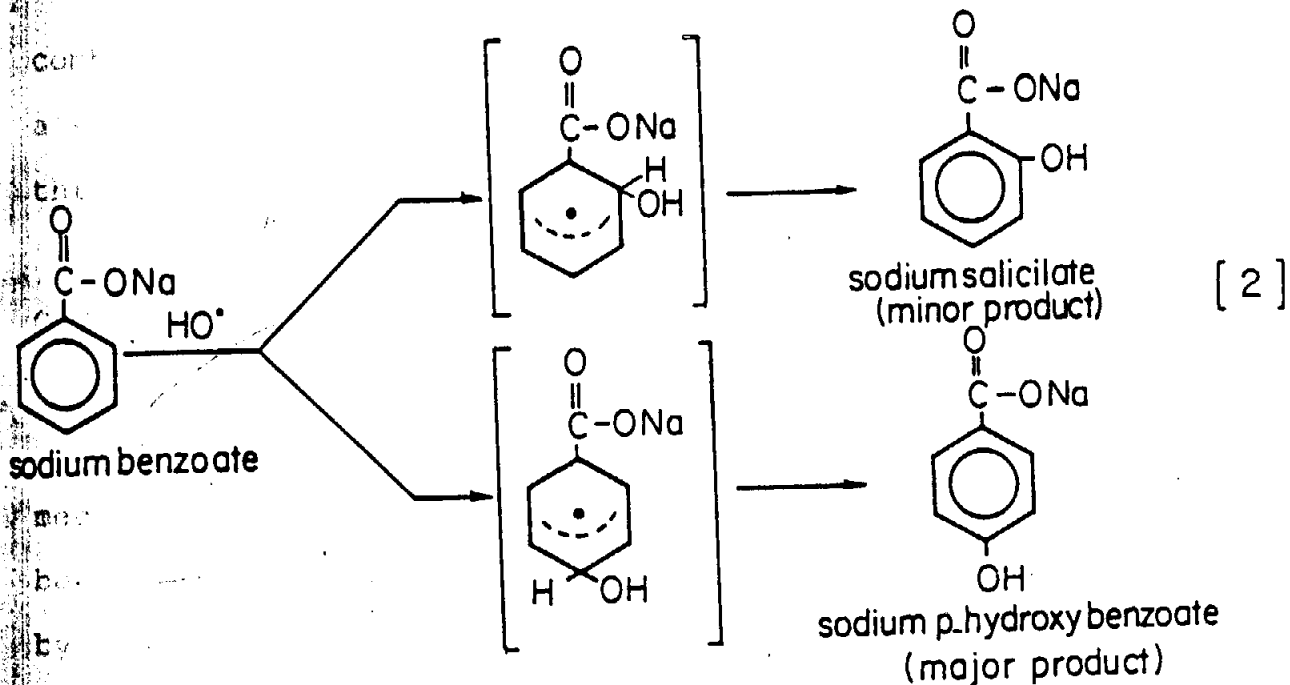
This mechanism is contrary to Abel's²³ original hypothesis involving a redox mechanism for the hydrogen peroxide decomposition, but is supported by the later work of Duke and Haas¹. The Raman spectra of alkaline peroxide solutions support the conclusion that the O-O bond of the perhydroxyl anion splits during the decomposition process²⁰.

1.1.2. The Base-Catalyzed Free Radical Mechanism of Peroxide Decomposition

The mechanisms described in subsection 1.1.1, which do not

involve free radical chain reactions, have been questioned in the majority of the more recent studies. Tanabe and Arata²⁴ consider the possibility of a dual mechanism for the decomposition of hydrogen peroxide in alkaline solutions. Experiments carried out in the absence of Na₄EDTA show a predominant chain reaction mechanism initiated by transition metals. On the other hand, in agreement with the earlier theories, a cyclic bimolecular mechanism, which involves the combination of a hydrogen peroxide molecule and its conjugate base to form a six-membered ring in the transition state, seems to be more important when Na₄EDTA is present²⁴. In a more recent publication, Csanyi *et al.*²⁵ contradicted this finding stating that the chain reaction mechanism is operative regardless of the presence of a chelating agent (Na₅DTPA).

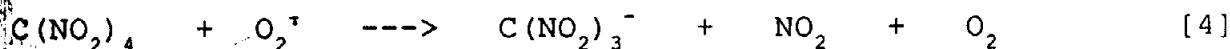
The free radical chain reaction mechanism has long been reported and supported by the actual determination of free radicals in alkaline solutions of peroxide. Electron paramagnetic resonance (EPR) measurements have been successfully used in the determination of hydroxyl radicals in this system^{26,27}. Hydroxyl radicals have also been determined under the same conditions by hydroxylation of benzene^{28,29} and of sodium benzoate³⁰ (eq. [2]) and by oxidation of the hydroxyl radical acceptor, p-nitrosodimethylaniline^{5,7,31-35} (RNO). The major products in the reaction of RNO with hydroxyl radicals appear to be nitro derivatives of the general type R(OH)NO₂ as well as one product with an intact NO group, possibly having an OH group in a meta-position to NO³² (eq. [3]).



4-nitrosodimethylaniline 3-hydroxy-4-nitrodimethylaniline 3-hydroxy-4-nitrosodimethylaniline
 (major product) (minor product)

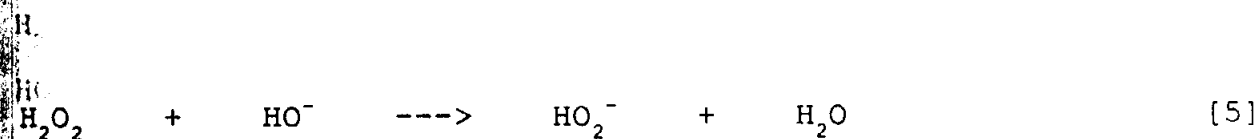
Superoxide anion radicals have been detected by EPR spectroscopy in weakly alkaline solutions of tetra-*n*-propylammonium hydroxide²⁷. These radicals have also been detected by the use of tetranitromethane^{34,36}. Tetranitromethane is very active towards one-electron reducing agents (e.g. superoxide anion radical) forming the stable nitroform anion which is easily detected by UV spectroscopy³⁷ (eq. 4). The

combined presence of hydroxyl and superoxide anion radicals in alkaline hydrogen peroxide solutions has also been confirmed through the oxidation of hydroxylamine to nitrite^{27,38}.



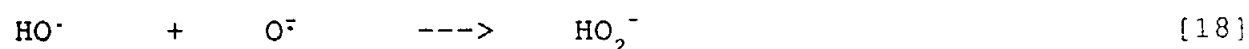
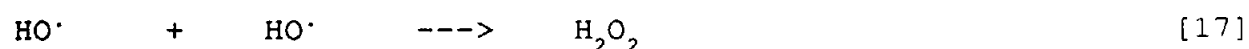
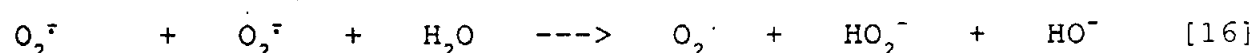
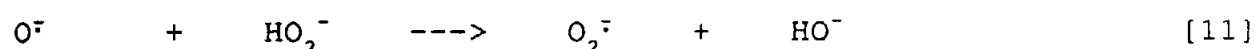
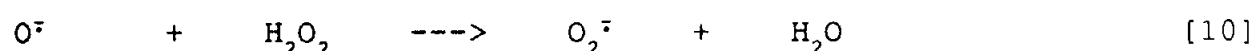
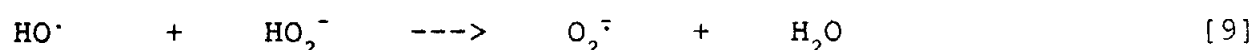
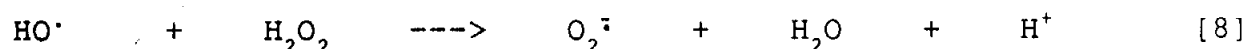
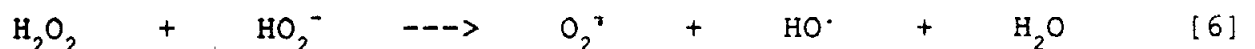
Although the existence of a free radical chain reaction mechanism has been established, a question that still remains to be answered is whether the generation of free radicals is induced by some catalytic species (e.g. transition metals)^{26-29,39-41} or by a reaction between dissociated and undissociated hydrogen peroxide^{25,42,43}.

Roberts *et al.*⁴² suggested that hydrogen peroxide decomposes by a free radical chain reaction mechanism involving the combination of dissociated and undissociated hydrogen peroxide. This reaction generates hydroxyl and superoxide anion radicals and is very dependent on the concentration of hydroxyl ions:



Using high purity chemical systems in conjunction with Na₅DTPA, Csanyi *et al.*²⁵ confirmed these results. The authors

rationalized the decomposition of hydrogen peroxide via a free radical reaction by the following set of equations:



The same authors claim that this chain reaction is promoted by the presence of metals which catalyze the rate of initiation by releasing additional hydroxyl and superoxide anion radicals. Furthermore, catalysis by transition metals displaces the pH corresponding to maximum decomposition which, in complete absence of impurities, is equivalent to the pKa of hydrogen peroxide,

i.e., 11.6 at 60° C. On the other hand, experiments performed with peroxide dismutase have created doubt as to the existence of an uncatalyzed process since superoxide anion radicals were not generated unless transition metals were added⁴¹.

According to Spalek *et al.*², the decomposition of hydrogen peroxide in alkaline solutions via a free radical chain reaction is indeed initiated by transition metals. The fact that hydroxyl ion concentration exerts a significant effect on the decomposition rate was explained by its influence on the activity of colloidal catalyst species that are probably the active sites for the decomposition. Strong evidence for a metal-induced chain reaction was presented by Koubek *et al.*²¹ and Galbacs *et al.*³⁵ who found that the decomposition of aqueous alkaline solutions of hydrogen peroxide is almost unmeasurable when the base is purified and Na₄EDTA is added to the system. The small loss of hydrogen peroxide under these conditions was a result of reactions between hydrogen peroxide and Na₄EDTA²¹.

The issue of the free radical chain reaction catalyzed by transition metals is addressed in the next section in connection with the effect of these metals on hydrogen peroxide decomposition.

1.2. Effect of Transition Metals

The majority of transition metals decompose hydrogen

peroxide. For example, hydrogen peroxide decomposition has been reported to occur under the influence of cerium^{44,45}, titanium^{44,46,47}, silver⁴⁸⁻⁵⁰, platinum^{48,50}, palladium^{48,50}, gold⁴⁸, nickel⁴⁹, cobalt⁵⁰⁻⁵², lead⁵¹, and zinc⁵³ but principally under the influence of iron, copper and manganese. Also, hydrogen peroxide decomposition has been noted as occurring on supported metals, e.g. alumina^{48,54,55}.

The particular effects of iron, copper and manganese and their combinations will be discussed in great detail in this review since they are the most important metals affecting hydrogen peroxide decomposition in pulp bleaching. Several theories have been advanced to explain the mechanism of hydrogen peroxide decomposition under the influence of these metals. Three theories have, however, obtained greater acceptance and they can be described as follows: 1) transition metals form unstable peroxides or complexes with perhydroxyl anions⁵⁶⁻⁵⁸, 2) transition metals decompose hydrogen peroxide by initiating a free radical chain reaction^{59,60}, 3) transition metals, in the form of colloidal metal hydroxides, decompose hydrogen peroxide heterogeneously via surface catalyzed reactions^{61,62}.

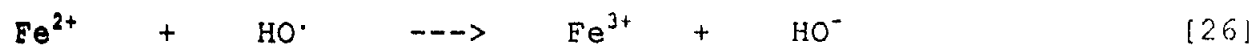
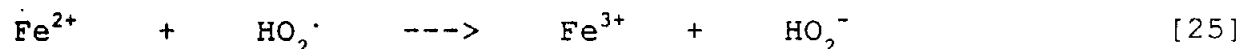
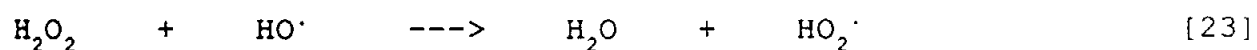
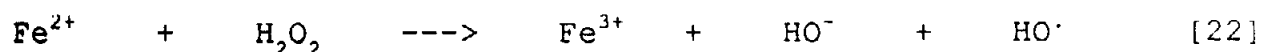
Recent work has demonstrated, however, that hydrogen peroxide decomposition may occur by different pathways depending upon the metal involved in the process³¹.

1.2.1. Iron

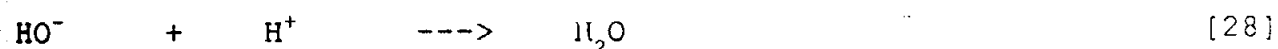
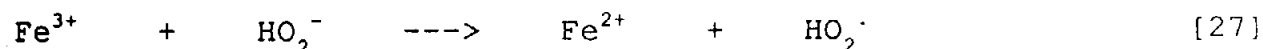
Much of the research on the iron-catalyzed decomposition of hydrogen peroxide has been concerned with decomposition in acidic solutions. To understand better the mechanism of hydrogen peroxide decomposition in alkaline solutions it is helpful to review current thinking concerning peroxide decomposition in acidic solutions.

The reactions between iron and hydrogen peroxide in acid solutions were first characterized by Haber and Weiss⁶³ and later revised by Weiss⁶⁰ who proposed the following reaction sequences for iron (II) and iron (III) ions:

Ferrous ion reactions:

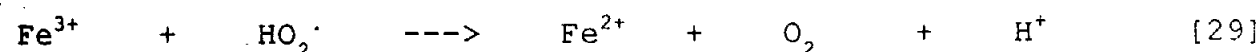
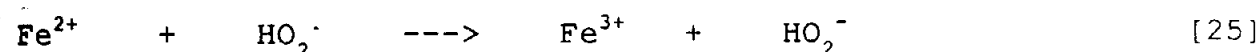
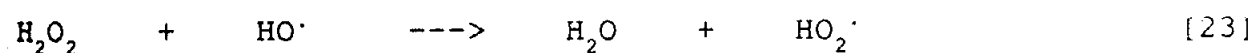
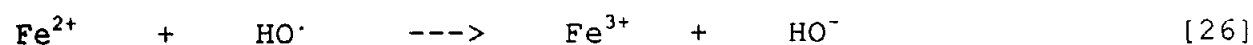
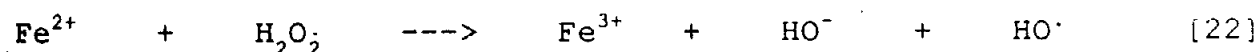


Ferric ion reactions:

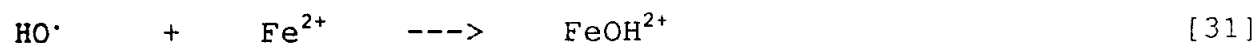
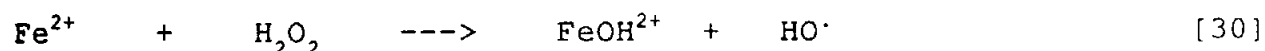


In both iron (III) and iron (II) catalysis, oxygen is

proposed to be evolved by a perhydroxyl radical reacting with hydrogen peroxide. Barb *et al.*⁶⁴ found, however, that the reaction producing oxygen is not that of perhydroxyl radical with hydrogen peroxide, but perhydroxyl radical with the iron (III) ion. The authors proposed the following alternative mechanism:



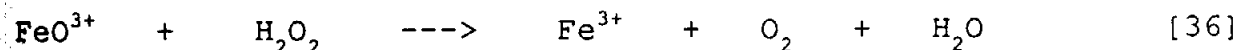
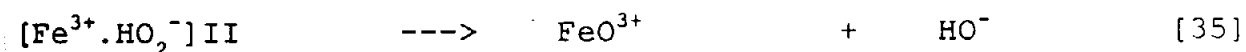
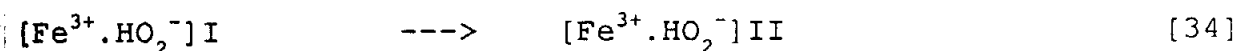
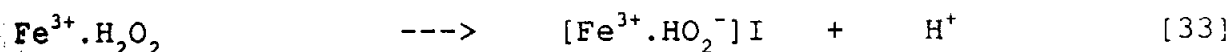
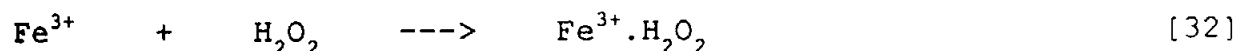
Uri⁶⁵ suggested that reactions [22] and [26] should be substituted by:



These modifications illustrate an important point which complicates the chemistry of inorganic ions, namely that the ions actually exist as solvated or complexed species or as several species in rapid equilibrium. However, detailed kinetic analysis performed by Barb *et al.*⁶⁴ revealed that reactions [30] and [31] are not very likely to occur.

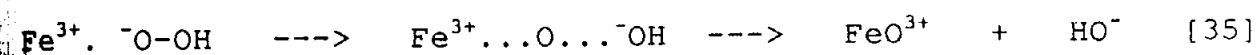
The mechanisms described immediately above, involving an

iron-initiated free radical chain reaction, have been supported by some authors^{66,67} but in many cases they are not very well accepted. EPR studies conducted with the iron (II)-hydrogen peroxide system did not reveal any spectra for hydroxyl or perhydroxyl radicals⁴⁴. An alternative mechanism proposed by Kremer and Stein⁵⁶⁻⁵⁸ does not involve the formation of free radicals as intermediates for hydrogen peroxide decomposition. This mechanism consists of the following steps:



At high $[\text{H}_2\text{O}_2]/[\text{Fe}^{3+}]$ ratios (10 to 300), the kinetic results are satisfactorily represented by a mechanism involving the first complex, (I), only in eq. [33]. At lower ratios (0.2 to 4.0) the second complex, (II), also becomes important, eq. [34].

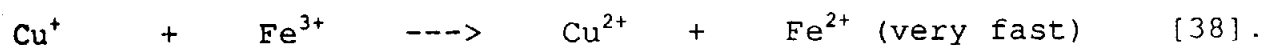
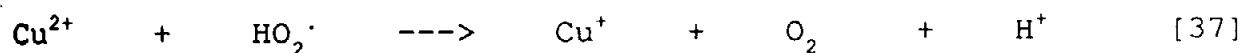
The catalytic role of iron (III) iron is attributed, at least in part, to its facilitating the breakage of the O-O bond of the perhydroxyl anion by complexing the liberated oxygen atom⁶⁸:



Support for this mechanism has been provided by kinetic studies performed by Kremer¹⁰, Jones⁶⁹ and Jortner⁷⁰.

As can be seen in the reaction sequence proposed above, there are two intermediate complexes in the decomposition of hydrogen peroxide catalyzed by iron (III) iron. The existence of these two complexes has been assumed to be the reason why copper has a promoting effect on hydrogen peroxide decomposition by iron. According to Kremer⁷¹, the promoting action of copper is due to its acceleration of the conversion of the primary to the secondary $\text{Fe}^{3+}.\text{HO}_2^-$ complex, eq. [34].

The promoting effect of copper on the iron-catalyzed decomposition of hydrogen peroxide has also been explained by a mechanism involving a free radical chain reaction^{64, 66, 72}. According to Barb et al.⁶⁴, the effect produced by copper (II) ions can be explained if they react at a higher rate than iron (III) ions in eq. [29] through the following pathway:



These two reactions amount to a catalysis of the reaction shown in eq. [29].

Contrary to what has been shown above, Krause⁶⁸ reported that iron (III) ions can inhibit hydrogen peroxide decomposition in the presence of copper ions.

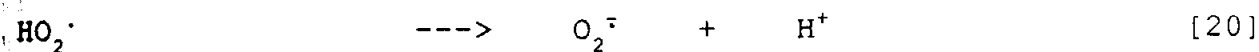
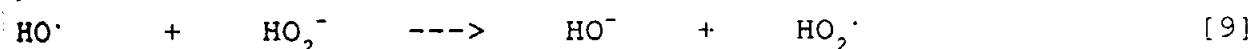
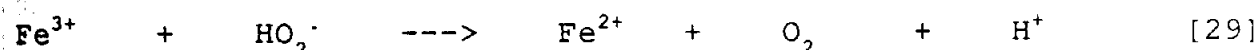
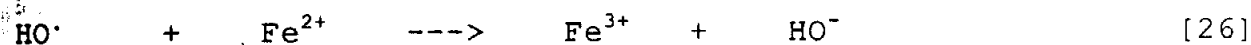
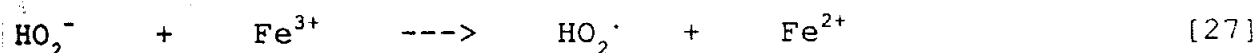
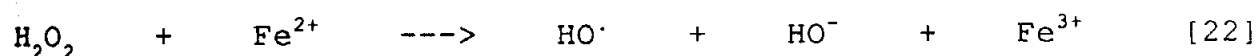
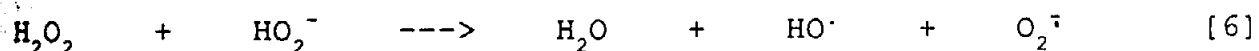
Through spectrometric and oxygen analysis of the iron (III) iron-hydrogen peroxide-water system, Lewis et al.⁷³ found

evidence for the existence of $\text{Fe}^{3+}(\text{H}_2\text{O})_5(\text{H}_2\text{O}_2)$, $\text{Fe}^{3+}(\text{H}_2\text{O})_5(\text{HO}_2^-)$ and $\text{Fe}^{3+}(\text{H}_2\text{O})_5(\text{HO}^-)$ in dilute solutions. In concentrated solutions of hydrogen peroxide, $\text{Fe}^{3+}(\text{H}_2\text{O})_4(\text{H}_2\text{O}_2)\text{HO}_2^-$ and $\text{Fe}^{3+}(\text{H}_2\text{O})_4(\text{H}_2\text{O}_2)_2$ were identified, the concentration of the latter being negligible. The authors suggest that the above-mentioned species are responsible for the iron-catalyzed peroxide decomposition.

To further complicate matters, Garten⁷⁴ found that the kinetic data cannot be reconciled with either a pure free radical cycle or with a pure non-free radical cycle, but is consistent with a combination of both. The author suggests that active intermediates in the propagation consist of dimerized products of iron (III) hydrolysis. Lebedev *et al.*⁷⁵ suggest that a free radical decomposition mechanism operates at low concentrations of iron, but that a non-radical mechanism predominates at high concentrations, and involves intermediate formation of a complex with two iron (III) ions, whose interaction involves an intramolecular transfer of electrons.

The mechanism of iron-catalyzed decomposition of hydrogen peroxide in alkaline solutions has not yet been studied with the necessary degree of detail. Most of the explanations for this mechanism are based on the principles of hydrogen peroxide decomposition in acid solutions. Isbell *et al.*⁷⁶ proposed a mechanism for the iron-catalyzed decomposition of hydrogen peroxide in alkaline solutions which is very similar to the oxidation-reduction mechanism presented by Weiss⁶⁰. This mechanism also takes into consideration the so-called

autodecomposition of hydrogen peroxide which cannot take place in acid solutions due to lack of hydrogen peroxide ionization. The reaction sequence proposed is shown below:



With an excess of hydrogen peroxide, the above reactions give rise to hydroxyl, perhydroxyl and superoxide anion radicals in a dynamic system in which iron (II) ions are oxidized by hydroxyl radicals, iron (III) ions are reduced by perhydroxyl radicals, and hydrogen peroxide is oxidized by superoxide anion radicals⁷⁶.

Nadezhedin et al.³⁴ found reaction [27] to occur between iron (III) ion and superoxide anion radicals rather than between iron (III) ion and perhydroxyl radicals in weakly alkaline media. This finding seems to be correct considering the fact that the pKa for the ionization of perhydroxyl radicals is approximately 4.4⁷⁷.

The pH corresponding to maximum decomposition of hydrogen peroxide in the presence of iron was found to be 11.6³⁵.

According to Nicoll and Smith¹⁸, the catalytic activity of iron (III) ions in alkaline solution does not increase regularly with increasing concentration and, at certain pH and concentration values, iron (III) ions actually act as peroxide stabilizers. The stabilization effect of iron (III) ions is explained as being caused by the formation of peroxides or complex per-ions which are comparatively stable¹⁸. The formation of iron (III) hydroxide at high concentrations of iron (III) ions causes rapid decomposition of alkaline solutions of hydrogen peroxide¹⁸. The highly-dispersed colloidal hydroxide is thought to be responsible for this effect⁶¹.

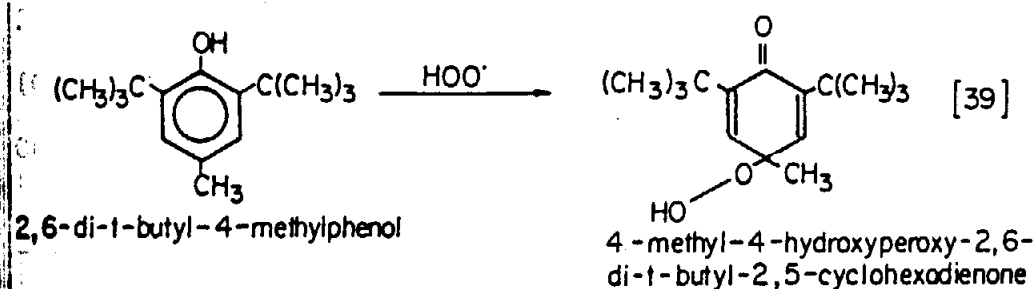
1.2.2. Copper

Hydrogen peroxide decomposition in the presence of copper increases with increasing copper concentration and alkalinity of the solutions¹⁸. According to Galbacs and Csanyi³⁵, maximum hydrogen peroxide decomposition in the presence of copper occurs at pH 12.0.

The catalytic activity of copper in the decomposition of alkaline hydrogen peroxide solutions has been explained as occurring through the formation of unstable peroxides⁶¹, formation of complexes with perhydroxyl ions^{15, 78, 79}, and formation of free radicals^{17, 21, 65, 80}.

Coppinger⁸¹ demonstrated the formation of perhydroxyl radicals in the cupric ion-catalyzed hydrogen peroxide

decomposition by adding the anti-oxidant, 2,6-di-*t*-butyl-4-methylphenol, to the reaction system. The product, 4-methyl-4-hydroperoxy-2,6-di-*t*-butyl-2,5-cyclohexadienone, was identified as arising from the reaction between the anti-oxidant and perhydroxyl radicals (eq. 39).

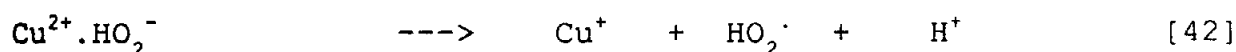
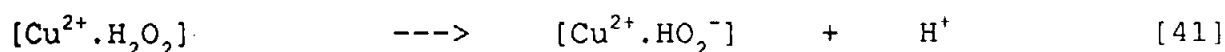
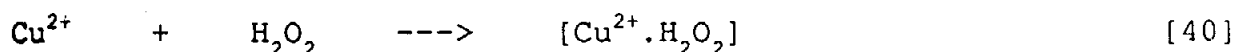


EPR studies performed by Vierke⁸² showed the existence of hydroxyl and superoxide anion radicals in solutions of hydrogen peroxide treated with cupric hydroxide. The superoxide anion radicals were thought to arise from the dissociation of perhydroxyl radicals and the hydroxyl radicals from the reaction between hydrogen peroxide and perhydroxyl radicals. An interesting observation was that the catalytically active copper compound was an unstable species which also gave a signal in the EPR spectrum⁸².

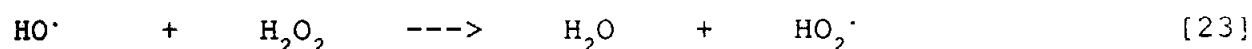
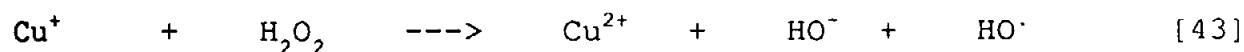
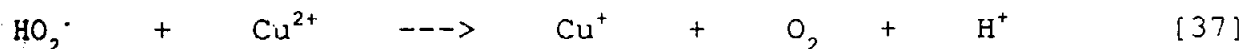
Using *p*-nitrosodimethylaniline as an acceptor for hydroxyl radicals in alkaline solutions of hydrogen peroxide, Ernestova³¹ concluded that copper-catalyzed hydrogen peroxide decomposition is indeed a free radical process. Berdnikov¹⁷ proposed a chain reaction mechanism for this process which is very similar to the

one presented by Barb *et al.*⁶⁴ for the iron-catalyzed hydrogen peroxide decomposition:

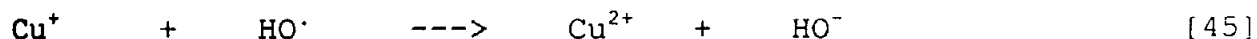
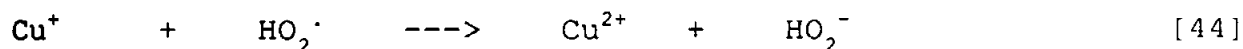
Initiation:



Chain propagation:

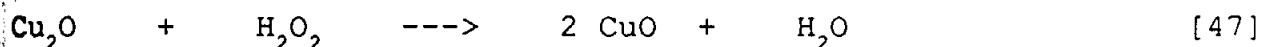
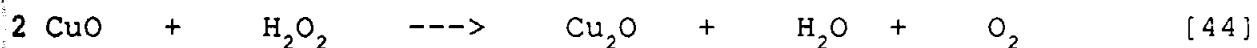


Chain termination:



This same reaction pathway has been reported in experiments where the initiation step was performed by photolysis in the presence of copper⁸³.

A different concept for peroxide decomposition catalyzed by copper has been put forward by Shashkov and Krylova⁸⁴. Working with a mixture of copper species (Cu^{2+} , Cu_2O , CuO and CuOOH), the authors concluded that hydrogen peroxide decomposition involves the following reactions:



Hydrogen peroxide decomposition via a copper peroxide intermediate was investigated by Glasner⁸⁵ who concluded that copper peroxide is formed by a simple addition of perhydroxyl radical to cupric hydroxide and has the formula CuOOOH . The formation of copper peroxide is promoted by increasing alkalinity and catalytic decomposition of hydrogen peroxide was shown to be proportional to the concentration of copper peroxide present at any moment in the solution. The rate of oxygen evolution was found to correspond approximately to one-half order with respect to hydrogen peroxide⁸⁵.

1.2.3. Manganese

Manganese has been found to have the most deleterious effect on hydrogen peroxide stability among the transition metals usually present during pulp bleaching^{86,87}. Also, it is often the most abundant transition metal in bleaching systems⁸⁶.

Peroxide stability in the presence of manganese is sharply reduced with increasing pH up to approximately 9.5^{14,15,35}. A further increase in pH results in an improvement in stability followed by a slight deterioration (Fig. 1). At a pH value around 10.5, the manganese is precipitated as manganese hydroxide and this may be the reason why improved stability is found at this pH¹⁴.

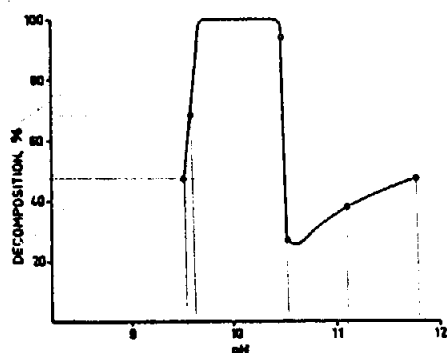
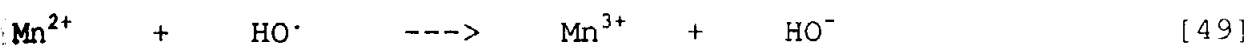
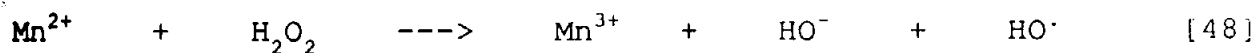


Figure 1. Decomposition of 0.040 M H_2O_2 solution containing manganese (0.2 ppm)¹⁴.

Manganese-induced decomposition of hydrogen peroxide has been explained in terms of unstable peroxide formation^{62,78}, free radical chain reactions^{29,65,88}, heterogeneous reaction with solid manganese dioxide⁶¹ and surface catalysis⁸⁹.

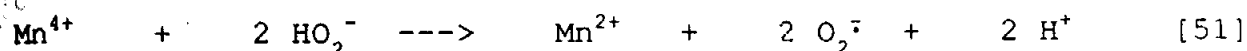
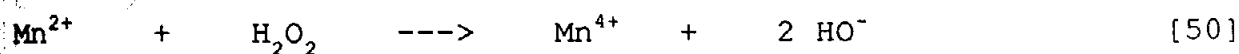
The free radical mechanism for decomposition of hydrogen peroxide in the presence of manganese has been described as follows⁶⁵:



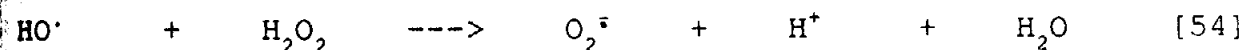
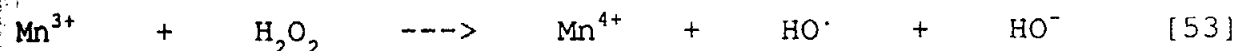
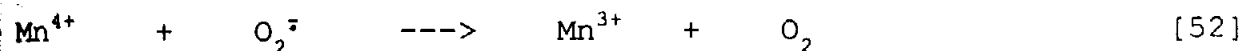
According to Sychev *et al.*⁹⁰, reaction [48] is not very likely to occur since it is a one-electron step and this requires the

generation of hydroxyl radicals before the formation of superoxide anion radicals which was found not to be the case. The authors therefore proposed the following modified mechanism:

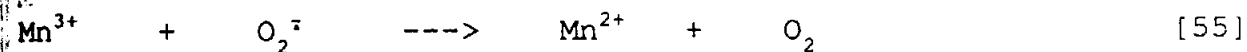
Initiation:



chain propagation:



chain termination:

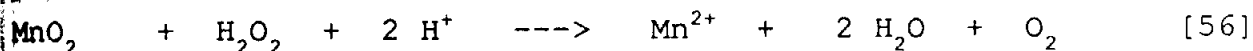


The free radical chain reaction mechanisms proposed above have been shown to be irrelevant in alkaline hydrogen peroxide solutions. Investigations carried out with the hydroxyl radical acceptor p-nitrosodimethylaniline and the heavy oxygen isotope ^{18}O have established, respectively, the non-existence of hydroxyl radicals in the intermediate stages of the sequence and the generation of oxygen without cleavage of the O-O bond in the hydrogen peroxide molecule⁹⁰.

In all probability, manganese does not exist predominantly in an ionic form in alkaline solutions. The exact forms of

manganese present in alkaline solutions as well as their effects on hydrogen peroxide decomposition are still not known with certainty but it is known that the addition of manganese in the form of Mn_3O_4 , Mn_2O_3 , MnO_2 or KMnO_4 to these solutions enhances hydrogen peroxide decomposition⁹¹. The decomposition was shown to be first order in peroxide in the presence of MnO_2 and orders of less than one in the presence of MnO , Mn_2O_3 and Mn_3O_4 ⁹².

According to Burmakina et al.⁵¹, manganese-catalyzed hydrogen peroxide decomposition in weakly alkaline solutions occurs by a two-electron transfer from the hydrogen peroxide molecule to internally-formed compounds as shown in the reaction sequence below:

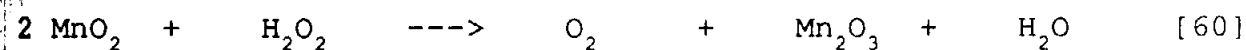
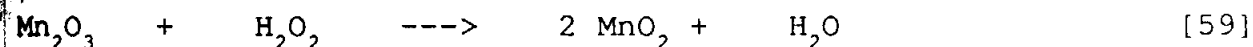


The theory of a surface catalysis has been advanced but not very convincingly explained. The only evidence that vaguely supports this theory was presented by Ismail and Constable⁹³ who found that the rate of heterogeneous hydrogen peroxide decomposition catalyzed by a manganese sesquioxide surface is proportional to the mass of the catalyst. Evidence contradicting this theory has been presented by Wolfram⁶¹ who found no change in the catalytic activity of manganese dioxide when it was gelatin-coated.

Particle size has also been shown to be important in the

effectiveness of manganese as a catalyst for hydrogen peroxide decomposition^{55, 61}. Wolfram⁶¹ found that decomposition rates of hydrogen peroxide in the presence of manganese dioxide of different particle sizes followed first order kinetics but increased in kinetic order with increasing degree of dispersion. The decomposition rate in the presence of the particles was much lower than in the case of manganese dioxide solutions and gels.

The decomposition of dilute aqueous hydrogen peroxide solutions on various supported manganese oxides catalysts seems to occur via a mechanism involving the simultaneous oxidation and reduction of the catalyst by hydrogen peroxide in which trivalent and tetravalent manganese take part⁷³. The proposed reaction sequence is shown below:

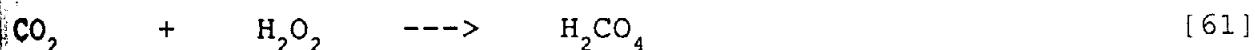


Broughton and Wentworth⁹⁴ found no catalysis of hydrogen peroxide decomposition by manganous solutions until manganese dioxide was formed. The oxidation of a manganous ion in solution by hydrogen peroxide is not very likely since it involves either the formation of the unstable manganic ion or a nucleus of solid manganese dioxide⁵⁵. However, manganous ions adsorbed on the surface of manganese dioxide may be more active in catalysis since on oxidation they become attached to the already-formed manganese dioxide lattice. The adsorbed manganous ion can either

take part in the reaction itself or create a site for the formation of a crystal of manganese sesquioxide.

1.3. Effect of CO_2 on Peroxide Decomposition

Navarro et al.¹¹ found that the rate of hydrogen peroxide decomposition is enhanced when a continuous stream of CO_2 is introduced into alkaline solution. In contrast to the effect of CO_2 , carbonate ions proved completely inactive. Furthermore, it was observed that the pH of unbuffered solutions initially adjusted to 12.0 decreased as the hydrogen peroxide decomposed. In the presence of CO_2 , the rate of hydrogen peroxide decomposition passed through a maximum between pH 11.5 and 11.7, just as in the absence of CO_2 . The following two-step mechanism was proposed for hydrogen peroxide decomposition in presence of CO_2 : (1) formation of peroxycarbonic acid by reaction of CO_2 with the undissociated hydrogen peroxide and (2) reduction of the percarbonic acid by perhydroxyl anions as illustrated below:



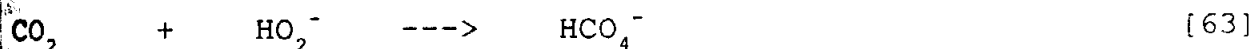
Since the bicarbonate anion is a much weaker base than the hydroxyl anion, it follows that the pH of the solution decreases as the decomposition progresses¹¹. This pH change is in contrast to the change observed during the so-called autodecomposition of alkaline hydrogen peroxide where the pH increases because of the

release of hydroxyl anions²³:



Laszlo *et al.*¹², however, have questioned the mechanism proposed by Navarro *et al.*¹¹ based on the following arguments:

(1) it is still not clear whether peroxy derivatives of carbonic acid are true peroxy compounds containing an HOO-group or that they contain active oxygen in the form of a hydrogen peroxide molecule of crystallization. The presence of the HOO-group activated by an acyl group is vital for the second step of the proposed redox reaction mechanism. (2) Usually, the pKa's of peroxycarboxylic acids are in the 6.0-9.0 range. If this range is also valid for peroxycarbonic acid, the pH where maximum decomposition take place should be between 8.8 and 10.3 rather than at 11.7. (3) The hydration of CO₂ is a slow process although it becomes much faster in the presence of hydroxide ions. By analogy, it is expected that perhydration with H₂O₂ is also a slow process, and consequently reaction [61] cannot contribute to the enhancement of the rate of decomposition of H₂O₂. In contrast, the perhydration would occur quickly in the presence of the strongly nucleophilic perhydroxyl anion and thus the mechanism can be visualized as follows:



After careful work, under the same conditions utilized by Navarro et al.¹¹, it was concluded that the rapid decomposition of hydrogen peroxide in aerated alkaline solutions is indeed induced by CO₂ but by a mechanism which does not involve formation of peroxyarbonates¹². Rather the induction of hydrogen peroxide decomposition by CO₂ occurs when transition metal impurities are transformed from their polynuclear oxohydroxo complexes into less aggregated carbonato complexes¹².

1.4. Effect of Stabilizers

1.4.1. Chelating Agents

It is well-known that chelating agents prevent hydrogen peroxide decomposition. The most widely-accepted concept is that the transition metals which catalyze peroxide decomposition are rendered inactive by the chelating agents^{14, 18, 86, 95-98}. Walling et al.⁶ point out, however, that some chelating agents, especially aminopolycarboxylates, can also act as scavengers of radicals which supposedly are intermediates in hydrogen peroxide decomposition^{27, 35, 99}.

The inhibition of alkaline hydrogen peroxide decomposition by certain chelating agents has been observed by several investigators^{21, 24, 25, 35, 96, 100-103}. The benefits of organic chelating agents are evident either when used as a pretreatment of mechanical pulps prior to peroxide bleaching or when used in peroxide bleaching formulations^{86, 96}. Allison¹⁰³ studied the

relative effectiveness of several organic chelating agents including three aminopolycarboxylates, the pentasodium salt of diethylenetriaminepentaacetic acid (Na_5DTPA), nitriloacetic acid (NTA), and the tetrasodium salt of ethylenediaminetetraacetic acid (Na_4EDTA). The results indicated that Na_5DTPA was the most efficient for increasing peroxide bleaching efficiency, especially when used as a pretreatment. In a similar study, Spitz⁹⁶ compared the stabilizing efficiency of trisodium hydroxyethylenediaminetriacetate (Na_3HEDTA), disodium hydroxyethyliminodiacetate (Na_2HEIDA), triethanolamine (TEA), trisodium nitriloacetate (Na_3NTA) and Na_5DTPA . With the exception of Na_3NTA and Na_5DTPA , no improvement in the stabilization of alkaline hydrogen peroxide by the chelating agents was observed in the presence of copper (II)⁹⁶. Overall, the best stabilizing performance was obtained with Na_5DTPA . Similar results have been obtained by Schroeter¹⁰⁴.

The effectiveness of several new organic sequestering agents including poly(α -hydroxyacrylic)acid (polylactone), myoinositol hexaphosphoric acid (phytic acid), Stabicol (a proprietary blend of aminopolycarboxylates), and diethylenetriaminepentamethylene-phosphonic acid (DTMPA) have also been investigated¹⁰³. With respect to pretreatments, chelating agent effectiveness was in the order $\text{DTMPA} > \text{Stabicol} > \text{Na}_5\text{DTPA} > \text{phytic acid} > \text{polylactone}$. However, the differences were very small. When the chelating agents were included in the bleaching formula, DTMPA was far more effective than any of the other stabilizers. Apparently DTMPA was

able to form strong and stable metal cation complexes under the prevailing bleaching conditions.

In a detailed study involving chelating and other stabilizing agents, Oldenroth¹⁰⁵ investigated the effect of Na_3NTA , Na_4EDTA , MgSiO_3 , $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ on the stability of hydrogen peroxide bleaching liquors in the presence of copper and iron. Na_3NTA strongly reduced the catalytic activity of iron but did not fully nullify it. Na_4EDTA , on the other hand, completely eliminated the catalytic action of iron. MgSiO_3 was as effective as Na_3NTA but likewise could not completely eliminate the catalytic action of the iron. When copper and iron were jointly added, none of the chelating agents gave perfect stabilization. Sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) had a better stabilizing action than either $\text{Na}_5\text{P}_3\text{O}_{10}$ or MgSiO_3 ⁶¹. Safonov et al.¹⁰⁶ claim that sodium pyrophosphate deactivates transition metals by forming complexes with them. Sodium pyrophosphate was shown to be an effective stabilizer only at pH values lower than 10.3 and this fact was explained by decomposition of the stable complexes at higher pH values¹⁰⁶.

In a recent study DeMaria¹⁰⁷ showed that the combination of gluconic acid and magnesium salts chelates iron more effectively than Na_5DTPA at pH 11. This combination was suggested as a replacement for sodium silicate in the bleaching of textiles.

Alkaline solutions of hydrogen peroxide are reportedly stabilized under the joint influence of Na_4EDTA and the hydroxides of magnesium, calcium and cadmium⁹⁶. An important

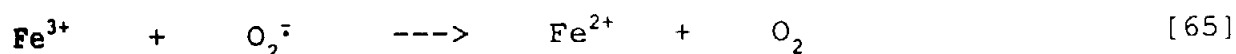
feature of these stabilizing systems is that the minimum stabilizing action is reached when the molar concentration of Na_4EDTA is equal to that of the divalent ion. Increased stability is obtained either with an excess of Na_4EDTA or with an excess of the divalent ion⁹⁸.

The magnesium salts of aminopolycarboxylic acids are very efficient hydrogen peroxide stabilizers¹⁰⁸. For optimum functioning, however, it is necessary that all of the carboxyl groups in the molecule be in the form of magnesium salt¹⁰⁸. The magnesium salt of Na_4EDTA , in particular, has been reported to be a very efficient hydrogen peroxide stabilizer^{16,108,109}. The combination magnesium sulphate-triethanolamine has also been shown to be a very good stabilizing system for alkaline hydrogen peroxide solutions¹¹⁰.

According to Hartler *et al.*¹⁴, an excess of calcium ions can have a deleterious effect on the chelation capacity of certain chelating agents. In some cases, the stability cannot be achieved even by adding large amounts of the chelating agent. The authors claim that Na_4EDTA can have good stabilizing action but amounts sufficient to chelate all transition metals have to be used.

An important fact established by several workers^{6,111-113}, is the ability of Na_4EDTA to form a complex with iron (III) which catalyzes hydrogen peroxide decomposition. The unstable complex formed is of the type $\text{Fe(III)[EDTA]O}_2^{3-}$ and decomposes readily^{6,114}. This same type of behavior has been observed with

$\text{Na}_5\text{DTPA}^{115-117}$ and DTMPA^{115} . A different explanation for the iron-catalyzed peroxide decomposition in the presence of chelating agents has been presented by Tien *et al.*¹¹⁸. According to these authors, the reaction



occurs only if iron is in the chelated form and, consequently, decomposition is faster in the presence of the chelating agent than in its absence.

Chelating agents can be decomposed in reactions with hydrogen peroxide^{73,119}. The decomposition of Na_4EDTA by such reactions was shown to be accelerated by copper ions⁹⁸. To avoid these reactions, the chelating agent reportedly must be completely saturated with divalent ions in order to inhibit the formation of unstable complexes with hydrogen peroxide⁷³. The addition of magnesium sulfate to the H_2O_2 - Na_4EDTA system reduced significantly the consumption of hydrogen peroxide by the chelating agent¹¹⁹.

1.4.2. Magnesium Compounds

Accumulated evidence indicates conclusively that magnesium compounds are effective stabilizers for alkaline hydrogen peroxide solutions^{13,14,18,29,102,120-124}. As shown by Reichert *et al.*¹²⁵, magnesium sulphate has a stabilizing effect over the pH range 9.0 to 12.0 and the effect is maximum at pH 9.7. The

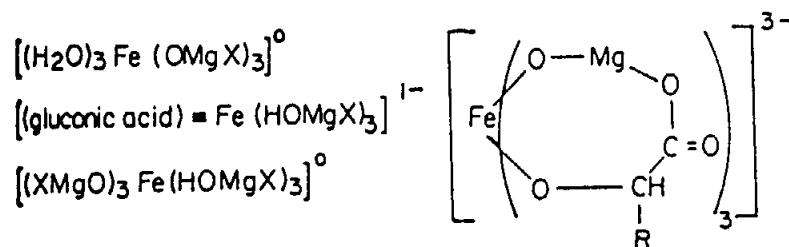
stability of alkaline hydrogen peroxide solutions in the presence of copper has been shown to increase with increasing amounts of magnesium sulphate¹⁸ but complete stabilization was estimated by extrapolation to be reached only if a 1000-fold excess of magnesium were added to the system¹²⁶. For cobalt the excess of magnesium was estimated to be 2000-fold¹²⁶. In the presence of iron and manganese, magnesium sulfate completely stabilized hydrogen peroxide when it was present in a molar concentration of 30- to 70-fold¹²⁶. Wolfram⁶¹ found that the addition of magnesium sulfate in the ratio of 3.2 Mg/Fe completely stabilizes alkaline solutions of hydrogen peroxide. Using polarography of metal complexes and ultraviolet analysis, Gilbert et al.¹²⁷ determined that between three and six moles of magnesium are needed to coordinate with one mole of iron. Krause and Kukiela¹²⁸, on the other hand, found magnesium hydroxide to be very effective in stabilizing hydrogen peroxide in the presence of copper but not in the presence of manganese.

The mechanism by which magnesium stabilizes hydrogen peroxide is still not clear. According to Sjostrom and Valtilla¹¹⁰, the stabilizing effect of magnesium is related to its ability to deactivate transition metal and this has been confirmed for cobalt and iron^{129,130}. In alkaline solutions, magnesium exists as an insoluble hydroxide which is believed to sorb transition metal impurities¹³¹. The insoluble hydroxide may also deactivate solid catalytic surfaces¹¹⁰.

Some authors have found, however, that the magnesium

hydroxide precipitate acts as a catalyst for hydrogen peroxide decomposition^{18,29,120}. Nicoll and Smith¹⁸ showed that magnesium hydroxide acts as a promoter for the catalytic activity of silver oxide. According to these authors, magnesium hydroxide acts as a support for finely-divided, catalytic silver oxide so that, in this instance, the colloidal properties of the hydroxide activated rather than inhibited hydrogen peroxide decomposition.

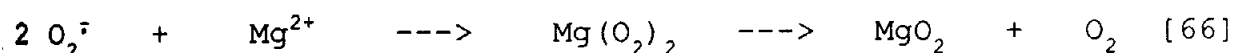
Gilbert *et al.*¹²⁷, on the other hand, claim that magnesium compounds act by forming stable, not readily oxidizable complexes with transition metals thereby inhibiting their catalytic action. Under alkaline conditions the formation of these stable coordination compounds occurs via "oxo" (-O-) and "hydroxo" (-OH-) bridges. The formation of these types of bonding is termed "olation" and "oxolation", respectively, and is well-documented in textbooks on coordination chemistry¹³². Examples of "oxo" bridges between iron and magnesium are presented in the iron-magnesium complexes depicted in Figure 2:



X = Hydroxide or Gluconic Acid Group.

Figure 2. Iron-magnesium complexes¹²⁷

The beneficial effect of magnesium has also been attributed to its ability to scavenge free radicals generated in the system, thereby preventing the propagation of the chain decomposition reaction^{133,134}. Isbell and Frush¹³³ proposed that magnesium dismutates superoxide anion radicals according to the following mechanism:



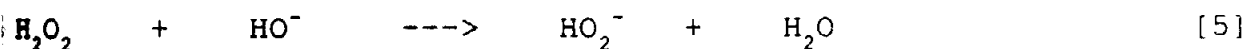
A similar mechanism has been proposed by Johnson *et al.*¹³⁵ for the dismutation of superoxide by lithium and calcium. The action of magnesium in peroxide stabilization appears comparable to that of superoxide dismutase in biological systems^{136,137}. However, experiments performed by Ericsson *et al.*¹³⁰ do not support the theory of superoxide dismutation.

Bregeon^{62,78}, suggests that magnesium ions form stable complexes with perhydroxyl ions inhibiting the hydrogen peroxide decomposition.

1.5. Effect of Buffers

Hydrogen peroxide was shown to decompose at a greater rate in the presence of pH buffers, as a consequence of the activation energy being lowered¹³⁸. The buffers used were borax (pH 9.0), sodium carbonate and sodium bicarbonate (pH 10.0), and a combination of sodium hydroxide and disodium hydrogen phosphate, Na_2HPO_4 , (pH 11.0). Hydrogen peroxide was shown to decompose at a rate 2 or 3 times higher in the buffered systems than in the

unbuffered ones. The authors explain the results considering the fact that in the unbuffered systems, the pH is lowered during the course of bleaching thereby lowering the rate of decomposition of hydrogen peroxide. For buffered systems, the concentration of hydroxyl ions is maintained constant throughout the reaction thereby maintaining also constant the concentration of perhydroxyl anions, eq. [5].



Because the concentration of perhydroxyl anions does not decrease throughout the bleaching process, the rate of decomposition in the buffered system is considerably higher than in the unbuffered system where the concentration of perhydroxyl anions decreases in the course of the reaction.

In contrast to what was shown in the previous work, Cates and Cranor¹³⁹ found that the rate of peroxide decomposition is decreased by approximately 75% when peroxide solutions are buffered at pH 10.5 with 100 mmolar Na_2HPO_4 .

1.6. Effect of Temperature

The rate of hydrogen peroxide decomposition increases with increasing temperature^{2,14,15,18,19,24,140,141}. Under the same conditions, hydrogen peroxide decomposition in alkaline solutions increased from 10 to 50% when the temperature was increased from 50° to 80° C¹⁸. According to Spalek *et al.*², the rate of hydrogen peroxide decomposition in alkaline media can be represented by a rate equation of the form:

$$-\frac{da}{dt} = k_1[H_2O_2] + k_0,$$

where a is the total hydrogen peroxide content in the solution. On increasing the temperature of reaction from 20° to 30° C, k_1 increased on average by 2.2 times and k_0 by roughly 3 times at equal hydroxyl ion concentration.

The pH dependence of the rate of hydrogen peroxide decomposition is independent of the temperature^{18,19,142}.

2. The Stability of Hydrogen Peroxide in the Presence of Sodium Silicate.

It is well-known that sodium silicate brings about a considerable improvement in the effectiveness of hydrogen peroxide bleaching by increasing brightness and reducing oxidant consumption^{13,14,143}. In addition, it has also been suggested that the inclusion of sodium silicate in peroxide bleaching reduces color reversion in mechanical pulps¹⁴⁴.

There is considerable uncertainty about the mechanism(s) through which sodium silicate enhances peroxide bleaching efficiency. A large number of theories have been proposed for the role of silicate, the following being the most widely accepted:

- (1) stabilization of hydrogen peroxide^{14,18,28,134,145-153}, (2) formation of more reactive peroxysilicates by interacting with peroxide¹⁴³, (3) direct interaction with lignin¹⁵⁴, (4) alteration of the mechanism of lignin oxidation through formation

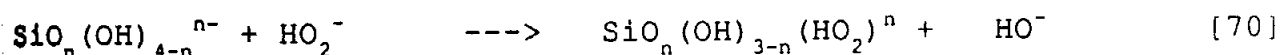
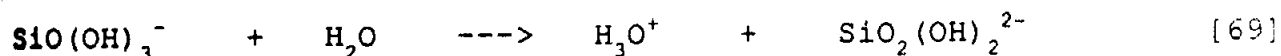
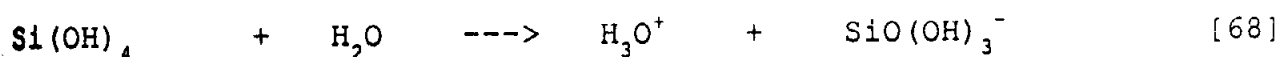
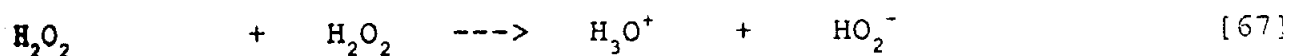
of new reactive species such as singlet molecular oxygen¹⁴⁶, (5) increasing of ionic strength¹⁴⁶, (6) increasing of alkalinity¹⁴⁶, (7) prevention of the formation of alkaline earth hydroxides which are catalysts for peroxide decomposition¹⁸, and (8) acting as a buffer, detergent, surfactant, flocculating, and anti-corrosion agent^{23, 28, 146-150, 154}.

The proposed theory that silicate interacts directly with the lignin has been seriously questioned since kinetic studies carried out by Lundqvist¹⁵⁵ have demonstrated that the rate of chromophore elimination during peroxide bleaching of groundwood is very little affected by the addition of silicate. Using transmission electron microscopy in combination with the EDAX technique, Graham *et al.*¹⁵⁶ have also partially discredited this hypothesis since they found that silicate does not penetrate the cell wall of the wood fibers.

On the other hand, the buffering properties of the sodium silicate have not been confirmed in peroxide bleaching of groundwood¹⁴⁶. It has also been suggested that the surface wetting, emulsification and flocculating properties of sodium silicate are unlikely to be the reason for the improved bleaching response of substrates to hydrogen peroxide¹⁵⁷.

Although a large number of investigators have reported data supporting the claim that hydrogen peroxide stability is enhanced in the presence of sodium silicate, some^{152, 158} have actually contended that sodium silicate destabilizes hydrogen peroxide. The peroxide destabilization has been explained by the formation of very unstable intermediates (eq. 67-70), peroxysilicates,

which decompose according to the reaction sequence below¹⁵²:



$$n = 0, 1 \text{ or } 2$$

Contrary to the foregoing conclusion, Nicoll and Smith¹⁸ have reported evidence indicating that silicate neither stabilizes nor destabilizes alkaline solutions of hydrogen peroxide. A part of these seemingly contradictory findings ultimately may be traceable to pH differences since Hartler *et al.*¹⁴ showed that, with increasing pH in the 10.0-13.0 range, silicate becomes increasingly less effective in stabilizing hydrogen peroxide. The transition metal impurities present in varying amounts in the various commercial silicates as well as the varying concentrations of calcium and magnesium present in the systems may also account for the different interpretations given the role of sodium silicate in hydrogen peroxide bleaching¹⁵⁹.

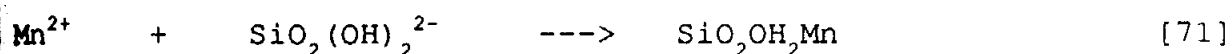
In a very recent publication, Kutney¹⁴⁶ reported the results of an exhaustive study in which the influence of seventy-five inorganic and organic compounds on the stability and effectiveness of hydrogen peroxide in the bleaching of groundwood pulp was examined. The additives included several organic chelating agents, free radical scavengers, and various other compound types. The conclusion drawn was that only a few had a

significantly positive effect on peroxide stability and none of them could match the efficiency of sodium silicate. Of the substances tested, only barium chloride, sodium nitrate, sodium hexafluorosilicate, sodium hypophosphite, succinimide, melamine, Na₅DTPA, and anthraquinone derivatives reduced peroxide consumption and improved pulp brightness in the absence of silicate. Furthermore, none of the silicate co-additives, including Mg²⁺ salts, had a significant positive effect on bleaching efficiency.

To explain the more-or-less accepted role of sodium silicate as a hydrogen peroxide stabilizer, several theories have been advanced: (1) sodium silicate retards the catalytic decomposition of peroxide through formation of stable complexes with transition metals, preventing their oxidation to higher oxidation states and thereby inhibiting the generation of free radicals^{152,153}, (2) sodium silicate retains transition metals in solution and prevents the formation of insoluble hydroxides which are catalysts for hydrogen peroxide decomposition¹⁸, (3) sodium silicate coats the transition metals with a protective layer whereby the heterogeneous surface catalysis of hydrogen peroxide is retarded or prevented^{147,149}, (4) sodium silicate passivates transition metals^{28,150}, (5) sodium silicate sorbs transition metals on its surface thereby rendering them catalytically inactive with respect to peroxide decomposition^{14,145,151}, (6) sodium silicate deactivates transition metals as a result of the metal ions entering the internal spaces between silicate chains and forming well-defined three-dimensional structures with the

ligands¹³⁴, (7) sodium silicate terminates reactions of hydrogen peroxide decomposition by binding free radicals and is itself polymerized in the process^{28,134}, and (8) sodium silicate and hydrogen peroxide form well-defined addition compounds, peroxysilicates, which are more stable than hydrogen peroxide itself^{143,152}.

Although the reaction of sodium silicate with transition metals to form stable complexes has been claimed as being the reason for the silicate action during peroxide bleaching^{152,153}, such compounds have never been isolated in actual bleaching conditions. An example of these proposed complexes is manganese metasilicate, formed as shown in equation [71]¹⁵³:



The hypothesis that silicate terminates free radical decomposition reactions arose from the fact that peroxide bleaching in the presence of barbituric acid, an efficient free radical scavenger, was as efficient as in the presence of sodium silicate¹³⁴. In contrast, Kutney¹⁴⁶ showed that barbituric acid, as well as many other organic reagents, had a detrimental effect on pulp brightness; very few free-radical scavengers had a positive impact on bleaching efficiency.

The reported syntheses of peroxysilicates typically involve concentrations of sodium silicate and peroxide far in excess of those prevailing in the peroxide bleaching of pulp^{152,160,161}. Hence, it remains to be demonstrated if and to what degree

peroxysilicates are significant in technical peroxide bleaching systems. It is important to distinguish between "true" peroxycompounds such as peroxydisulfate salts which contain O-O bonds (Fig. 3) and substances such as sodium percarbonate ($2 \text{ Na}_2\text{CO}_3 \cdot 3 \text{ H}_2\text{O}_2$), sodium perborate, and sodium perphosphate that contain H_2O_2 of crystallization¹⁶². Both type of compounds hydrolyze to give hydrogen peroxide upon dissolution in water. Several investigators¹⁶²⁻¹⁶⁴ have synthesized silicate peroxyhydrate salts but, there is no experimental evidence currently available to support the existence of genuine peroxysilicates.

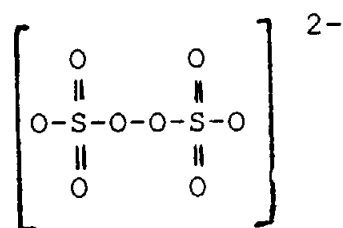


Figure 3. "True" peroxycompound (peroxydisulfate)¹⁶².

Blaschette and Saad¹⁴³ suggested that the formation of peroxysilicates is the reason for the improved peroxide bleaching action in the presence of sodium silicate. The authors assumed that these compounds are stronger oxidants (higher redox potential) than peroxide itself. Burton¹⁶¹ found no evidence that such complexes are better bleaching agents than conventional hydrogen peroxide-sodium silicate mixtures. The hypothesis that peroxysilicates are more active bleaching agents was almost totally discarded in recent work by Graham *et al.*¹⁵⁶. Using transmission electron microscopy in combination with the EDAX

technique, the authors concluded that silicate does not penetrate the cell wall during bleaching. If silicate does not penetrate the fiber wall it is evident that a major portion of the lignin will not be available to react with any peroxysilicate that may be formed.

The effectiveness of sodium silicate as a stabilizer for hydrogen peroxide has been reported to be dependent on several variables. Strel'tsov and co-workers¹⁶⁵ observed that peroxide bleaching efficiency in the presence of sodium silicate solutions containing magnesium and calcium increased as a function of the molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$. Raskina et al.²⁸ found an increase in hydrogen peroxide stability as a result of increasing the sodium silicate/total alkali ratio from one to two. According to the authors, sodium silicate with a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of two has a greater tendency to undergo polymerization and, as a consequence, it is more efficient in binding the free radicals present in the system. Soldatkina et al.¹⁶⁶, on the other hand, found better stabilization of the hydrogen peroxide when "depolymerized" silicates were used instead of regular "water glass". This finding was rationalized on the bases of the lower capacity of the depolymerized silicates to form intermediate products and by the lower sodium hydroxide content which reportedly accelerates the hydrogen peroxide decomposition via a free radical mechanism. The authors¹⁶⁶ also showed that the rate of copper- and iron-catalyzed peroxide decomposition in the presence of silicate and magnesium or silicate and calcium is lower for "depolymerized"

silicate than for "water glass".

The degree of hydrolysis of sodium silicate is another factor affecting its performance as a hydrogen peroxide stabilizer¹⁶⁷. The stabilization action is increased by increasing the concentration of sodium silicate or by the addition of reagents such as ammonium chloride which increase the hydrolysis of sodium silicate. Thus, a significant increase in hydrogen peroxide stability was obtained by increasing the silicate-alkali ratio from 1.0 to 1.6 which in turn increased the degree of hydrolysis of sodium silicate by a factor of two¹⁶⁷.

The action of sodium silicate in a bleach has often been attributed to its colloidal properties by means of which catalytic ions are sorbed and thus prevented from initiating hydrogen peroxide decomposition. However, a number of organic colloids, some of them acidic in nature and therefore capable of forming salts with transition metals, were found incapable of effectively stabilizing alkaline solutions of hydrogen peroxide¹⁸. The compounds tested included methylcellulose, carboxymethylcellulose, hydroxyethylcellulose, poly(methacrylic acid), starch and dextrin. Even in combination with sodium silicate, the solutions of which certainly exhibit colloidal properties, the organic colloids showed no effective potential for hydrogen peroxide stabilization¹⁸. Nevertheless, the presence of large amounts of a colloidal precipitate may result in the absorption of some catalytic materials which would otherwise initiate hydrogen peroxide decomposition. Such effects may possibly be obtained in the case of the hydroxides of alkaline

earth metals¹⁸.

The stabilizing capacity of sodium silicate was shown to be affected by macromolecular substances. Thus, under the influence of cotton fibers, sodium silicate stabilized hydrogen peroxide much more efficiently than in its absence²⁸.

2.1. Effect of Stabilizers

The accumulation of siliceous deposits on equipment is a major problem associated with the application of sodium silicate in pulp and textile bleaching. Consequently, considerable effort has been directed toward the development of peroxide bleaching systems containing as low an amount of silicate as possible. In this context, magnesium salts and chelating agents play an important role. In addition, other compounds have been investigated. Thus, Bassilios *et al.*¹⁶⁸ reported that sodium aluminate, NaAlO_2 , functioned efficiently as a stabilizing agent for hydrogen peroxide. The authors claimed that alumina precipitates were more easily removed from an apparatus than were silicate scales. Other investigators have utilized organic chelation reagents and/or surfactants as substitutes for sodium silicate. Organophosphonates have also been shown to be effective peroxide stabilizers¹⁶⁹. Kowalsky¹⁷⁰ prepared buffered peroxide bleaching solutions containing sodium tripolyphosphate and sodium diethylenepenta(methylenephosphonic acid). Gottlieb¹⁷¹ replaced 50% of the sodium silicate used in a single-stage textile

bleaching process with a proprietary organic sequestrant/dispersant. This procedure prevented silicate deposition on cotton and cotton-polyester fabrics. The use of quaternary alkyl ammonium salts has been reported to improve the stability of hydrogen peroxide¹⁷².

2.1.1. Magnesium Compounds

In the absence or near absence of transition metals, magnesium and, to a lesser extent, calcium are effective stabilizers of alkaline hydrogen peroxide solutions in their own rights. In combination, however, magnesium and sodium silicate are generally found superior to either component alone, especially in the presence of large amounts of transition metals^{16,119,125,152}.

The concentration of magnesium becomes unimportant above a certain value^{16,109}. However, in the presence of copper ions, hydrogen peroxide stabilization with sodium silicate is very dependent on the magnesium concentration¹⁰⁹. Under bleaching conditions, Burton¹⁶¹ found that magnesium sulfate can partially replace sodium silicate, especially when the latter is used at lower than optimum levels.

Blaschette and Saad¹⁴³ suggest that the enhancement of hydrogen peroxide stability in the combined presence of sodium silicate and magnesium sulfate is a result of the formation of colloidal dispersions of sparingly-soluble Ca- and Mg-silicates. Calcium and magnesium salts reduce the solubility of silicate in water dramatically¹⁷³. Three mechanisms have been proposed to

account for the enhanced stability of peroxide in the combined presence of silicate and magnesium or calcium. First, alkaline earth silicates may function as sequestration agents by bonding transition metals, such as iron, copper and manganese that catalyze peroxide decomposition¹⁴³. Second, alkaline earth metals react with silicate forming a colloidal suspension which sorbs transition metals thereby preventing the metal-catalyzed peroxide decomposition¹⁴⁵. Third, colloidal magnesium silicate particles may bind free-radical intermediates formed during transition metal-catalyzed peroxide decomposition^{28,134}.

2.1.2. Chelating Agents

Chelating agents are usually introduced in the bleaching process as a pretreatment step. Ali et al.¹⁵⁴ and Allison¹⁰³ have reported that the pretreatment of pulp with a chelating agent (Na_5DTPA) reduces significantly the demand for sodium silicate in the subsequent bleaching operation. Very little has been published regarding the use of chelating agents in combination with sodium silicate and magnesium salts in the bleaching formula. Bambrick¹⁰² showed that Na_5DTPA significantly enhanced the stability of bleaching liquors containing magnesium sulfate and sodium silicate even in systems where large amounts of transition metals were added ($\text{Fe} = 40$, $\text{Mn} = 40$ and $\text{Cu} = 2\text{ppm}$). Burton¹¹⁵ has shown that Na_5DTPA and DTMPA , when contained in a bleaching formula, were more efficient peroxide stabilizers than silicate in the presence of copper and manganese but, in the

presence of iron, all of the stabilizers were inefficient.

Allison¹⁰³ studied the effect of three different amino-polycarboxylate chelating agents (Na_5DTPA , Na_3NTA and Na_4EDTA) on hydrogen peroxide stability in the presence and absence of sodium silicate. Na_5DTPA was shown to be the most effective and its effectiveness in the presence of sodium silicate was higher at low concentrations of the latter. The author also found that DTMPA provided superior peroxide protection during silicate-free bleaching and resulted in bleaching efficiency similar to that found in conventional peroxide bleaching with 5.0% silicate addition. However, the high cost of DTMPA made silicate-free bleaching more expensive than conventional peroxide bleaching with silicate. Replacement of sodium silicate with DTMPA during refiner bleaching resulted in less efficient bleaching and lower final brightness. DTMPA did not provide adequate peroxide protection under the harsh conditions of high temperature and increased metallic contamination associated with refiner bleaching.

Chelating agents have been shown to be more effective in peroxide bleaching when used in the pretreatment of the pulp than when applied with the liquor in the bleaching formulation¹⁰³. This finding is explained based on the fact that, in the case where the chelating agent is applied in the bleaching formula, some metal cations in a high valence state, e.g. iron (III) and manganese (IV), though complexed with the chelating agent, can still induce hydrogen peroxide decomposition¹⁷⁴. A further

Indication of the validity of this theory was demonstrated in recent work by Whiting *et al.*¹⁰⁰ who showed that pulp washing after chelation is very important in the peroxide bleaching of pretreated pulps.

2.2. Effect of Transition Metals

It seems certain that sodium silicate does not directly stabilize hydrogen peroxide¹⁸. However, sodium silicate is capable of forming complexes with a large number of metal ions and these complexes have definite effects on the catalytic process by which hydrogen peroxide decomposes in alkaline solutions¹⁸.

The effect of transition metals depends on the particular species, its concentration and the pH of the hydrogen peroxide solution¹⁸. Sodium silicate is reported to have a negative effect on hydrogen peroxide stability in the presence of copper at pH 10.5¹⁸. The addition of silica to alkaline hydrogen peroxide solutions containing copper promotes decomposition by a factor of two⁶¹. In the presence of iron no difference in hydrogen peroxide stability was observed at pH 10.6 but, with increasing pH up to 12.0, the stability decreased to a greater degree in the presence of sodium silicate than in its absence^{14,18}. Hydrogen peroxide decomposition catalyzed by iron was shown to decrease slightly with the addition of silica gel, and this beneficial effect was explained by the adsorption of active iron micelles by the silica rendering them inactive⁶¹. In the presence of manganese, sodium

silicate has been shown to be a good stabilizer of hydrogen peroxide; the beneficial effect has been explained as being due to formation of manganese metasilicate which prevents the oxidation of manganese to higher oxidation states^{152,153}.

The effect of combinations of transition metals on peroxide decomposition is complex and, hence, difficult to predict^{18,153}.

Sodium silicate is reported to have a positive effect on hydrogen peroxide stabilization in the combined presence of copper and iron and, to a lesser extent, retards hydrogen peroxide decomposition in the presence of copper and manganese^{152,153}. The combined presence of sodium silicate and magnesium sulfate stabilizes hydrogen peroxide completely regardless of the transition metal combination present¹⁵³.

The reason for the higher rate of hydrogen peroxide decomposition in the presence of mixed catalysts than when the catalysts are added separately is not clear. Kanter et al.¹⁵³ attribute the phenomenon to the formation of joint intermediate products and coprecipitation of metal hydroxides. Nicoll and Smith¹⁸ claim that extremely unstable complex peroxides containing more than one metal may form. It is possible that a mixture of the colloidal hydroxides of two or more metals may have unusual potency in promoting surface catalysis¹⁸.

The effect of the order of chemical addition on hydrogen peroxide decomposition was studied in a solution comprised of magnesium sulfate, sodium silicate, sodium hydroxide, iron (III) hydroxide and hydrogen peroxide¹⁸. Higher hydrogen peroxide

stability was obtained when sodium silicate was available to react with both magnesium and iron before the addition of sodium hydroxide. Lower stability resulted when the order of addition of reagents permitted the formation of insoluble magnesium hydroxide before addition of the iron. Intermediate stability was obtained when the order of addition was such as to permit the formation of some iron (III) hydroxide. From these results it would appear that the chief function of sodium silicate in those solutions was to maintain the metal ions, iron and magnesium, in a soluble state and to prevent the formation of insoluble iron (III) hydroxide¹⁸.

3. The Effect of Transition Metals in Mechanical Pulps on Peroxide Decomposition

In hydrogen peroxide bleaching of mechanical pulps, part of the peroxide is consumed in oxidation reactions, part is decomposed into water and oxygen and, finally, a portion of it remains unchanged in the spent bleaching liquor. The exact amount of peroxide decomposed under bleaching conditions is difficult to determine because the high consistencies used do not allow for accurate determination of the amount of oxygen released which is the conventional way to assess decomposition. However, measurements carried out at low consistencies indicate that as much as one-third of the peroxide's bleaching capacity may be lost in decomposition reactions during bleaching^{13,119}.

The cause of peroxide decomposition during bleaching is well

known. It involves substances present in the pulpwood, bleaching chemicals, process equipment and mill water which catalytically initiate the decomposition reaction^{87,175}. The enzyme catalase, a common by-product of bacteria in pulps, has been shown to produce this effect^{125,176}. Trace amounts of transition metals such as iron, copper and manganese found in the bleaching system also cause serious detrimental effects on peroxide stability⁸⁶.

The principal source of transition metals in the bleaching system is the pulpwood⁸⁷. However, these metals have proven to be relatively inactive as catalysts for peroxide decomposition⁸⁶. The metals present in mill waters are more likely to have an accelerating effect on peroxide decomposition during bleaching⁸⁶.

Transition metals in pulpwood may originate from two principal sources. First, they are absorbed by the growing tree where some of them play a vital physiological role^{177,178}. Secondly, they may be absorbed from saws, from mud picked up on the logs, or by erosion of grinding linings and refiners¹⁷⁹. Finger bars, broken off and ground with the wood often represent a serious source of iron contamination in the case of stonegroundwood (SGW)¹⁸⁰. Erosion of refiner plates, on the other hand, is an important source of iron in thermomechanical pulps (TMP)¹⁸¹.

The amount and type of transition metals picked up by the pulp during mechanical pulping vary tremendously with the process, wood origin and wood species. Gupta and Mutton¹⁸⁰

reported that the grinding of black spruce wood increased the iron content from 5.3 to 30, copper from 0.14 to 8.1, and zinc from 6.9 to 10.0 ppm. Simultaneously, the content of manganese decreased from 87 to 60 ppm. Rothenberg and Robinson¹⁸¹ showed that the refining of Norway spruce wood in the thermomechanical process increased the iron content from 10 to 90, copper from 4 to 22, and manganese from 14 to 17 ppm. The stone grinding of the same wood increased the iron content to 45, copper to 23, and decreased the manganese content to 7 ppm. TMP obviously is in greater contact with metals, especially iron, than is SGW¹⁸¹. Trace metal analysts for iron, copper and manganese in SGW obtained from eastern Canadian woods revealed that manganese was present in higher concentrations⁸⁶. SGW made from New York State Norway spruce wood showed a significantly higher concentration of iron than of manganese¹⁸¹.

The effectiveness of transition metals as peroxide catalysts depends on their type, concentration, physical condition and chemical composition. Dick and Andrews⁸⁶ claim that among iron, copper and manganese, the latter has the most deleterious effect on peroxide stability. The authors contend that manganese, which usually comes entirely from the wood, is loosely complexed with wood components. Iron and copper, on the other hand, are more firmly held by the pulp. Although present in the original wood, these two metals are also absorbed during grinding or refining from process equipment and from mill water⁸⁶. The fact that iron and copper are more tightly held by the pulp has been confirmed by the results of Robinson et al.¹⁸²

The mechanism of goethite formation involves a series of equilibria which may be changed drastically depending upon temperature and pH of the iron solutions. The pale violet hexaquon of iron (III) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, forms in acidic solution of iron (III) salts whose anions have low coordinating ability.¹⁸³

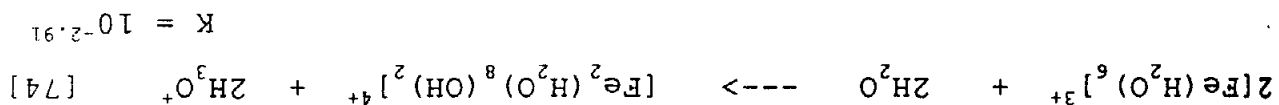
manufacture of mechanical pulps.¹⁸¹

aging of the iron (III) iron, e.g., by the heat produced in the transformed to the crystalline form under conditions which caused that some or all of the amorphous iron in the pulp can be by colloidal amorphous iron (III) ion. It has also been shown crystalline iron (III) ion, goethite, while weak bonds are formed results indicate that strong bonds are formed by colloidal in the adsorption of iron (III) ions on mechanical pulps. The It has been shown¹⁸¹ that both strong and weak bonds are formed mechanisms of adsorption and binding of these metals by the pulp. mechanical pulps has encouraged considerable research on the The difficulty encountered in removing iron and copper from of the copper from TMP and 17% from SGW.¹⁸²

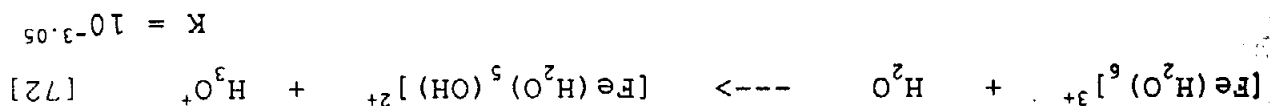
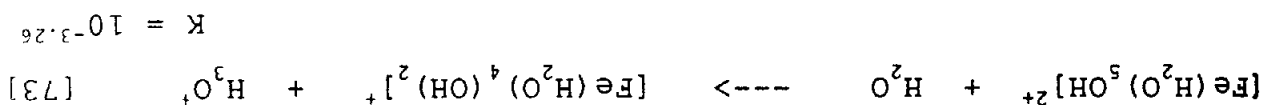
removing copper from SGW or TMP but acidic treatment removed 65% temperature. Na_5DTPA treatment was entirely ineffective for the amount removed depending on acid concentration, time and completion. Oxalic acid treatment proved the most effective, with desorb the iron from SGW, but removal never approached TMP. Additional and more drastic treatments were performed to removed iron from SGW while only a minor amount was removed from which showed that neither dilute HCl nor Na_5DTPA treatments

Once formed, the crystals of goethite are very difficult to dissolve even under optimum conditions. Cornell et al.¹⁸⁸

Rothenberg¹⁸⁷ of iron by TME has been thoroughly discussed by Robinson and effect of pH on the aging of iron solutions and on the adsorption accelerated by heating or raising the pH of the solutions. The Fe_2O_3 , and amorphous iron (III) ion oxide^{184,186}. The aging is crystals in much lesser amounts are also crystals of hematite, α -predominantly goethite (α -FeOOH)^{184,185}. Included with these precipitates occurs, eventually producing crystals which are oxide¹⁸³. When these solutions are allowed to stand, aging of the colloidal gels and finally precipitate as hydrous iron (III) species formed initially, are later converted to amorphous When the pH increases much above 2.0, more highly condensed



solutions based on the following equilibrium:
A binuclear species also forms from these strongly acidic



according to the following equilibria:
The ion then readily undergoes hydrolysis in the initial stages

found that, in aqueous solution, the surface layer of oxides, including goethite, consists of hydroxyl groups which are coordinated to iron atoms. Hydroxyl groups are, therefore, plentifully available in crystalline goethite to bond to hydroxyl groups in pulp. Furthermore, the authors suggest that the initial step in the dissolution of goethite is the attack on the free surface hydroxyl groups by protons.

Although the mechanism of adsorption of iron (III) iron on the pulp suggests an interaction between hydroxyl groups of goethite and pulp, there is still a considerable amount of controversy as to how iron is attached to mechanical pulps and in what chemical form it is present. Ogiwara and Kubota¹⁸⁹ claim the existence of two types of iron in mechanical pulps. The easily removable type, which is combined by weak ionic bonds to the carboxyl groups of the cellulosic material, is believed to be iron (II) iron. The more tenaciously held iron, which is joined by strong chelate bonds to the carbonyl groups of the cellulosic material, is probably iron (III) iron. The authors^{189,190} have also found that calcium ions show the same behavior as iron (II) iron and that ceric ions behave similarly to iron (III) iron. The adsorption of either calcium or iron (II) iron to cellulose occurs very rapidly and does not depend upon variables such as time, temperature or concentration. With iron (III) and ceric ions, on the other hand, the adsorption is much more influenced by the treatment temperature, time and concentration. In closely related work, Rothenberg and Robinson¹⁸¹ have also demonstrated

There have been no reports on the mechanisms of copper adsorption and binding by mechanical pulps. It is well known, nevertheless, that copper can easily form complexes with cellulose and cellulose derivatives¹⁹³⁻¹⁹⁶. The reaction of

not known¹⁸³. explanations is the fact that the hydroxide $Fe(OH)_3$ as such is negatively-charged cellulose micelles. The only drawback to these adsorption of positively-charged iron (III) hydroxide micelles by hydroxyl groups of iron (III) hydroxide or possibly by the hydrogen bridges between the hydroxyl groups of cellulose and the concluded instead that bonding takes place either through the strong bonding of iron (III) iron to cellulose. They workers¹⁹² have shown that carbonyl groups are not involved in In contrast to the opinions of Ogiwara and Kubota¹⁸⁹, other

pulps^{113,180,181,191}. hand, have proven very ineffective in removing iron from 0.1-0.5 % chelating agent) with Na_5DTPA or Na_4EDTA , on the other Na_4EDTA . Conventional pretreatments (30 min, room temperature, after treatment of the pulp for 3 days at 80° C with 1.0% iron content of kraft pulp could be reduced from 106 to 2 ppm aminopolycarboxylates. Sjöström and Valttilä¹²⁶ showed that the chelation of this iron in the pulp by chelating agents such as chelation of iron (III) iron by the pulp finds parallel in the The effect of temperature, time and concentration on the necessary.

that in order to adsorb iron (III) iron tightly to the pulp, higher temperatures, higher pH values or, prolonged times are

Cu(OH)_2 with cellulose under alkaline conditions is actually a way of synthesizing copper-cellulose complexes¹⁹⁷. Copper hydroxide reacts with the two secondary hydroxyl groups of glucose units forming well-defined compounds.

The distribution of the transition metals in the pulpwood fibers is not yet known. However, the distribution of these metals in wood tissues has been thoroughly investigated by Saka and Goring¹⁹⁸. By using transmission electron microscopy coupled with energy dispersive x-ray analysis (TEM-EDAX), the authors determined that almost all of the transition metals were localized and concentrated in the torus and half-bordered pit membrane regions. The total content of inorganic constituents decreased in the order, torus > half-bordered pit membrane > middle lamella > ray parenchyma cell wall > tracheid secondary wall. Overall, the concentration of inorganic constituents in earlywood was higher than that in latewood for each of the morphological regions studied¹⁹⁸.

STABILIZING SYSTEMS
CHAPTER II - HYDROGEN PEROXIDE STABILITY IN THE ABSENCE OF

FACTORS AFFECTING HYDROGEN PEROXIDE STABILITY IN THE BRIGHTENING
OF MECHANICAL AND CHEMIMECHANICAL PULPS

1. INTRODUCTION

One of the main drawbacks in using hydrogen peroxide for pulp brightening is its tendency to decompose with concomitant loss of brightening capacity. Under certain conditions, this loss may represent as much as one-third of the peroxide's oxidative capacity¹³. Additionally, the products of the hydrogen peroxide decomposition (O_2 , $HO\cdot$, and $O_2^{\cdot-}$) may participate in chromophore-producing reactions¹⁹⁹.

The mechanism of hydrogen peroxide decomposition under brightening conditions is not completely clear. Many efforts have been made to clarify this issue, but a satisfactory answer has not yet been achieved mainly because of contradictions concerning the homogeneous or heterogeneous character of the reaction^{200,201}, its pH dependence^{1,21,24} and kinetics^{202,203}, and the rate-influencing effects of potential impurities³⁵. Basically, five mechanisms have been proposed to account for the decomposition reaction, the first three being the most widely accepted: (1) a base-catalyzed ionic mechanism^{1,20}, (2) a base-catalyzed free radical mechanism⁴², (3) a transition metal-catalyzed free radical mechanism⁷⁶, (4) a transition metal reaction with perhydroxyl anions to form unstable peroxides or complexes⁵⁶⁻⁵⁸, and (5) a heterogeneous surface-catalyzed reaction caused by colloidal transition metal hydroxides^{61,62}.

It is possible that more than one mechanism is operative during brightening. For example, a recent investigation has demonstrated that peroxide decomposition catalyzed by transition

metals occurs by different pathways depending upon the metal involved³¹. In this regard, special attention must be paid to the mechanisms of peroxide decomposition catalyzed by iron, copper and manganese because they usually are present in relatively large amounts during the brightening of mechanical pulps. It is unreasonable, however, to assume that all five proposed mechanisms are operative during brightening.

The right choice of suitable stabilizing systems for peroxide brightening liquors as well as of appropriate brightening conditions depends upon the mechanism of peroxide decomposition. Therefore, a full understanding of this mechanism is of fundamental importance.

The objective of this investigation was to clarify the mechanism of peroxide decomposition under brightening conditions. To achieve this goal a systematic repetition and re-evaluation was undertaken of several reported studies which produced often-conflicting information relating to the influence of various factors affecting peroxide stability under conditions relevant to pulp brightening. These factors included peroxide concentration, pH, pH control, temperature, chemical purity, ionic strength, chelating agents, free radical concentration, and transition metal solubility and concentration.

2. MATERIALS AND METHODS

2.1. Reagents

All of the chemicals used in this study were reagent grade. Additional purification of sodium hydroxide solutions was performed to remove traces of transition metals. The solutions were purified by using the complexing agent, phenyl-2-pyridyl ketoxime, according to the method proposed by Trussel and Diehl²⁰⁴. Hydrogen peroxide solutions were not purified. The metal contents of the various solutions are shown in Table 1. The water used throughout all the experiments was doubly-distilled.

TABLE 1. Concentrations of Metals in Hydrogen Peroxide and Purified and Unpurified Sodium Hydroxide Solutions.

Chemical Solution	Metal Concentration, ppm				
	Fe	Cu	Mn	Ca	Mg
H ₂ O ₂ 1 M	0.014	<0.01	<0.01	0.06	<0.01
Unpurified NaOH 1 M	0.12	0.013	<0.01	0.06	0.03
Purified NaOH 1 M	0.02	<0.01	<0.01	0.08	0.03

In experiments involving the addition of transition metals to the reaction systems, the following salts were used : FeCl₃ · 6 H₂O, CuSO₄, and MnSO₄ · H₂O. A 0.005 M solution of each metal was prepared by dissolving the salt in 0.1 M HCl.

In the ionic strength experiments, variation of ionic strength was achieved by adding varying amounts of sodium chloride to the reaction mixture.

2.2. Peroxide Decomposition Tests

The reactions were carried out in polyethylene bottles previously cleaned by washing with aqua regia and then rinsing several times with doubly-distilled water. All glassware used for handling and transfer of chemicals was washed using this same procedure.

Solutions containing all chemicals except hydrogen peroxide were heated to the desired temperature and the required amount of hydrogen peroxide was then added. After the addition of peroxide, the reaction vessels were immersed in a water bath maintained at the desired temperature ($\pm 1^\circ \text{C}$) and the reactions allowed to proceed. At the end of each reaction the solutions were cooled and hydrogen peroxide residuals were measured in duplicate using the iodometric procedure described by Kraft²⁰⁵. Hydrogen peroxide decomposition was calculated as the difference between added and residual hydrogen peroxide. All results reported are averages of duplicate experiments.

In all experiments, the order of addition of the chemicals was as follows: (1) water, (2) transition metals, (3) sodium hydroxide, and (4) hydrogen peroxide, with stirring between additions.

2.3. pH Measurement and Control

The pH measurements were uniformly carried out at the reaction temperature. A Fisher electrometer model 380 equipped with a temperature-resistant Accu-pHast combination electrode

(Fisher Scientific) was used for the measurements. For the experiments in which pH values were kept constant throughout the reaction, a Fisher automatic titrimeter model 381 was used. The titrant was 0.1 N HCl.

2.4. Determination of Hydroxyl and Superoxide Anion Radicals

The measurement of hydroxyl radicals was performed according to the procedure described by Baxendale and Magee ²⁰⁶, which consists of the hydroxylation of benzene by hydroxyl radicals formed during peroxide decomposition. At the end of each reaction the excess benzene was extracted with hexane and the phenols formed in the reaction were extracted with ether and determined by high-pressure liquid chromatography (HPLC) using a 10 cm/ 8 mm Radial-PAK C₁₈ cartridge column (Waters Assoc.) as the stationary phase and a mixture of 55% methanol and 45% water (2 mL/min) as the mobile phase. The HPLC unit was manufactured by Waters Associates and was composed of the following elements: automated gradient controller, model 680; pumps, model 510; absorbance detector, series 440; universal liquid chromatography injector, model U6K; and data module, model 740.

Superoxide anion radical concentration was determined by electron paramagnetic resonance (EPR) spectrometry. Samples were withdrawn from the reaction mixture at a pre-determined time, placed in 4-mm (ID) EPR cells, purged with nitrogen, and immediately frozen in liquid nitrogen. The EPR measurements were

made at approximately 120 K temperature with an E-line Varian spectrometer Model E9. With the exception of receiver gain, the following EPR conditions were kept constant throughout the experiments: time constant = 1 s, scan time = 1 min, modulation amplitude = 0.8 G, modulation frequency = 100 KHz, microwave power = 56 mW, and microwave frequency = 9.0895 GHz. The radical concentration was determined by comparison of the area under the absorption curve for the superoxide anion radical with that for 2,2'-diphenyl-1-picrylhydrazyl (DPPH) in benzene.

2.5. Ultrafiltration of Transition Metal Solutions

Samples (200 mL) of 0.34 mM solutions of iron, copper, and manganese were prepared at pH 9.8, 10.8, or 11.8 from 0.005 M solutions of these metals. The solutions were then heated to 50°C, allowed to stand for 120 min and then ultrafiltered through 02 Diaflo membranes (Amicon Corp.) of 1000 molecular mass cutoff. After 95 % of the solution volume had been filtered, the residues remaining on the membranes (retentates) were washed 6 times with 10-mL portions of purified sodium hydroxide solutions having the same pH. The original filtrate and washings were combined to provide a total of 250 mL. The 10 mL of solution retained on the membranes was diluted to 250 mL with an aqueous NaOH solution having the same pH value. The transition metal content of the filtrates and retentates was subsequently determined.

2.6. Determination of the Metal Content of the Solutions

The iron, copper and manganese contents of the solutions were determined by flame atomic absorption spectroscopy with Zeeman effect background correction. The concentrations of calcium and magnesium were determined by conventional flame atomic absorption spectroscopy. A Perkin-Elmer spectrophotometer model 403 was used for the measurements.

3. RESULTS AND DISCUSSION

3.1. Effect of Reaction Variables on Peroxide Decomposition

3.1.1. Hydrogen Peroxide Concentration

Hydrogen peroxide concentrations in the range 0.040 to 0.392 M which correspond to 0.41 to 4.0% peroxide on o.d. pulp at 25% consistency were selected as bracketing the range most commonly used in commercial brightening.

The effect of 0.040 and 0.098 M hydrogen peroxide concentrations on its extent of decomposition at 50° C in the pH range 9.8 to 11.8, is shown by the plots in Figures 4-8. A slightly greater extent of peroxide decomposition was observed at the higher initial concentration, the difference being more significant (~5%) at pH 10.8 where decomposition was more pronounced (Fig. 6).

For all practical purposes, the differences in the extent of peroxide decomposition observed for the two concentrations were

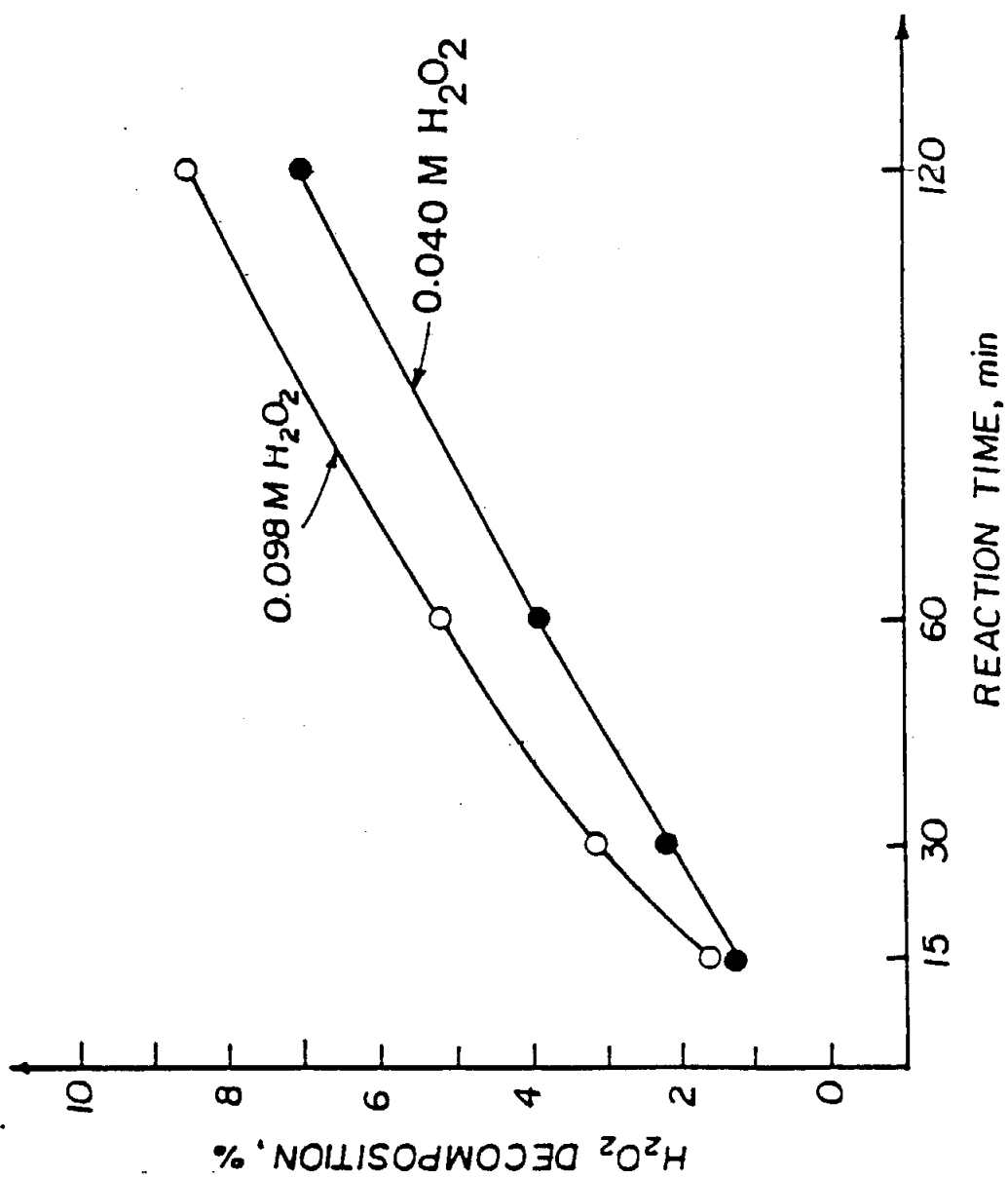


Figure 4. Effect of concentration on the extent of H_2O_2 decomposition. (initial pH 9.8, 50°C).

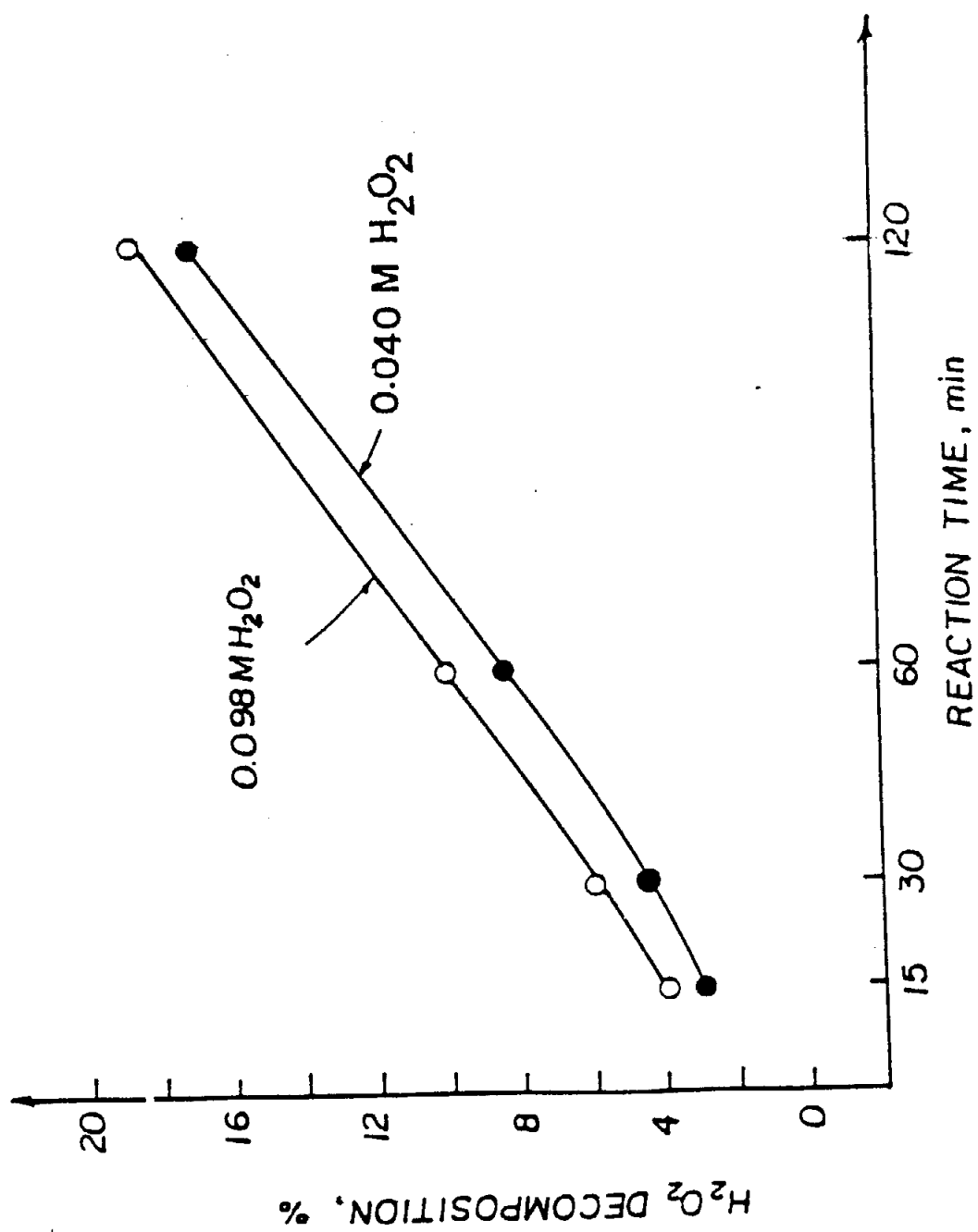


Figure 5. Effect of concentration on the extent of H_2O_2 decomposition. (initial pH 10.3, 50°C).

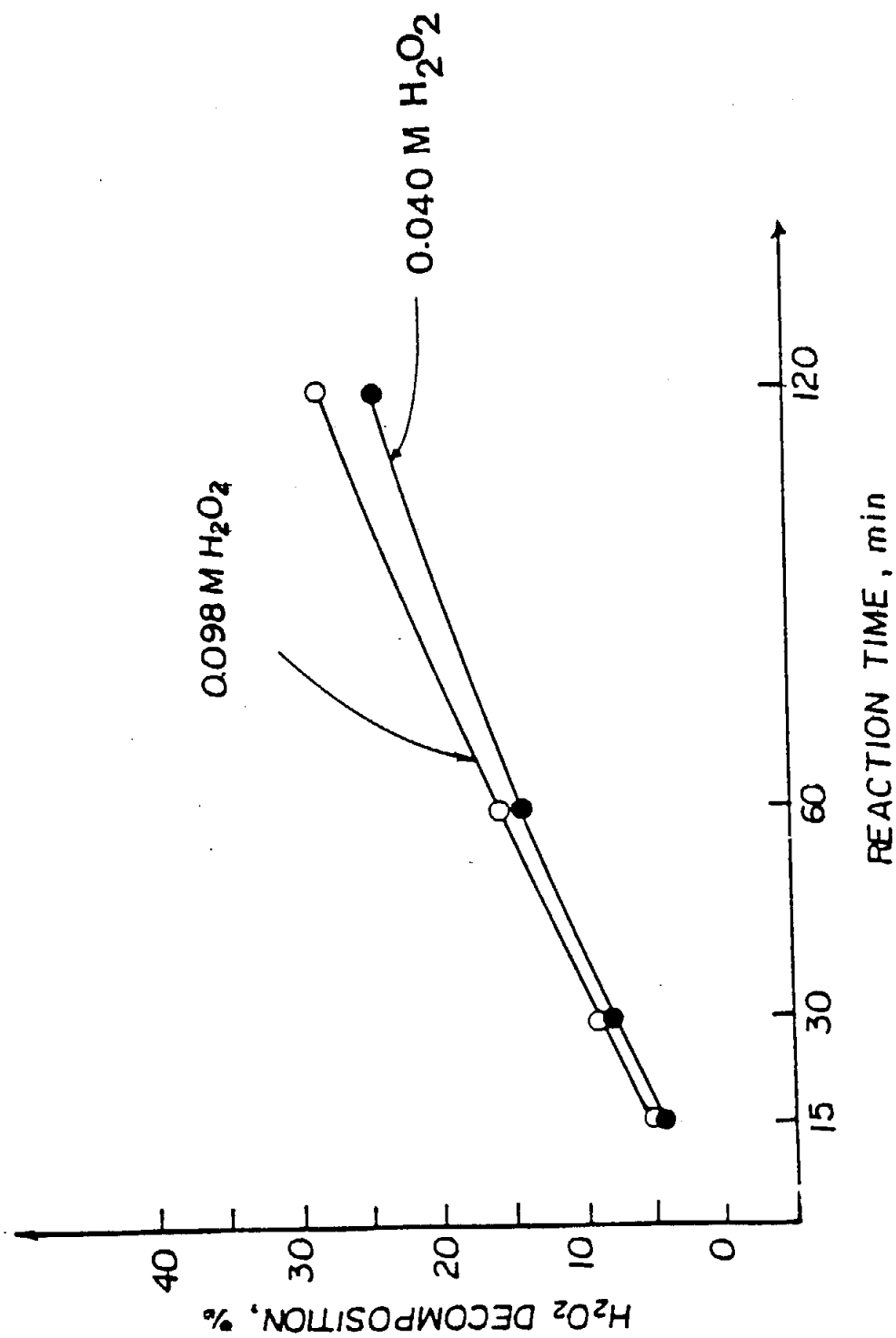


Figure 6. Effect of concentration on the extent of H_2O_2 decomposition. (initial pH 10.8, 50°C).

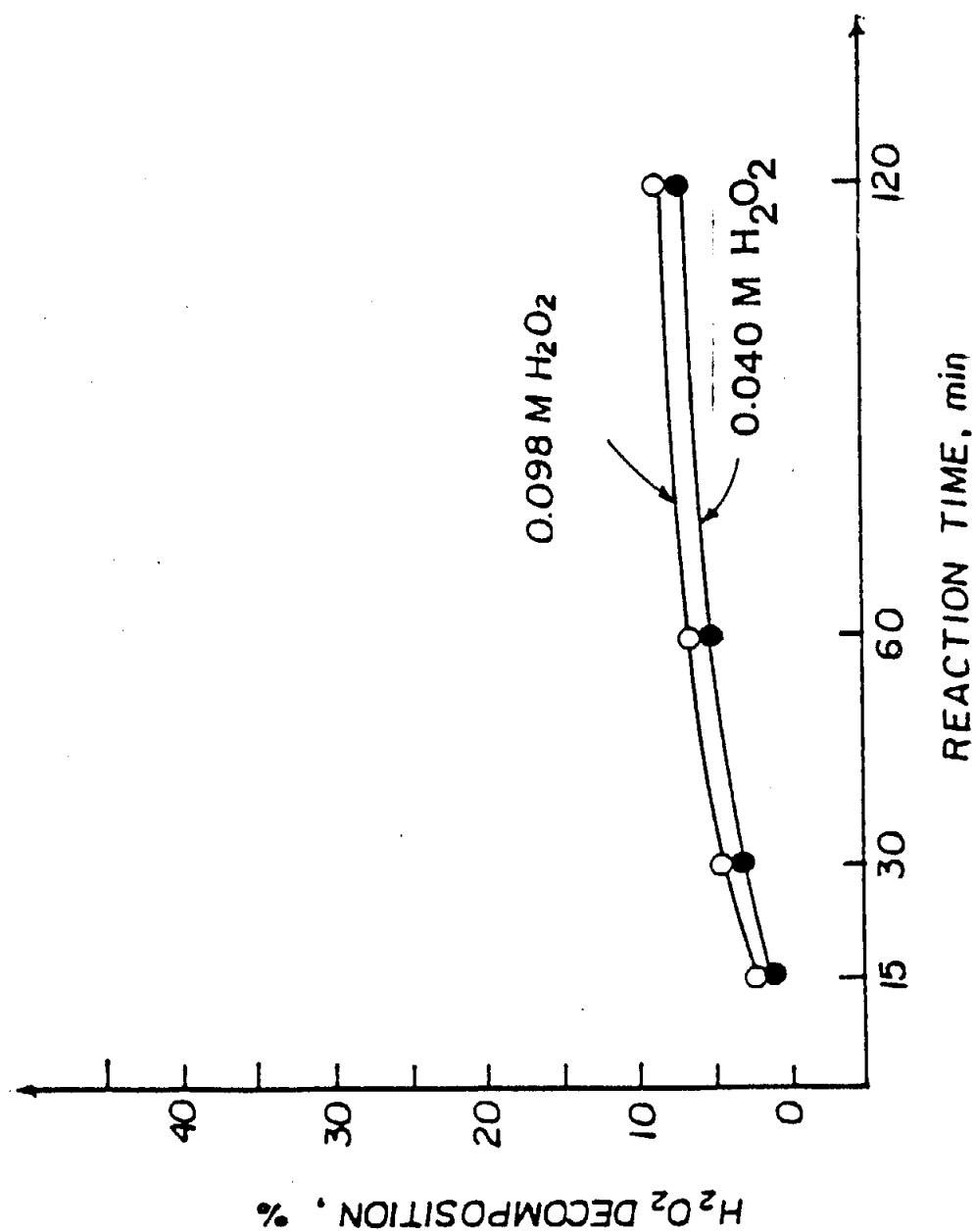


Figure 7. Effect of concentration on the extent of H_2O_2 decomposition. (initial pH 11.3, 50°C).

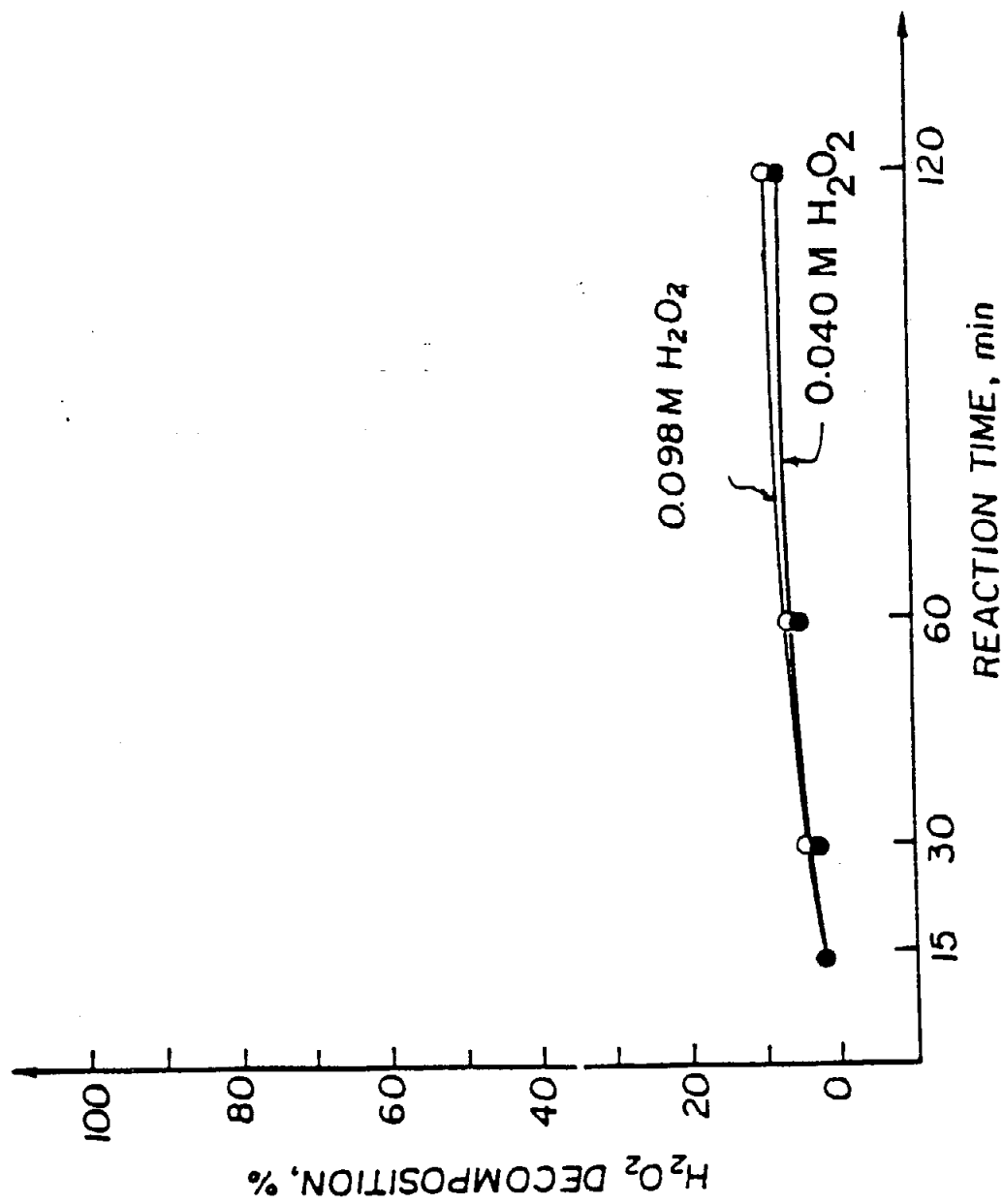


Figure 8. Effect of concentration on the extent of H_2O_2 decomposition. (initial pH 11.8, 50°C).

not very significant. In order to establish whether the extent differences were real, a broader range of peroxide concentrations (0.040 - 0.392 M) was investigated. The results presented in Table 2 show that peroxide decomposition is indeed influenced by its initial concentration; decomposition more than doubled as a result of increasing peroxide concentration from 0.098 M (1% H_2O_2 on o.d pulp at 25% consistency) to 0.392 M (4% H_2O_2 on o.d. pulp at 25% consistency). These findings contradict the results of the kinetic studies of Duke and Haas¹ which showed no dependence of peroxide decomposition on its initial concentration in the range of 0.1 to 1.1 M.

TABLE 2. The Effect of Concentration on the Decomposition of Hydrogen Peroxide. (initial pH 10.8, 50° C, 120 min).

H_2O_2 Conc., M	H_2O_2 Decomposition, %	Final pH
0.040	23.2	10.9
0.098	28.5	11.0
0.196	40.0	11.2
0.294	51.8	11.4
0.392	59.2	11.5

The increase in pH observed with increasing decomposition (Table 2) is a result of the generation of hydroxyl ions as illustrated in equation [1], section 1.1.1.

3.1.2. pH Control

To investigate the proposed theory that hydroxyl ions

enhance peroxide decomposition^{139,150}, a study was undertaken in which the pH of the system was kept constant over the entire course of the reaction in the absence of buffers. The hydroxyl ions generated in the decomposition reaction were neutralized by automatic titration with hydrochloric acid. The results show that control of pH reduced decomposition slightly at lower pH values but enhanced it at pH values above 11.0 (Fig. 9). Although the differences in decomposition were too small to be a matter of concern, the trend was in the expected direction. At pH values above 11.0, peroxide decomposition decreases with increasing pH and, therefore, it is to be expected that by preventing the pH from rising above this level during the reaction, decomposition should, in fact, increase as shown in the figure.

3.1.3. Ionic Strength

Ionic Strength (I) of a solution is defined as:

$$I = 0.5 \cdot \sum C_i \cdot Z_i^2$$

where C_i is the molar concentration of the ions of the type i and Z_i is their valence²⁰⁷.

Ionic strength had no effect on peroxide decomposition within the range studied (0 - 1.0 M) (Fig. 10). Under actual brightening conditions, I values higher than 1.0 are unlikely to exist; thus, this variable has no effect during peroxide brightening as far as peroxide stability is concerned. However, ionic strength has been shown to have a small positive effect in

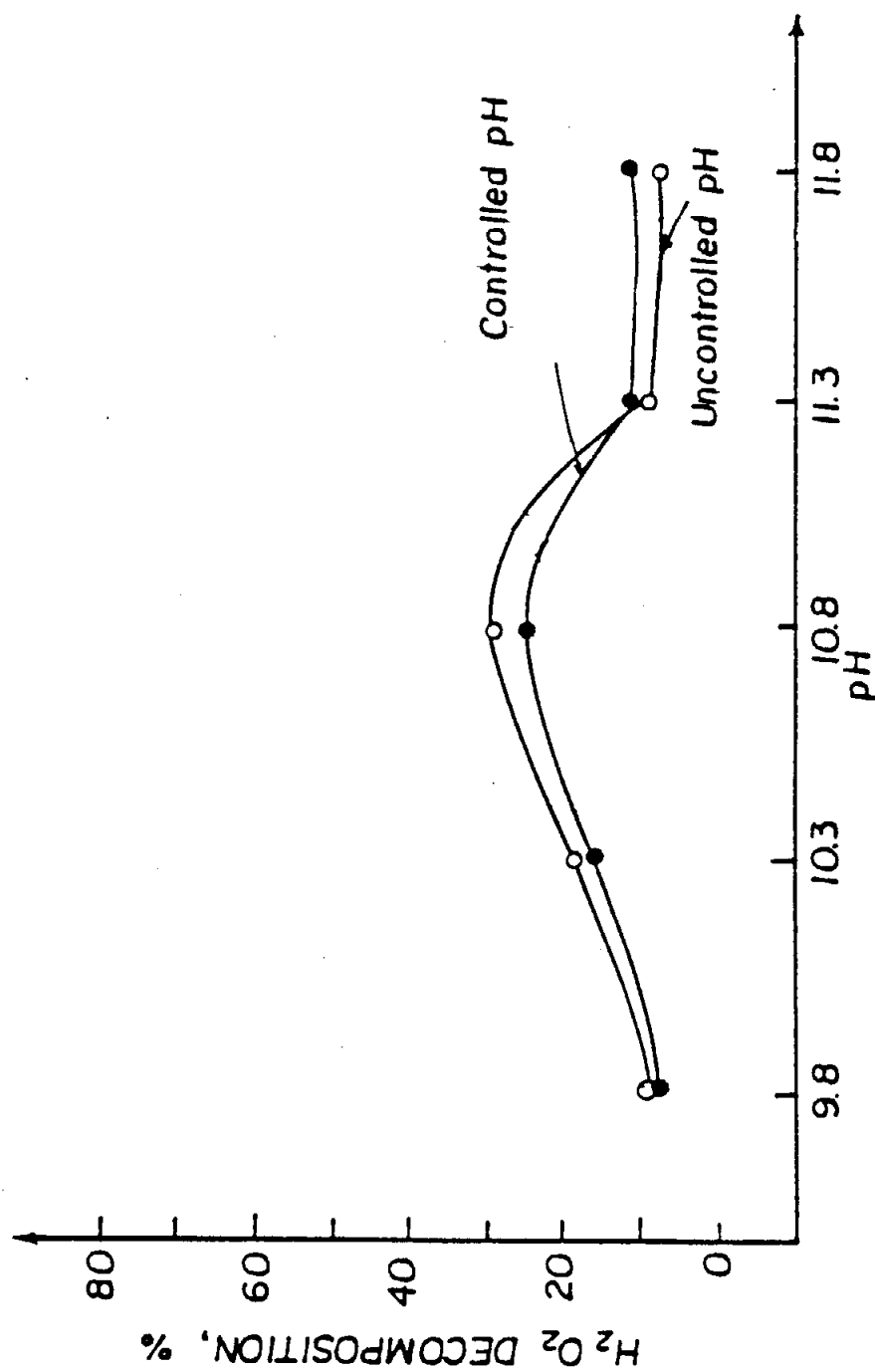


Figure 3. Decomposition of 0.098 M H_2O_2 under pH-controlled and pH-uncontrolled conditions. (50° C, 120 min).

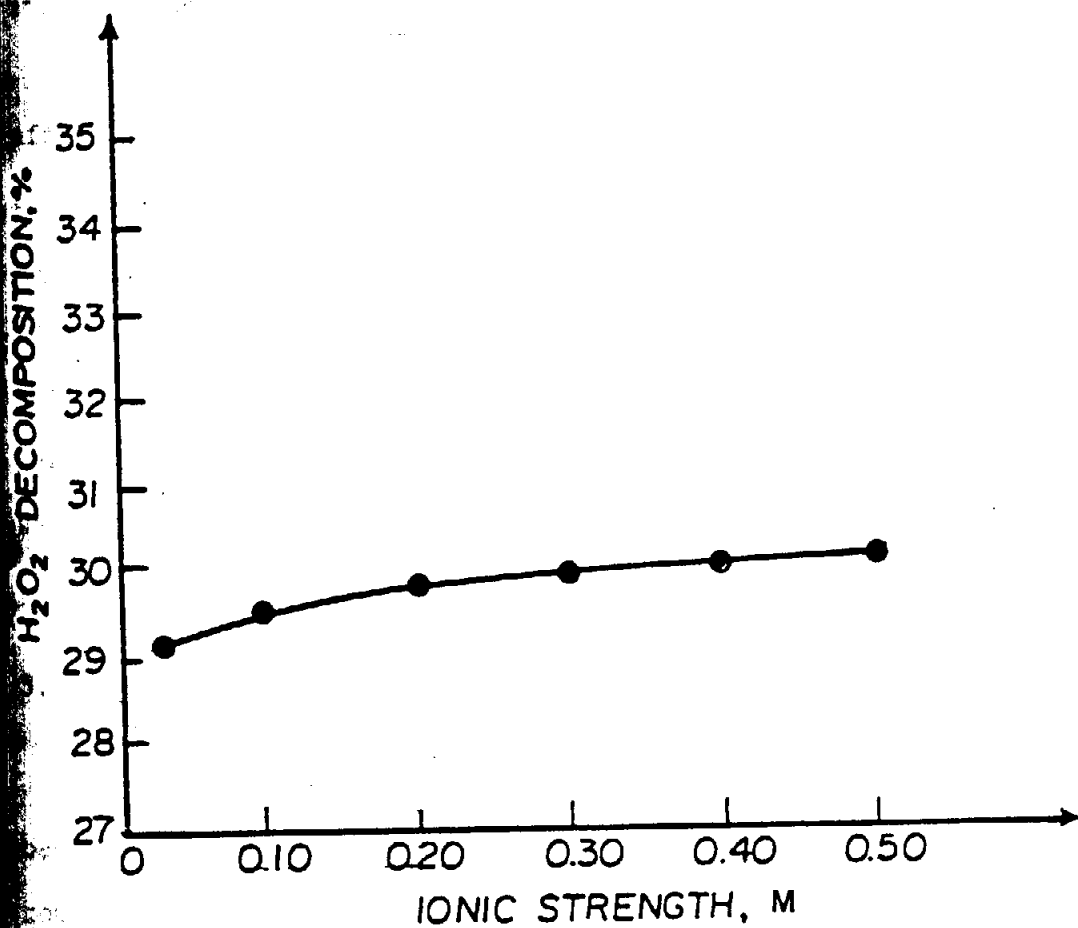


Figure 10. Effect of ionic strength on the decomposition of 0.098 M H₂O₂. (initial pH 10.8, 50° C, 120 min).

pulp brightening. Lundqvist¹⁵⁵ observed a slight decrease in the light absorption coefficient of spruce groundwood by increasing the ionic strength from 0.2 to 2.0 M. Kutney¹⁴⁶ attributed 20% of the brightness gain of groundwood to the increase in the ionic strength resulting from the addition of sodium silicate.

Alkaline hydrogen peroxide stability has been shown to be affected by the type of anion in solution²⁸. For example, sulfate anions are much more harmful to peroxide stability than are chloride anions²⁸. Therefore, the effect of ionic strength on peroxide stability has to be interpreted carefully since the anion of the salt used for ionic strength variation may influence peroxide stability. In this particular study, chloride anions were used to adjust ionic strength values since this anion has been shown to have a very small effect on peroxide stability²⁸.

3.1.4. Temperature

Temperatures of 50° and 60° C were chosen for this study because they are typical of those most generally used in commercial brightening²⁰⁸. The results in Figure 11 show that peroxide decomposition was enhanced approximately three-fold by increasing the temperature from 50° to 60° C. The decrease in peroxide stability with increasing temperature was also observed when transition metals were added to the solutions (Figs. 12-14). However, only in the case of copper (Fig. 13) was the effect as severe as that observed in the absence of added metals. No explanation for this fact has yet been found.

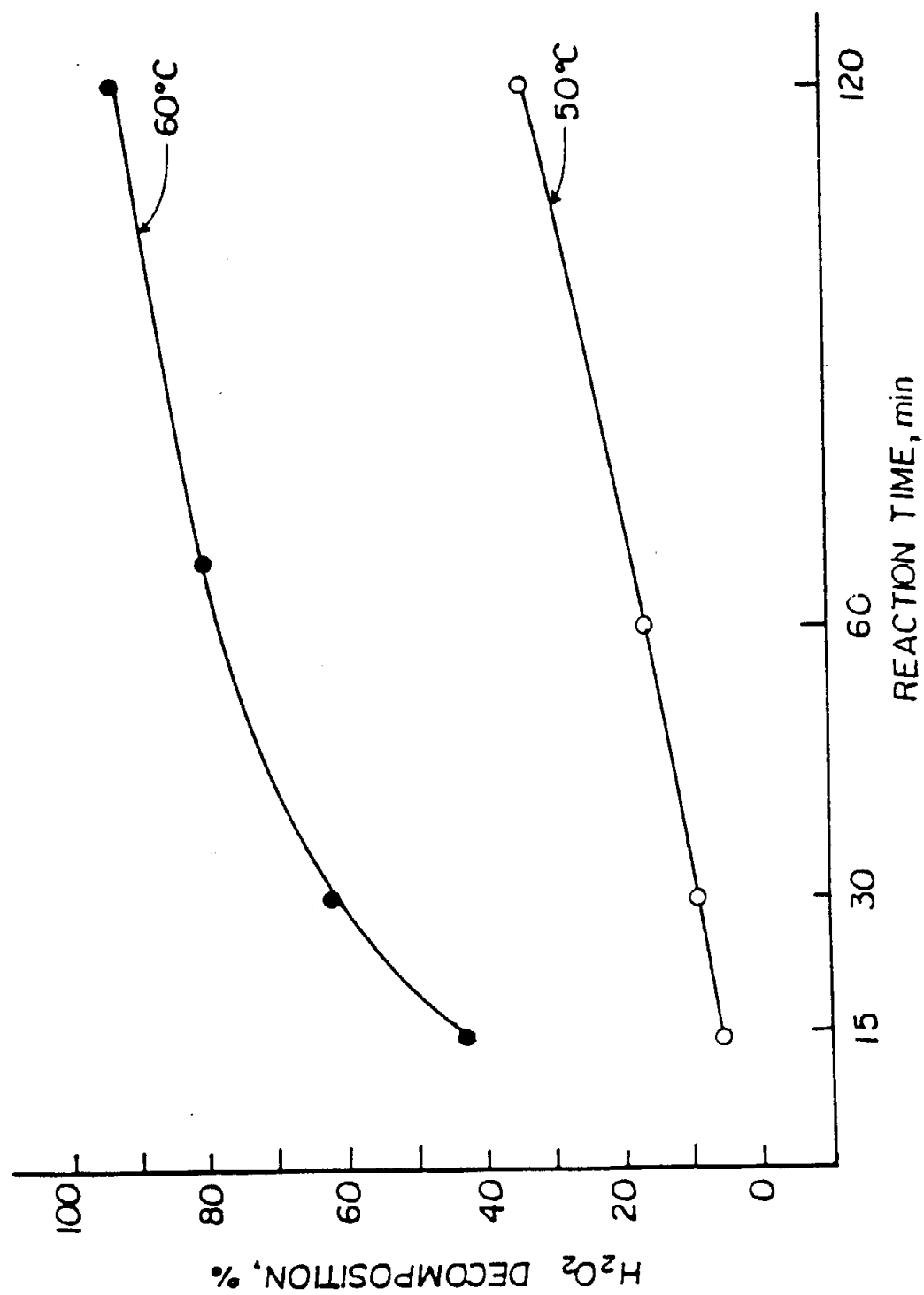


Figure 11. Effect of temperature on the extent of decomposition of 0.098 M H_2O_2 . (initial pH 10.8, 50°C).

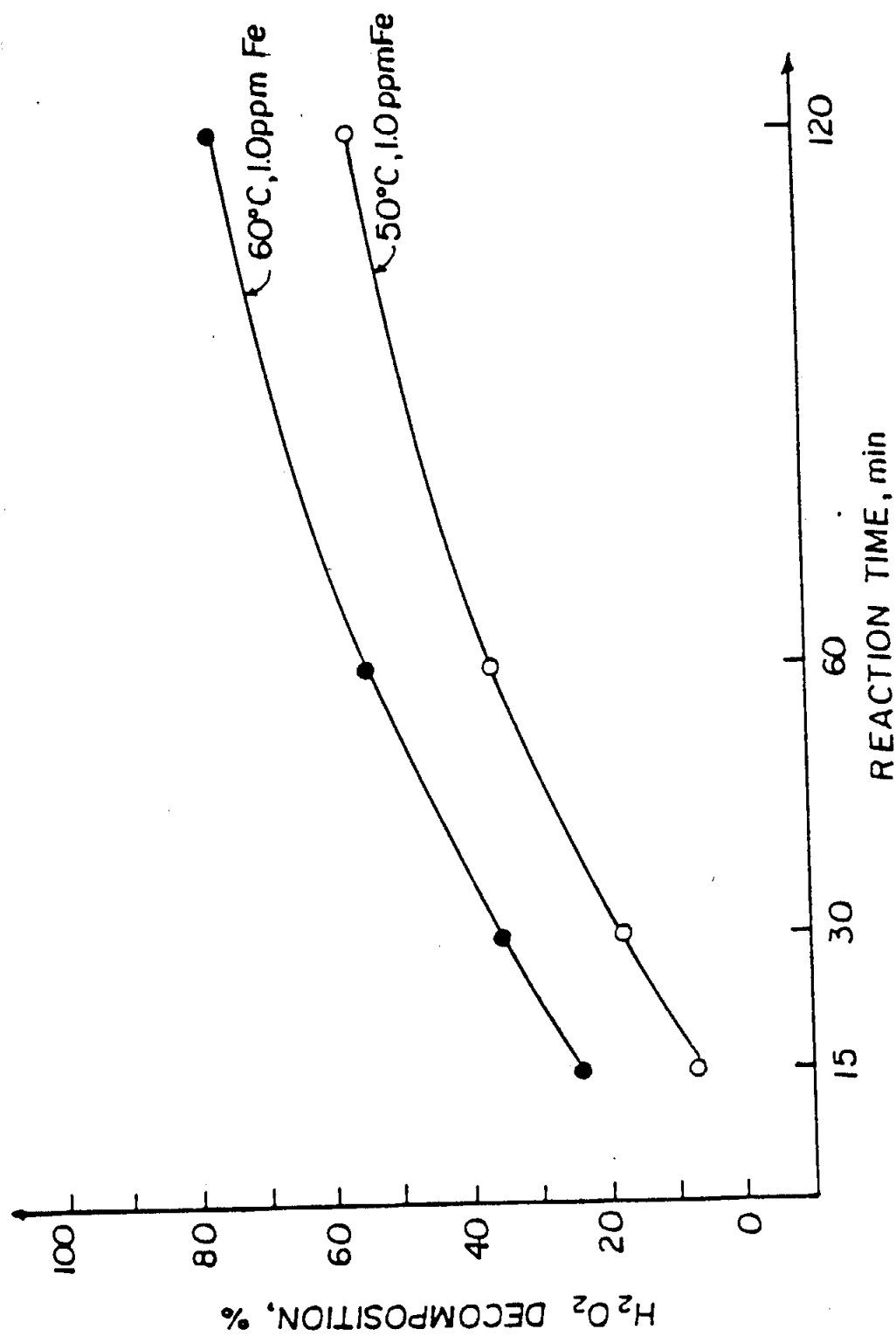


Figure 12. Effect of temperature on the extent of decomposition of 0.098 M H_2O_2 in the presence of iron. (initial pH 10.8, 50° C).

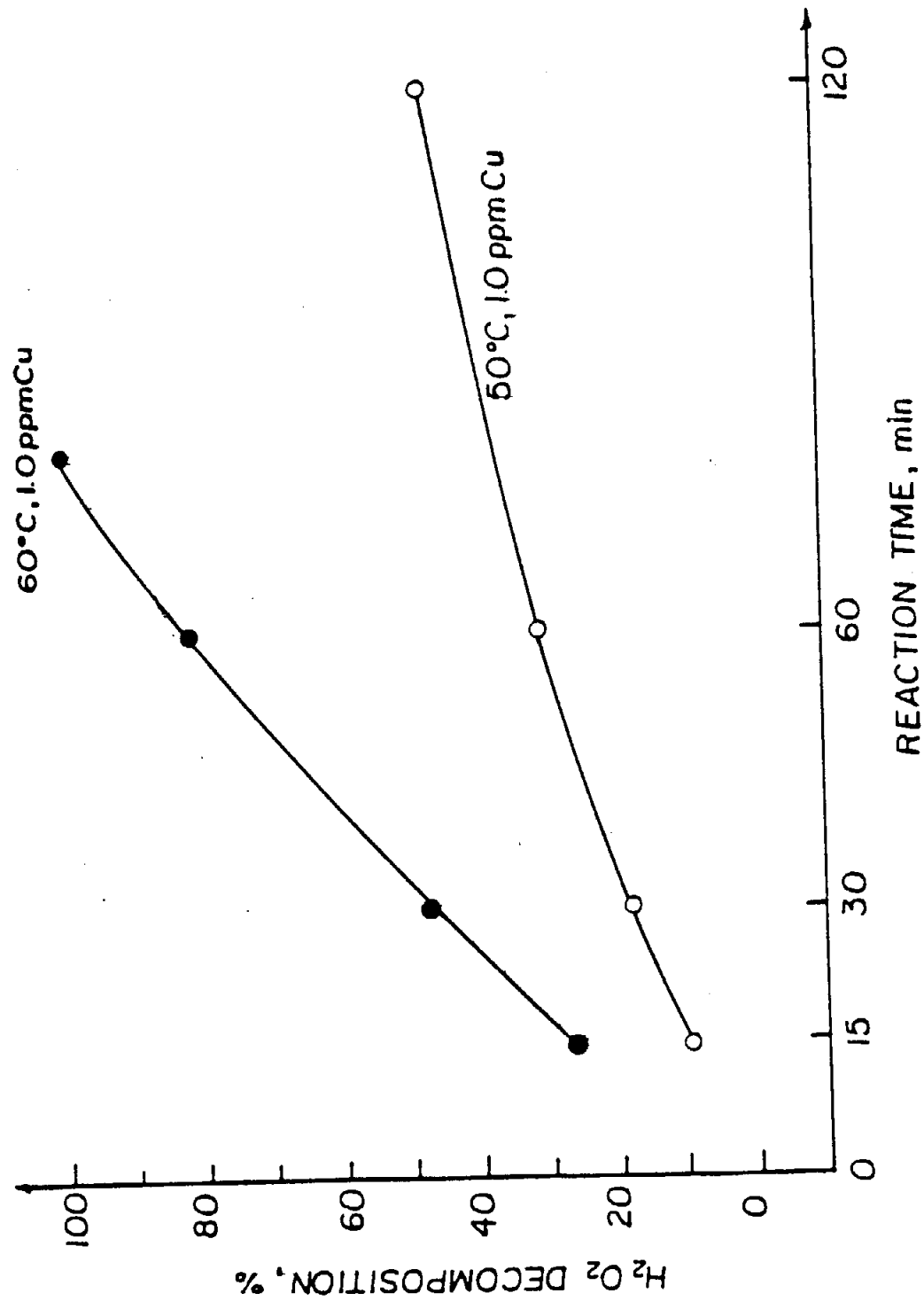


Figure 13. Effect of temperature on the extent of decomposition of 0.098 M H_2O_2 in the presence of copper. (initial pH 10.8, 50°C).

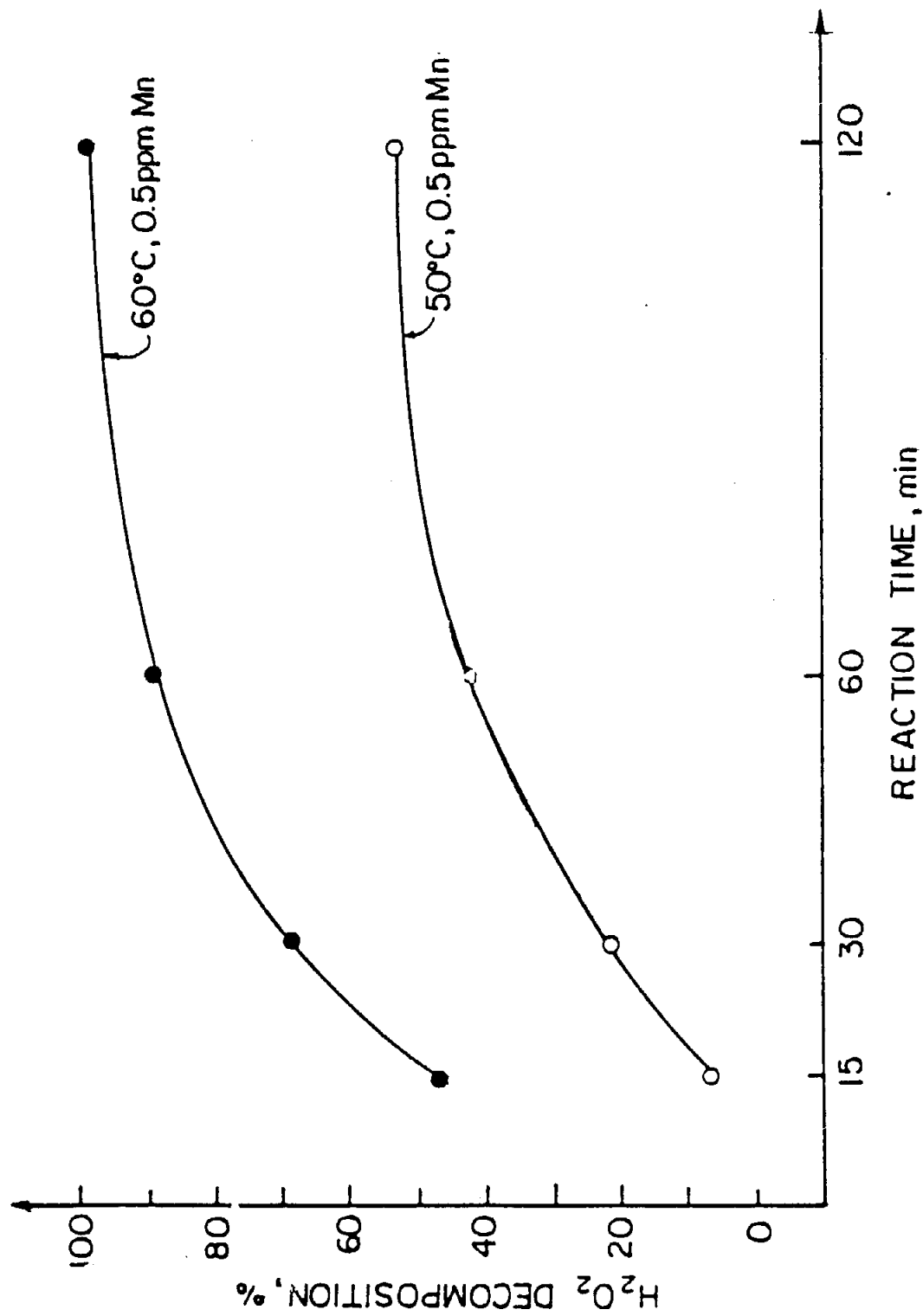


Figure 14. Effect of temperature on the extent of decomposition of 0.098 M H_2O_2 in the presence of manganese. (initial pH 10.8, 50°C).

3.2. Effect of Transition Metals on Peroxide Decomposition

3.2.1. Iron

The effect of varying iron concentration on peroxide decomposition at various pH levels is shown in Figure 15. At low concentration (0.5 ppm) iron acted as a peroxide stabilizer when the pH of the solutions was below 10.8. This trend has been observed by other workers¹⁸ but no explanation has been offered. Iron concentrations above 1.0 ppm increased hydrogen peroxide decomposition regardless of pH.

It is important to note that the catalytic activity of iron is greatly enhanced at pH values above 10.8. This behavior was initially postulated as being due to the redissolution of iron above this pH value with a resultant increase in the concentration of soluble iron, a more active catalyst for peroxide decomposition. To investigate this hypothesis, the solubility of iron solutions in the pH range 9.8 to 11.8 was assessed through an ultrafiltration experiment. A schematic representation and the results of this experiment are presented in Scheme 1 (page 93) where it is evident that undetectable amounts of iron were found in the filtrates of the solutions indicating that essentially no soluble iron exists in the pH range 9.8 to 11.8. Therefore, the enhanced peroxide decomposition observed at a pH above 10.8 is not caused by changes in iron solubility.

The reaction of iron with perhydroxyl ion, forming readily-decomposed iron-peroxide complexes has been proposed⁵⁶⁻⁵⁸. If

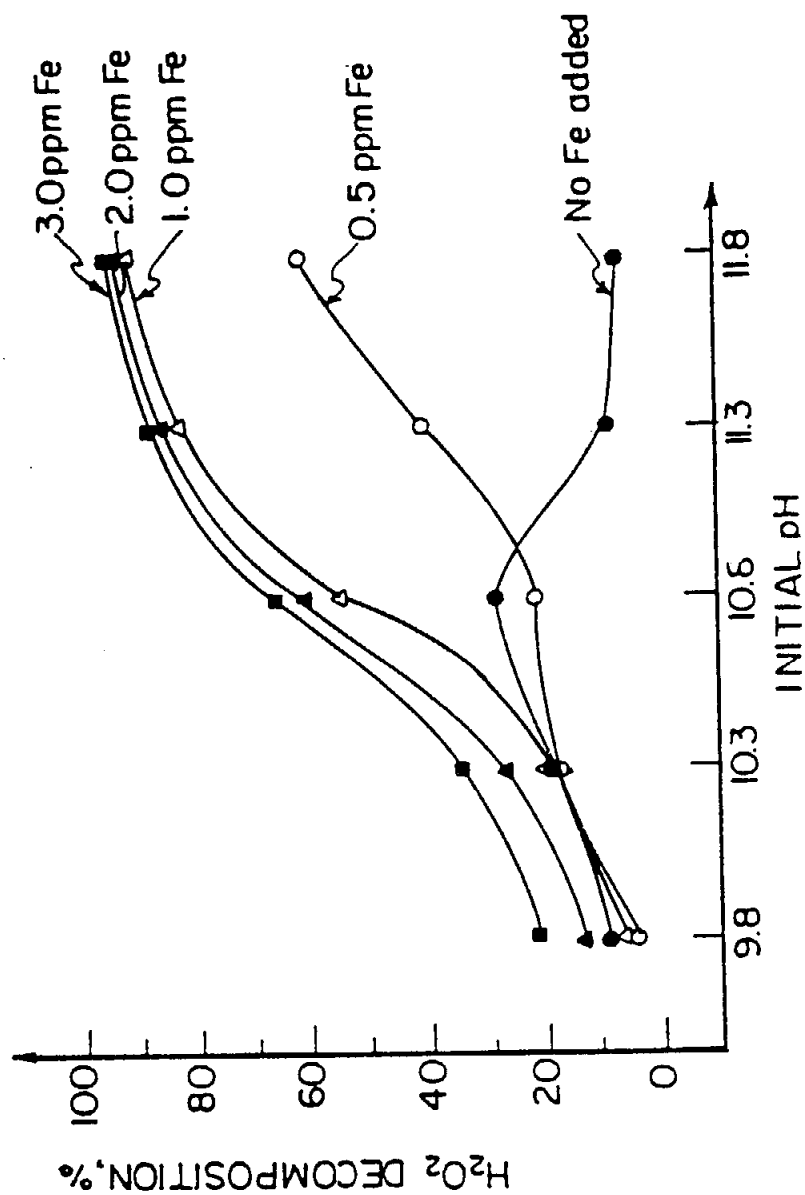


Figure 15. Effect of iron concentration on the decomposition of 0.098 M H_2O_2 . (50°C, 120 min).

the validity of this theory is assumed, higher pH values should result in higher decomposition extents because of the greater ionization of the peroxide. However, experiments conducted in the presence of iron with the same perhydroxyl ion concentration at pH 11.0 and 12.0 revealed that the extent of peroxide decomposition is much higher at pH 12.0 (Fig. 16), indicating that the amount of perhydroxyl anion present in the system is not the real cause of the increased peroxide decomposition at the higher pH value. In the above experiment the initial concentrations of hydrogen peroxide required to produce the same initial concentration of perhydroxyl anions at the two different pH values were calculated based on the assumption that the degree of peroxide ionization is 69% and 93% at pH 11.0 and 12.0, at 60°C, respectively¹⁴.

Changes in the composition and morphology of the iron residues with increasing pH were initially thought to be the cause of the enhanced peroxide decomposition at pH values above 10.8. However, the results presented in Table 3 partially discredit this hypothesis since the nature of the anion did not affect peroxide decomposition to any extent, and it is known that the composition and the morphology of the solid iron are strongly dependent on the nature of the anions in solution²⁰⁹.

All of the attempts made in this study to explain the greater effectiveness of iron as a peroxide catalyst at higher pH values in the range 9.8 to 11.8 failed. A more detailed investigation in this area emphasizing especially the effect of particle size of iron precipitates on peroxide decomposition and

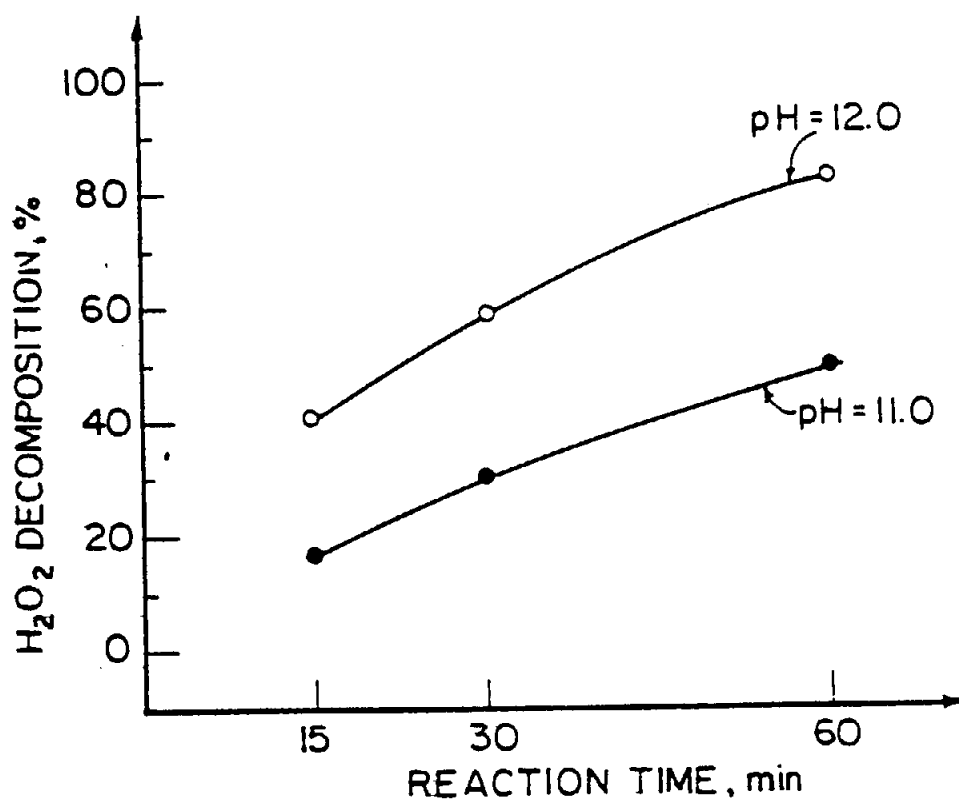


Figure 16. Effect of pH on the extent of H_2O_2 decomposition at equal initial perhydroxyl anion concentrations in the presence of iron. ($HO_2^- = 0.067$ M, Fe = 20 ppm, 60° C).

the effect of pH on the particle size of these precipitates seems to be in order.

TABLE 3. The Decomposition of 0.098 M H_2O_2 by Iron (III) Chloride, Iron (III) Nitrate, and Iron (III) Sulfate. (initial pH 10.8, RT, 120 min, Fe = 20 ppm).

Anion	H_2O_2 Decomposition, %
Sulfate	23.2
Chloride	24.0
Nitrate	22.9

3.2.2. Copper

At pH values below 10.8, the effectiveness of copper as a catalyst for peroxide decomposition was very similar to that of iron, but at higher pH values (10.8-11.8) copper became more deleterious to peroxide stability (Figure 17). The reason for the rather sharp increase in the catalytic activity of copper at the higher pH values is not known. As in the case of iron the increase in perhydroxyl anion concentration associated with increasing pH was shown not to be the cause for enhanced decomposition at higher pH values (Fig. 18). Moreover, ultrafiltration of copper solutions at pH values of 9.8, 10.8 and 11.8 demonstrated that the solubility of copper is not affected to any measurable extent by the pH (Scheme 1 - page 93). Therefore, differences in copper solubility do not explain the enhanced decomposition of peroxide at the higher pH values.

A possible explanation for the rather sharp enhancement of

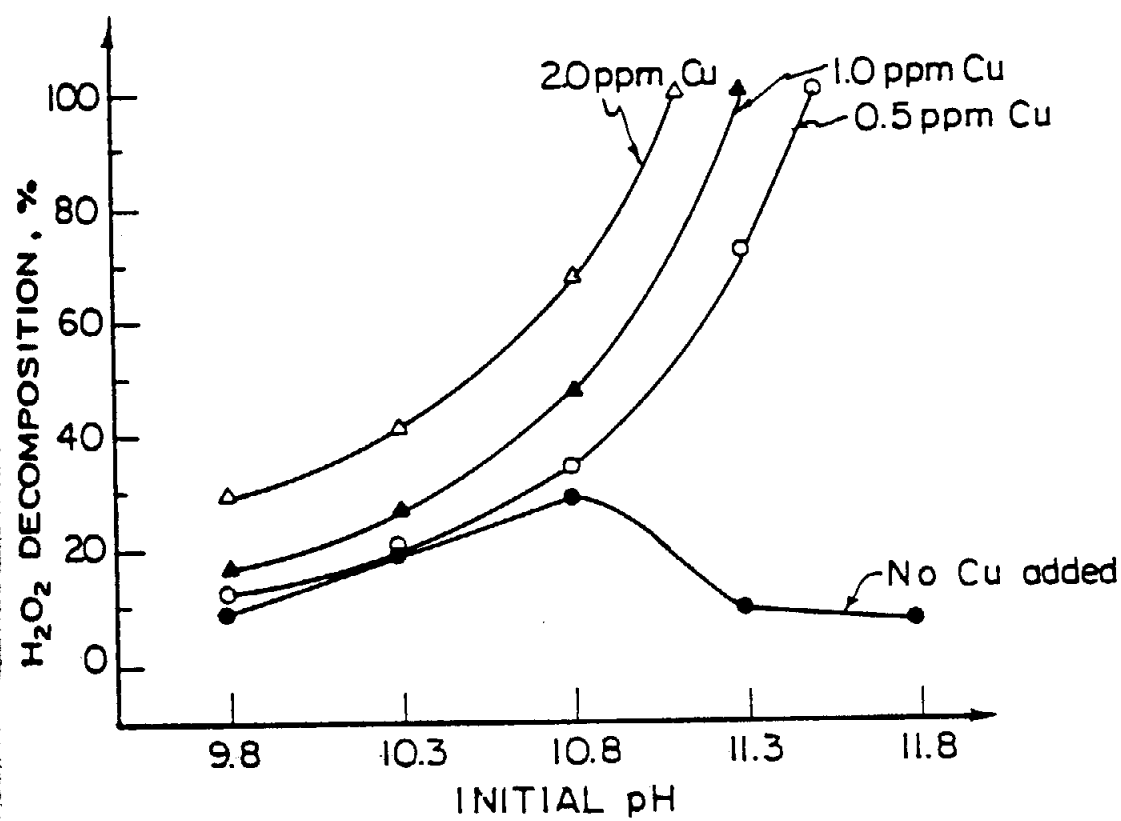


Figure 17. Effect of copper concentration on the decomposition of 0.098 M H_2O_2 . (50° C, 120 min).

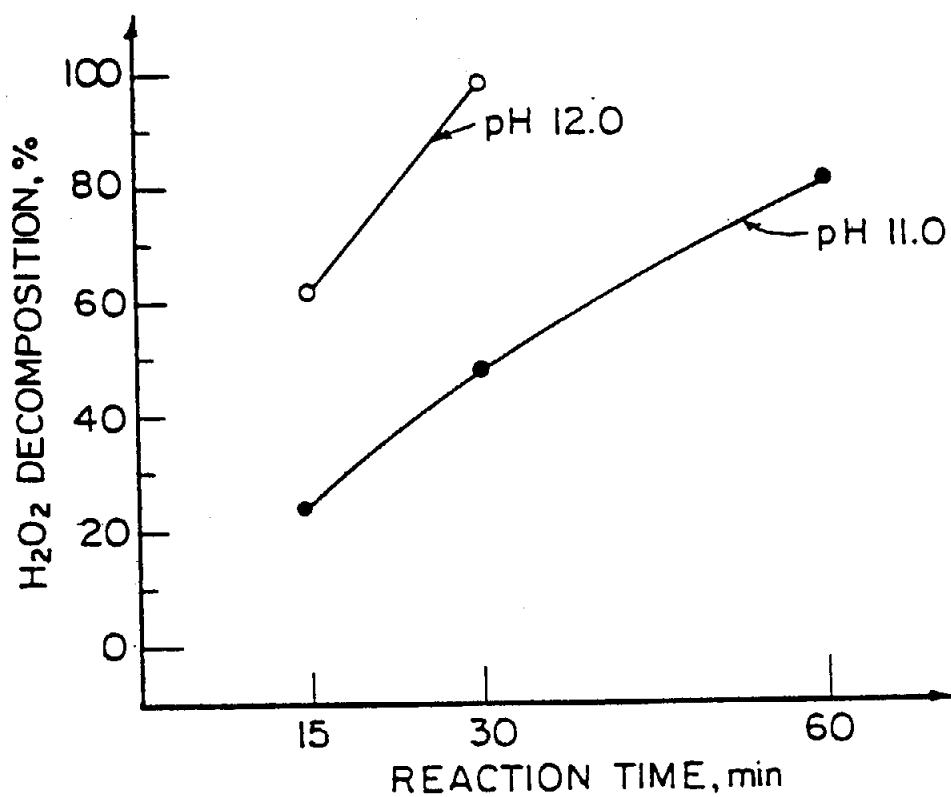


Figure 18. Effect of pH on the extent of H_2O_2 decomposition at equal initial perhydroxyl anion concentrations in the presence of copper. ($\text{HO}_2^- = 0.067 \text{ M}$, $\text{Cu} = 20 \text{ ppm}$, 60°C).

peroxide decomposition with increasing pH above 10.8 in the presence of copper may involve changes in the particle size of the copper (II) oxide precipitates which are formed under these conditions. This hypothesis needs to be investigated since the effect of pH values above 10.8 on copper (II) oxide particle size is not known nor is the effect of copper (II) oxide particle size on peroxide decomposition.

3.2.3. Manganese

Among the transition metals studied, manganese was the most effective catalyst for peroxide decomposition. For example, at pH 9.8 and 50° C, 0.5 ppm of manganese was sufficient to decompose all of the hydrogen peroxide in 2 hours (Fig. 19). The effect of pH on peroxide decomposition in the presence of manganese was very irregular. In the pH range investigated (9.8-11.8), a maximum and a minimum amount of decomposition was found at pH 9.8 and 10.3, respectively, regardless of the manganese concentration. The very high decomposition observed at pH 9.8 was first thought to be caused by manganese present in the form of free ions which supposedly catalyze peroxide decomposition rapidly via a redox mechanism⁶⁵. However, ultrafiltration experiments performed with manganese solutions showed that the solubility of manganese is extremely low in the pH range 9.8 to 11.8 (Scheme 1 - page 93). Thus, the hypothesis of a free ion-catalyzed reaction via a redox mechanism at pH 9.8

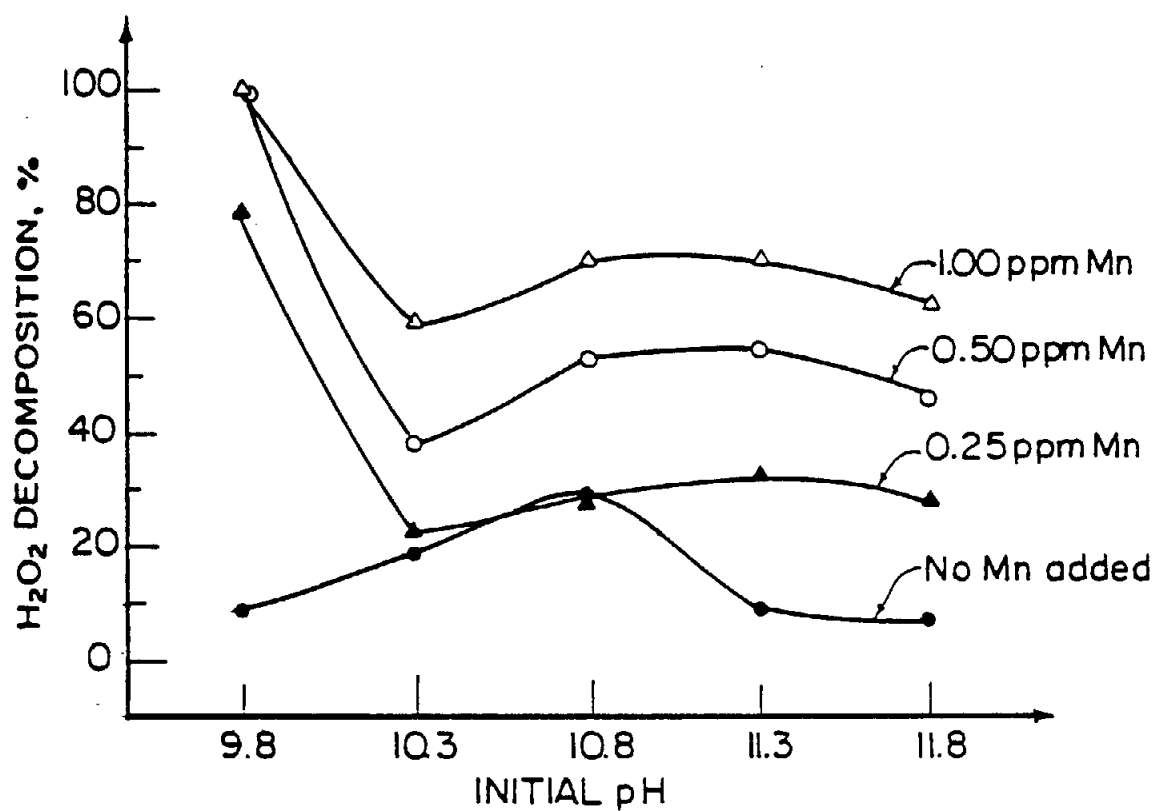
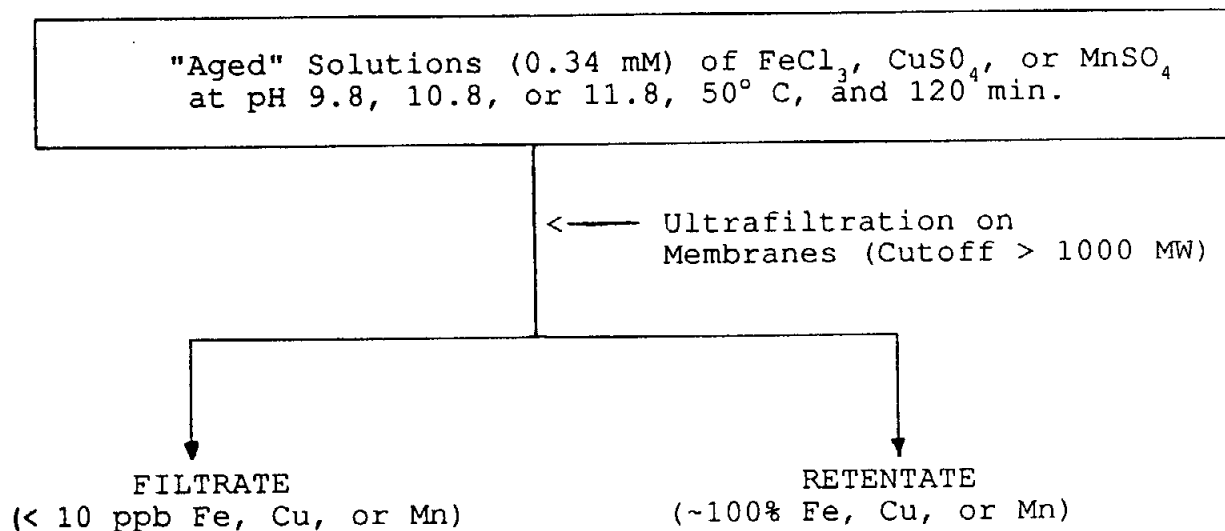


Figure 19. Effect of manganese concentration on the decomposition of 0.098 M H_2O_2 . (50° C, 120 min).

was discarded. Minimum decomposition at pH 10.3 has also been found by others and attributed to the formation of insoluble manganese hydroxide which supposedly is not an effective catalyst for peroxide decomposition¹⁴. At the concentrations of manganese used, however, the maximum yield of manganese hydroxide is obtained at a pH near 9.5²¹⁰; thus, minimum decomposition should have occurred at pH values lower than 10.3.



Scheme 1. The solubility of iron, copper, and manganese solutions.

The most likely manganese species in the pH range from 9.8 to 11.8 is manganese dioxide which is a very efficient peroxide catalyst^{61,146}. Manganese dioxide may exist in several chemical forms depending upon the pH of the solution²¹¹; this fact might explain its different catalytic activity at various pH levels.

The decomposition probably occurs via formation of unstable alkali peroxymanaganates (IV)²¹².

The fact that manganese is a very severe catalyst for peroxide decomposition at lower pH values (<10) is a matter of great concern in the peroxide brightening of mechanical pulps. The reactions of peroxide with pulp may lower the pH of the brightening system, initially in the range 10.5 to 11.0, very rapidly to values equal to or lower than 10. If manganese is not removed from the brightening system by any sort of pretreatment, this drop in pH may result in a large enhancement of its catalytic activity in the latter phases of the reaction.

3.2.4. Metal Combinations

The catalytic activities of iron, copper, and manganese combinations were investigated. Results comparing the individual and combined effects of the metals on the amount of peroxide decomposition are presented in Table 4. The concentrations of the transition metals were chosen in such a way that the sum of the individual effects of each metal and the decomposition of hydrogen peroxide in the absence of transition metals did not exceed 100%. Although the results obtained are interesting, a more thorough investigation of this topic is needed in order to draw any conclusion since the method used to asses synergism between metals is not applicable for all metal concentrations.

TABLE 4. Individual and Combined Effects of Transition Metals (Fe, Cu and Mn) on the Decomposition of 0.098 M H_2O_2 . (initial pH 10.8, 50° C, 120 min).

Metal Combination	H ₂ O ₂ Decomposition, %					Combined Effects
	Individual Effects					
	No Added Metals	Fe ¹	Cu ¹	Mn ¹	Total	
Fe + Cu + Mn	29.0	-7.0	5.0	-1.0	26.0	100.0
Fe + Cu	29.0	-7.0	5.0	-	27.0	100.0
Fe + Mn	29.0	-7.0	-	-1.0	21.0	68.0
Cu + Mn	29.0	-	5.0	-1.0	33.0	85.0

¹ Fe = Cu = 0.5 ppm, Mn = 0.25 ppm

3.2.5. Aging of the Metals

"Aged" transition metal solutions were prepared by boiling 0.005 M solutions of the transition metal salts for 3 h at pH 6.5. The pH value of 6.5 was selected in order to reproduce the pH conditions prevailing in the wood pulp and process water which are the sources of most of the transition metals found in pulp brightening. Metal solutions designated as "fresh" were prepared by dissolving the transition metal salts in 0.1 M HCl. Of the metals studied, iron was the only one whose catalytic activity was changed by the aging treatment (Table 5). The sharp decrease

In the catalytic activity of the iron solution caused by the aging may be explained by the formation of insoluble hydrous iron oxide which is a less severe catalyst for peroxide decomposition than is iron (III) ion. It should be pointed out that the iron present in nature or in pulp brightening very likely exists in the form of an insoluble hydrous iron oxide and therefore catalyzes peroxide decomposition at a lower extent.

TABLE 5. Decomposition of 0.098 M H_2O_2 by "Fresh" and "Aged" Solutions of Iron, Copper, and Manganese. (initial pH 10.8, 50° C).

Transition Metal	H_2O_2 Decomposition, %	
	"Fresh" Metal	"Aged" Metal
Fe (20 ppm) ¹	85.9	31.8
Cu (2 ppm) ¹	64.7	65.5
Mn (5 ppm) ²	85.9	83.6

¹ 2 h reaction

² 30 min reaction

The aging of the copper solution did not result in any significant change in its catalytic activity. These results can be explained by the fact that the catalytic activity of copper (II) ions is probably the same as that of the copper (II) oxide which is formed by the aging of the solutions.

Manganese does not "age" (i.e., forms no precipitate)

upon boiling the manganese (II) salt solutions at pH 6.5 for 3 h. Thus, it should not be expected that aging would cause any significant changes in its catalytic activity. Under alkaline brightening conditions, however, manganese "ages" to form manganese dioxide because the pH of the brightening liquors is usually above 10. The conversion of manganese (II) ion to manganese dioxide is a fast reaction at a pH above 10; thus, the active species during brightening is insoluble manganese dioxide.

Under the neutral conditions prevailing in biological systems, iron and copper will certainly exist in the form of insoluble hydroxides or oxides. Manganese, on the other hand, will exist in the form of free ions and that may explain why this metal is so easily removed from pulps simply by acid washing or by chelation.

3.3. Mechanistic Considerations

Three basic mechanisms have been proposed to explain peroxide decomposition under brightening conditions : (1) a base-catalyzed ionic mechanism involving the combination of undissociated hydrogen peroxide and its conjugate base (perhydroxyl anion) to form a six-membered ring in the transition state (Fig. 20)^{1,20}, (2) a base-catalyzed free radical chain reaction mechanism involving hydroxyl and superoxide anion radicals (Fig. 21)⁴², and (3) a transition metal ion-catalyzed free radical chain reaction mechanism involving hydroxyl and superoxide anion radicals (Fig. 22)⁷⁶.

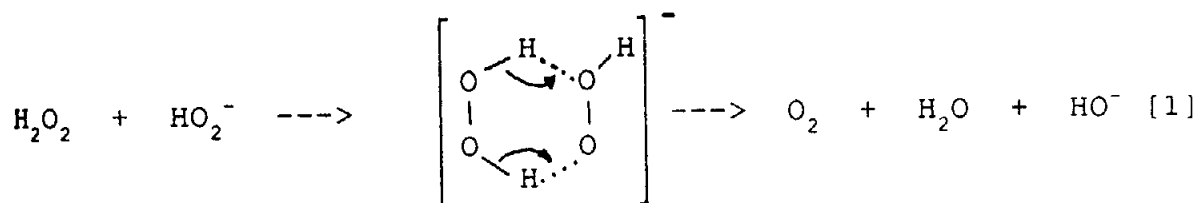
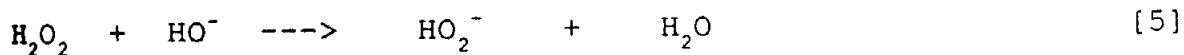


Figure 20. The proposed base-catalyzed ionic mechanism of peroxide decomposition²⁰.

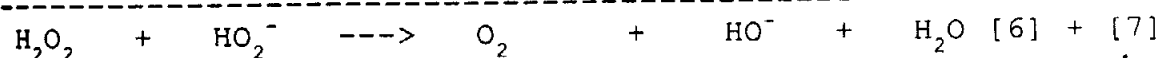
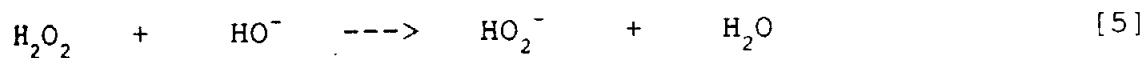
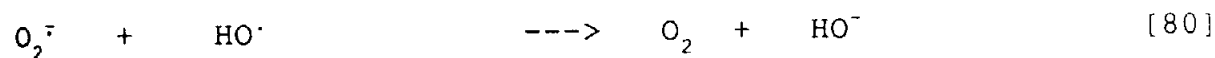
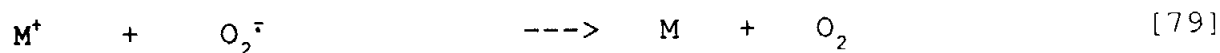
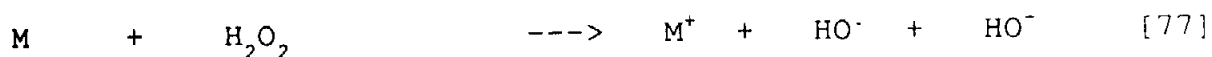


Figure 21. The proposed base-catalyzed free radical mechanism of peroxide decomposition⁴².



M = transition metal ion

Figure 22. The proposed transition metal ion-catalyzed free radical mechanism of peroxide decomposition⁷⁶.

In order to determine whether or not any of these mechanisms were applicable under brightening conditions, the effects of pH, chemical purity, chelating agents, free radical concentration, and transition metal solubility on peroxide decomposition were investigated.

3.3.1. Effect of pH and Chemical Purity on Peroxide Decomposition

The base-catalyzed mechanisms (Figs. 20 and 21) cited in section 3.3 predicts that maximum peroxide decomposition should occur at the pKa of the hydrogen peroxide where half of it is ionized in the form of perhydroxyl anion. The results presented in Figure 23, with purified or unpurified sodium hydroxide, show that maximum peroxide decomposition occurs at a pH value around 11.0. This finding is not in complete agreement with any of the two proposed mechanisms since the pKa of hydrogen peroxide at 50° C is approximately 11.5²¹³. The bell-shaped curve (Fig. 23) has been found by different researchers but there is no agreement as to the pH value where maximum decomposition takes place^{1,14,18,35}. The origin of this controversy probably is related to the varying purity of the chemicals used by various workers. Since the catalytic activity of the individual transition metals and their combinations is dependent upon pH³⁵, maximum decomposition will be strictly dependent on the amount and composition of the contaminants introduced with the chemicals and water.

Previous purification of the sodium hydroxide used in the various reactions to remove traces of transition metals resulted

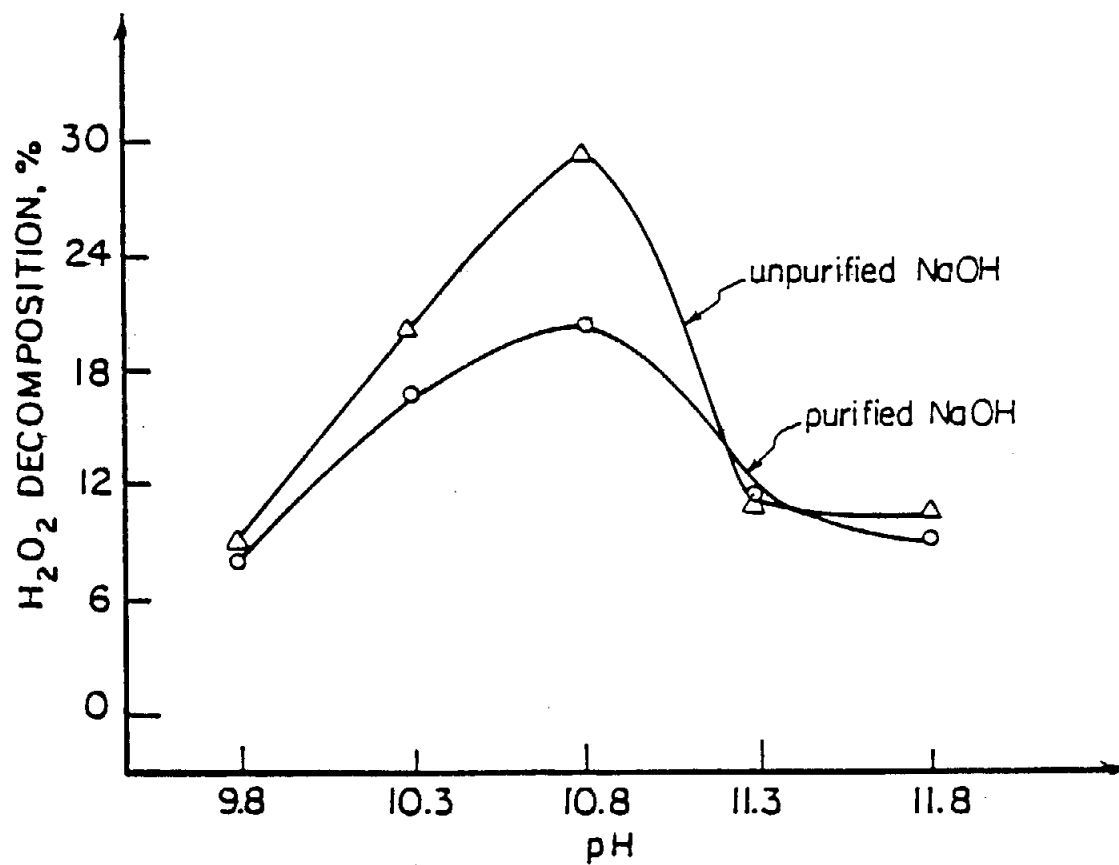


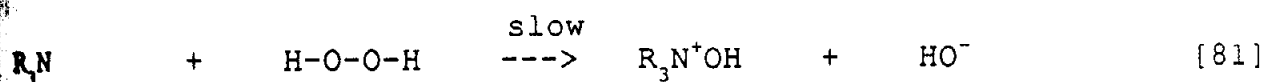
Figure 23. Effect of pH on the decomposition of 0.098 M H_2O_2 in purified and unpurified NaOH solutions. (50°C , 120 min).

approximately in a 10% decrease in peroxide decomposition at pH 10.8. This decrease in decomposition demonstrates the existence of transition metal-catalyzed reactions. However, the fact that peroxide decomposition was not completely eliminated by purification of the sodium hydroxide indicates that either the solutions were not completely free of transition metals or that base-catalyzed decomposition reactions were operative.

In order to determine whether or not transition metals were the actual cause of the residual peroxide decomposition even after purification of the sodium hydroxide, the effect of two chelating agents was investigated.

3.3.2. Effect of Chelating Agents on Peroxide Decomposition

The two chelating agents chosen for study were the pentasodium salt of diethylenetriaminepentaacetic acid (Na_5DTPA) and triethanolamine (TEA). Na_5DTPA is frequently used commercially in the brightening of mechanical pulps while TEA is a very effective chelating agent at pH values above 10.0²¹⁴. The effect of chelating agent concentration on peroxide decomposition at pH 10.8 is shown in Table 6. Concentrations of Na_5DTPA as low as 0.034 g/L were sufficient to completely stabilize peroxide solutions. Higher concentrations of Na_5DTPA resulted in small losses of peroxide. Such losses have been previously reported¹¹⁹, and probably are the result of peroxide consumption by reaction with Na_5DTPA . The reaction of peroxide with tertiary amines is well-documented in the literature²¹⁵, eqs. [81] and [82].



TEA, on the other hand, was not able to completely prevent the decomposition of hydrogen peroxide. Similar to Na_5DTPA , TEA consumes hydrogen peroxide. As noted in Table 6, it was impossible to find a concentration of TEA capable of completely stabilizing hydrogen peroxide without consuming it.

TABLE 6. The Effect of Chelating Agent Concentration on the Decomposition of 0.098M H_2O_2 . (initial pH 10.8, 50° C, 120 min).

Chelating Agent, g/L	H ₂ O ₂ Decomposition, %	
	Na ₅ DTPA	TEA
1.700	7.6	13.8
0.340	1.5	6.7
0.170	0.7	3.8
0.034	0.0	3.9
0.000	29.0	29.0

The effect of pH on peroxide stability in the presence of Na_5DTPA and TEA is shown in Figure 24. It is seen that Na_5DTPA is a very good stabilizer up to a pH 10.8 but is ineffective at higher values. TEA, on the other hand, showed nearly the same performance over the total pH range investigated (9.8-11.8) but

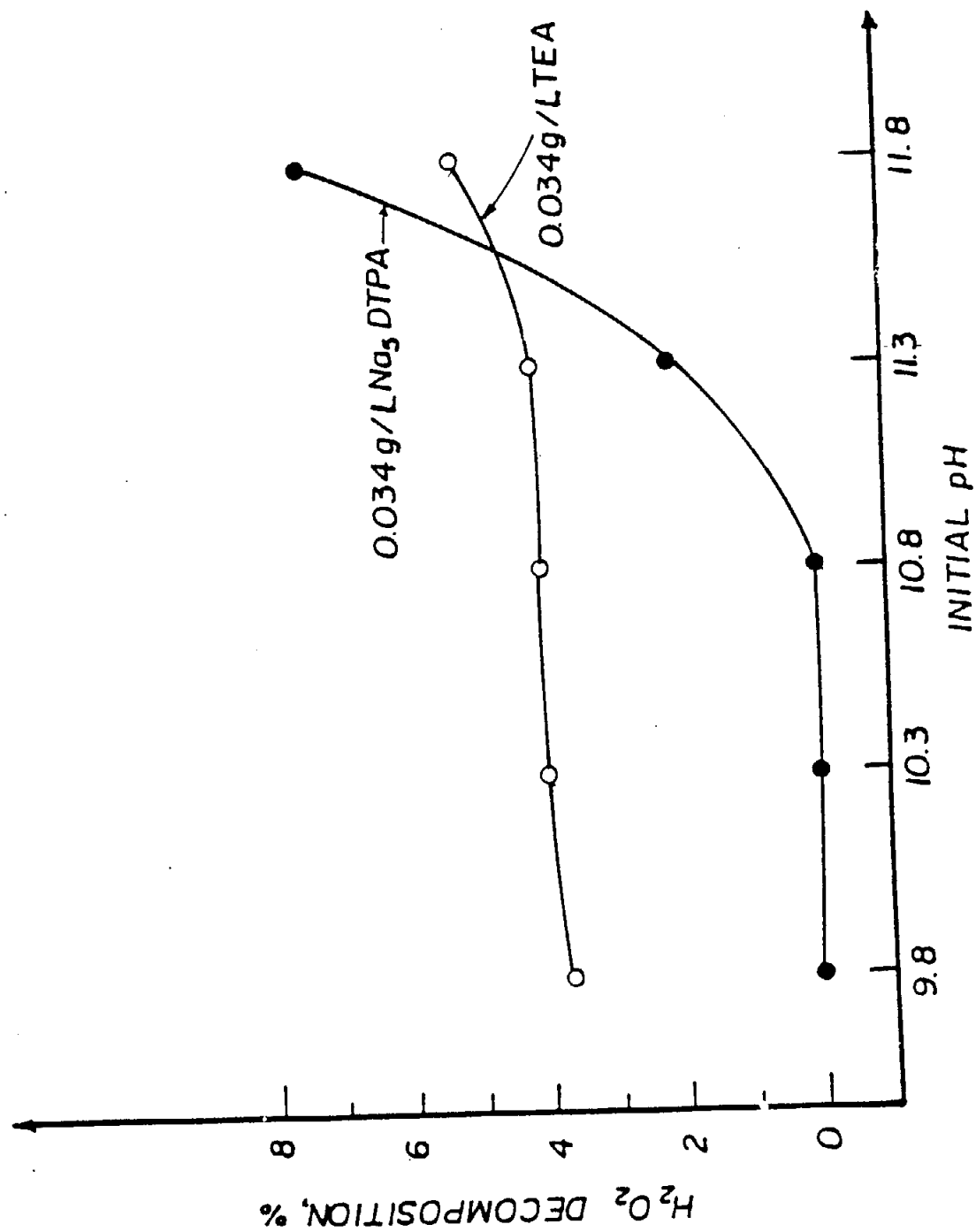


Figure 24. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of Na_5DTPA or TEA. (50° C, 120 min).

was slightly less efficient than Na_5DTPA at pH values lower than 11.0. It should be pointed out that in order to compare accurately the capacities of Na_5DTPA and TEA to stabilize peroxide, the concentrations of the chelating agents added to the reaction must be calculated based on their chelation equivalents. However, the fact that concentrations in g/L were used in these particular experiments does not make this comparison inaccurate since the amounts of Na_5DTPA and TEA used were in large excess of the amount actually needed to chelate the metal impurities present in the highly purified alkaline solutions.

The poor stabilizing action of Na_5DTPA at higher pH values is, in all likelihood, the result of competing reactions involving the formation of transition metal hydroxides and metal chelation itself²¹⁴. The hydroxides are more readily formed at higher pH values and act as effective catalysts for peroxide decomposition¹⁸.

The results discussed above indicate that TEA is indeed a better chelating agent than Na_5DTPA at high alkalinities, but it is significantly less effective in the pH range (10.0-11.0) where pulp brightening is usually performed. Therefore, Na_5DTPA seems to be the more appropriate chelating agent in such circumstances.

The fact that the addition of Na_5DTPA stopped peroxide decomposition altogether supports the concept of a transition metal-catalyzed reaction since base-catalyzed reactions are very unlikely to be inhibited by chelating agents. It has been suggested, however, that Na_5DTPA may function as a free radical

scavenger⁶ thereby preventing the propagation of the base-catalyzed free radical chain reaction. Obviously, if Na₅DTPA functions as a free radical scavenger, the base-catalyzed free radical mechanism cannot be ruled out. The reaction of free radicals with Na₅DTPA most likely occurs at the tertiary amine group²¹⁵. However, since the addition of other tertiary amines such as p-nitrosodimethylaniline (PNDA) and triethylamine, which are not chelating agents, to alkaline hydrogen peroxide solutions was not found to improve peroxide stability to any extent (Table 7), the reaction of Na₅DTPA with free radicals through the tertiary amine group must be of minor importance or non-existent.

TABLE 7. The Effect of the Concentration of p-Nitrosodimethylaniline (PNDA) and Triethylamine (TEA) on the Decomposition of 0.098 M H₂O₂. (initial pH 10.8, 50° C, 120 min).

Tert. Amine, M . 10 ⁴	H ₂ O ₂ Decomposition, %	
	PNDA	TEA
6.0	28.3	25.1
2.0	25.7	23.0
0.2	21.3	21.0
0.1	19.2	20.0
0.05	19.7	20.6
0.00	20.0	20.0

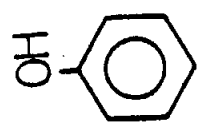
The fact that Na₅DTPA stabilizes peroxide probably by chelation of transition metals indicates that peroxide

decomposition during brightening is indeed a transition metal-induced reaction. A large variety of transition metals may be present during mechanical pulp brightening; thus, it is difficult to predict the exact mechanism of decomposition under brightening conditions because each metal may catalyze the reaction in a different way. The mechanism proposed in Figure 22, which involves a free radical chain reaction, has been widely accepted. To help confirm the validity of this mechanism, the concentrations of hydroxyl and superoxide anion radicals were determined in the absence of added metals and in the presence of iron, copper and manganese, generally the most abundant transition metals in pulp brightening systems.

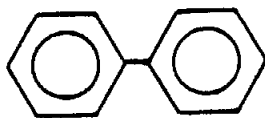
3.3.3. Concentrations of Hydroxyl and Superoxide Anion Radicals in Alkaline Solutions of Peroxide

Hydroxyl radicals were determined by hydroxylation of benzene. The reaction of benzene with hydroxyl radical proceeds by direct addition to yield a free radical intermediate²¹⁶, the hydroxycyclohexadienyl (HCD) radical. Phenol can be formed from the HCD radical by dismutation or by oxidation (eq. [83]). A second major product, biphenyl, is the result of dimerization and dehydration²¹⁷. Biphenyl production is suppressed by oxidizing agents such as oxygen and hydrogen peroxide²¹⁸. An alternative method for determining hydroxyl radical was also used in this study. It consisted of the decolorization of the hydroxyl radical acceptor, p-nitrosodimethylaniline, according to the procedure

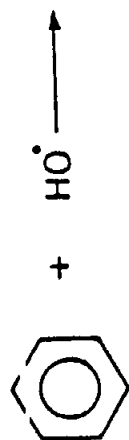
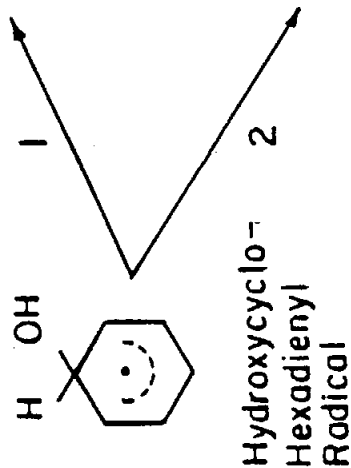
[83]



Phenol



Diphenyl



Benzene

described by Kraljic and Trumbore³². The results obtained by this procedure were similar to those obtained through the benzene hydroxylation method (Table A-1, Appendix A).

Superoxide anion radicals were determined by EPR spectrometry. The superoxide anion radical was identified by comparing the spectroscopic splitting factor (g) and line width of its EPR signal with those reported in the literature. The g value of 2.0038 and line width of 10.5 G obtained in this work are within the range reported in the literature for the superoxide anion radical which is 2.0015-2.0040 and 9-15 G for g and line width, respectively^{82,219}. The EPR signal for the superoxide anion radical is shown in Figure 25. The concentration of superoxide anion radicals was measured after 10-min' reaction because the largest concentrations of the radical were detected at approximately this time (Figs. 26 and 27). The sharp decrease in the concentration of the radicals after 10-min' reaction probably results from their consumption in side reactions to generate new radicals and oxygen (eqs. [7] and [23]).

The amount of superoxide anion radical generated in a given time is directly related to the final peroxide decomposition values. This can be observed in Figure 28 where values of peroxide decomposition and superoxide anion radical concentration are plotted against pH; it is clear that the pH at which maximum peroxide decomposition occurs coincides with the pH for maximum generation of superoxide anion radical, either in the presence of copper or in the absence of added transition metals. The results in Table 8 reveal that hydroxyl and superoxide anion radicals

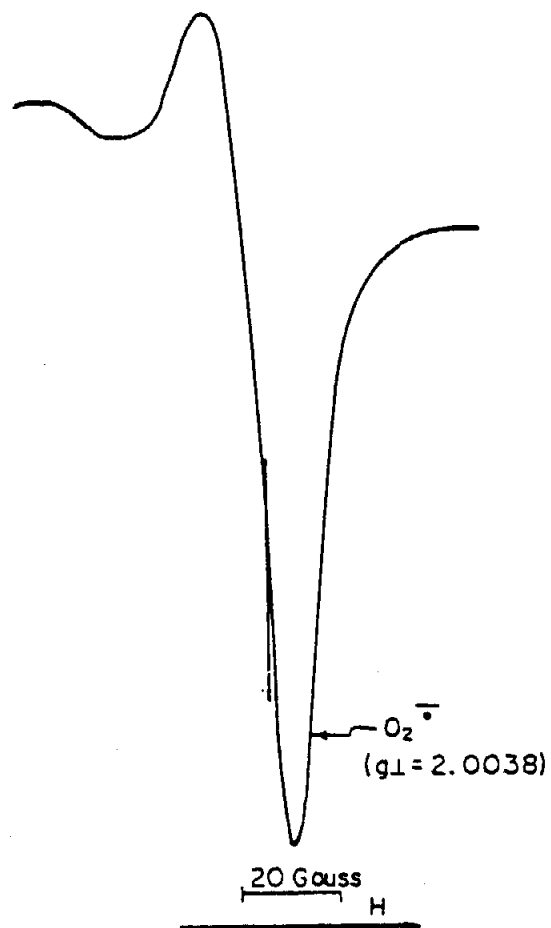


Figure 25. Second derivative EPR spectrum of superoxide anion radical obtained upon decomposition of 0.49 M H_2O_2 . (initial pH 10.8, 50° C, 10 min). EPR measurements made at 120 K. Vertical line indicates the position of DPPH signal.

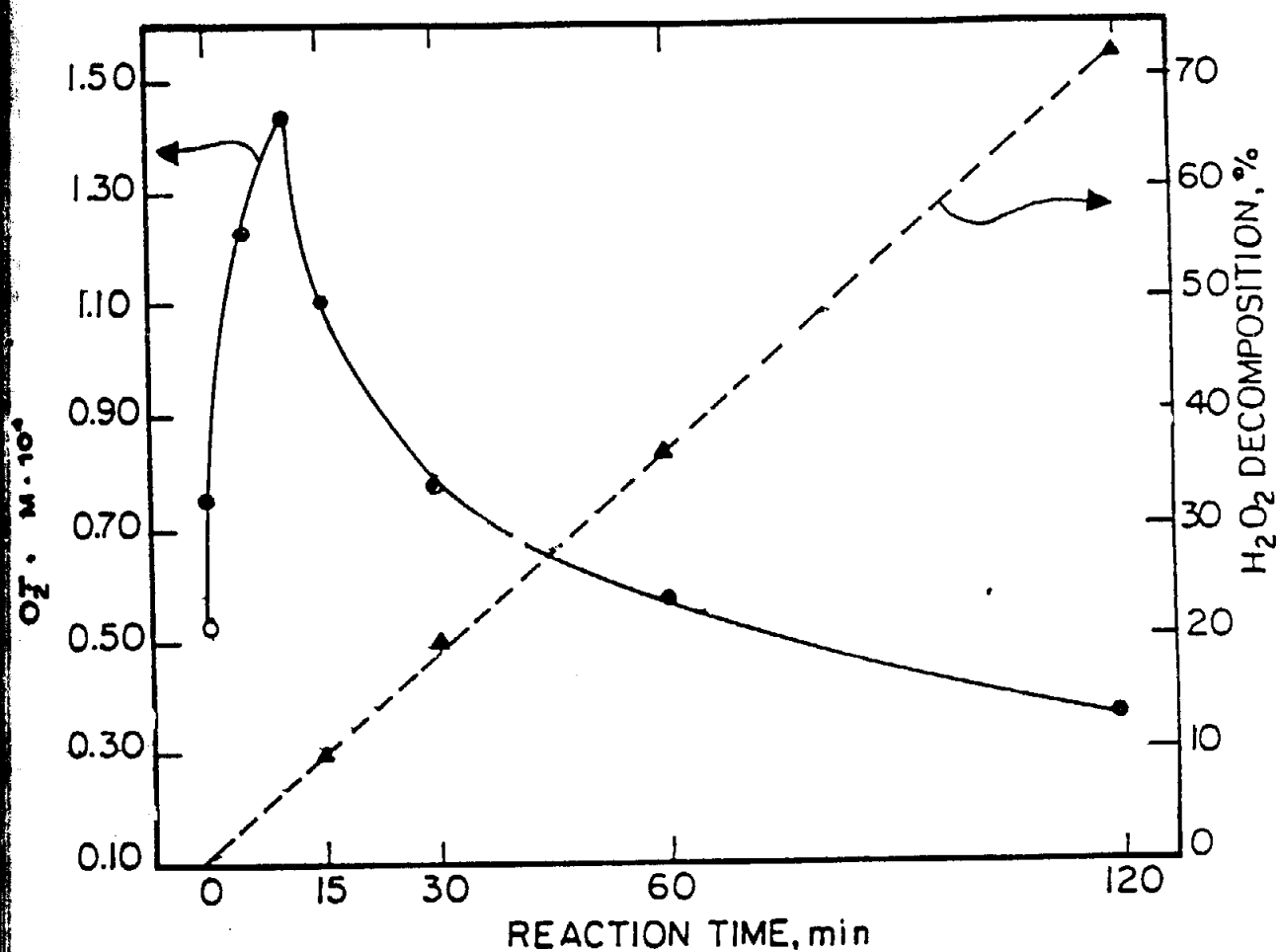


Figure 26. Rates of superoxide anion radical generation and of decomposition of 0.49 M H_2O_2 . (initial pH 10.8, 50 °C).

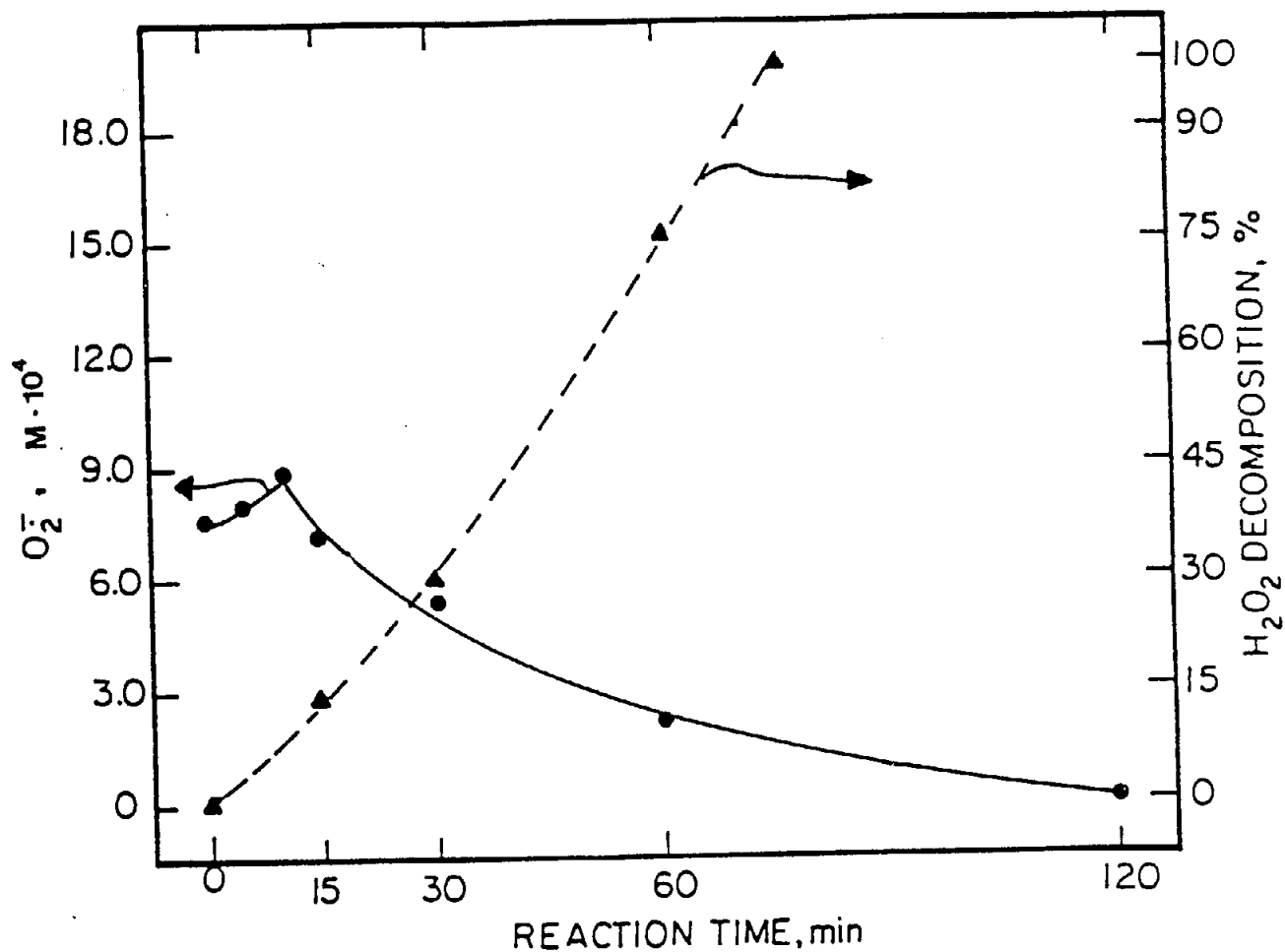


Figure 27. Rates of superoxide anion radical generation and of decomposition of 0.49 M H_2O_2 in the Presence of of Copper. (Cu = 3.5 ppm, initial pH 10.8, 50° C).

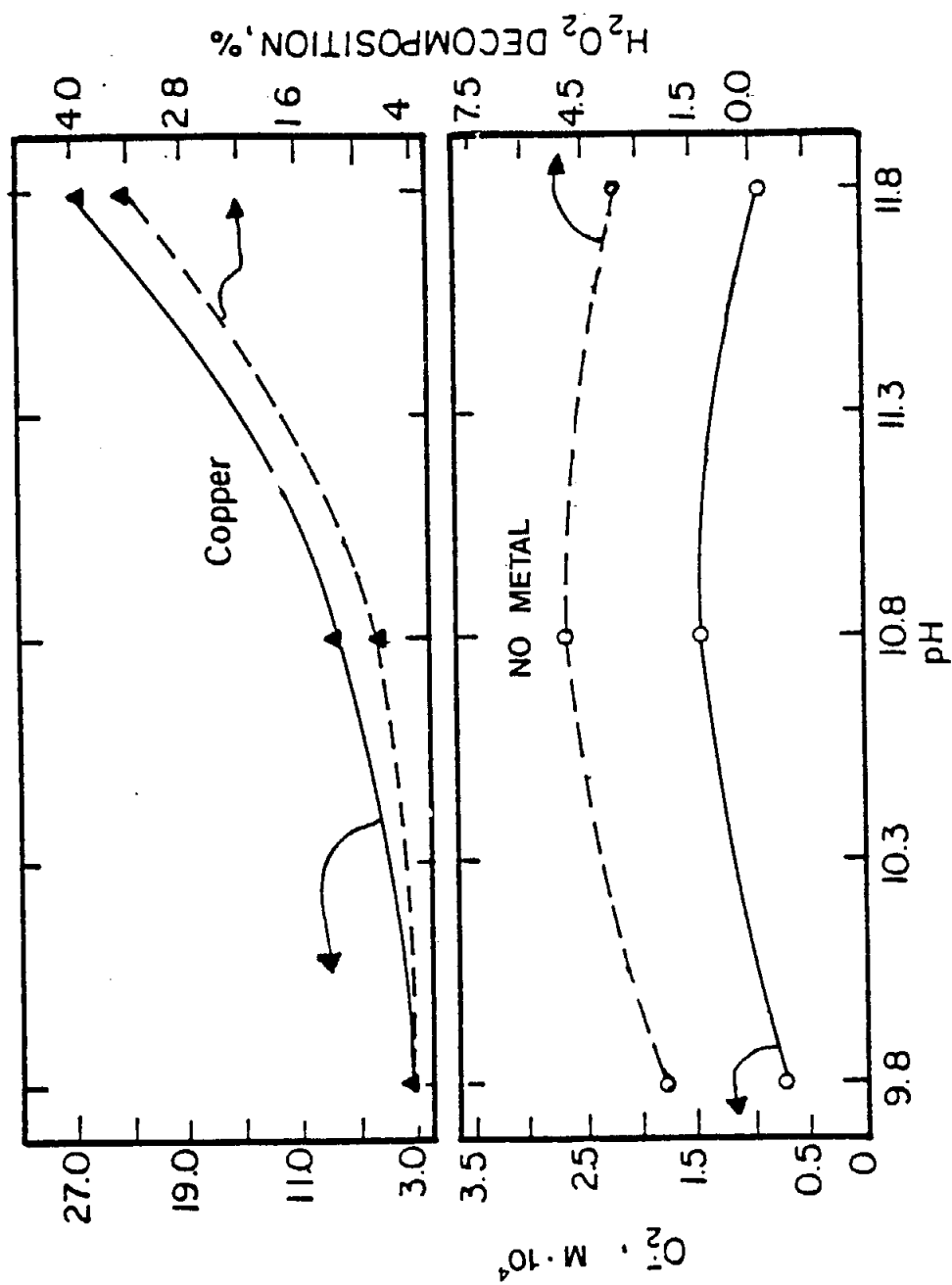
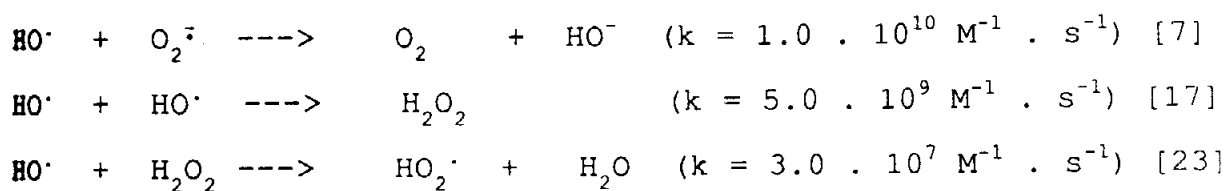


Figure 28. Effect of pH on the superoxide anion radical generation and decomposition of 0.49 M H_2O_2 in the presence and absence of copper. (50° C, 10 min, Cu = 3.5 ppm).

occur even when peroxide is decomposed in the absence of added transition metals. The formation of these radicals was probably induced by transition metal impurities contained in the reactants and water used in the reactions even though the sodium hydroxide was purified prior to use. The amounts of hydroxyl and superoxide anion radicals found in the system without added transition metals were very small considering the amount of peroxide decomposition. This probably results from a combination of two factors: (1) mechanisms other than free radical chain reactions may be operative and (2) a part of the radicals may have been consumed in side reactions and, thus, were not detected by the techniques used. Indeed, the consumption of radicals in side reactions is very likely since the rate constant for the hydroxylation of benzene ($6.7 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ at pH 10.5 and 50°C)²¹⁶, for instance, is lower than the rate constant for at least one of the most common side reactions occurring with hydroxyl and superoxide anion radicals during peroxide decomposition, eqs. [7], [17], and [23].



On the other hand, EPR spectrometry is not a very suitable technique for the accurate determination of superoxide anion radical concentration. It can be observed in Table 8 that the values for superoxide anion radical concentration can deviate as much as 40% from the average value. It should also be pointed

out that in order to have measurable readings for superoxide anion radical concentration by the EPR technique, a hydrogen peroxide concentration (0.49 M) considerably higher than that usually present in pulp brightening had to be used.

TABLE 8. The Amounts of Hydroxyl and Superoxide Anion Radicals Detected when Hydrogen Peroxide is Decomposed in the Presence and Absence of Transition Metals. (initial pH 10.8, 50° C).

Metal Added	Radical Concentration, M . 10 ⁴	
	Hydroxyl ¹	Superoxide Anion ²
None	9.4 (12.5) ³	1.4 ± 0.6 (5.0)
Iron	1.2 (57.0)	0.2 ± 0.1 (8.1)
copper	34.3 (28.0)	8.9 ± 2.8 (7.2)
Manganese	3.4 (54.0)	0.1 ± 0.06 (9.7)

¹ Determined by measurement of the amounts of phenol generated during peroxide decomposition in the presence of benzene for 2 h. (H₂O₂ = 0.098 M, Fe = 18.8, Cu = 0.7 and Mn = 0.3 ppm).

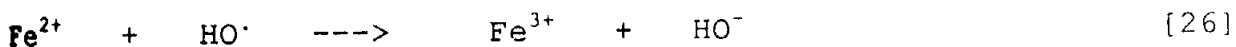
² Determined by EPR spectrometry after 10-min' reaction. (H₂O₂ = 0.49 M, Fe = 94 ppm, Cu = 3.5 ppm and Mn = 1.5 ppm).

³ Values in parentheses indicate % of peroxide decomposition.

Peroxide decomposition in the presence of copper resulted in the formation of large amounts of free radicals. It is not clear whether or not a free radical chain reaction is the only mechanism operative during the copper-catalyzed peroxide decomposition but, judging by the amount of radicals generated, it must play an important role. This finding is in agreement with results reported by Ernestova and Skurlatov³¹ who, using a

different technique, also found significant amounts of hydroxyl radicals in copper-catalyzed peroxide decomposition.

When hydrogen peroxide decomposed in the presence of iron and manganese, the generation of hydroxyl and superoxide anion radicals was inhibited. Even considering the fact that decomposition was higher in the presence than in the absence of these two metals or in the presence of copper, the amounts of radicals generated were considerably smaller. These results indicate that either peroxide decomposition catalyzed by iron and manganese does not involve a free radical mechanism or that these metals somehow trap the radicals that are generated during the reaction thereby preventing their determination. Indeed, EPR spectra for hydroxyl and perhydroxyl radicals in the Fe^{2+} - H_2O_2 system have not been found⁴⁴. Also, it has been shown that the addition of Fe^{2+} to the Ti - H_2O_2 system resulted in a decrease in the intensity of the EPR signal²²⁰. The decrease in hydroxyl radical concentration occurring when iron (II) is added to acidic hydrogen peroxide solutions has been attributed to the following reaction⁴⁴:



A previous study⁵¹ has shown that peroxide decomposition induced by manganese does not involve formation of radicals. It was established that hydroxyl radicals are not formed in the intermediate stage of the reaction between H_2O_2 and Mn^{2+} and that the hydrogen peroxide is transformed to O_2 without oxygen-oxygen bond cleavage during decomposition. Therefore, it is likely that

peroxide decomposition catalyzed by manganese occurs by a two-electron transfer from the H_2O_2 to the reaction intermediates.

Manganese and iron, which are the transition metals usually present in the largest amounts in the brightening system, do not decompose peroxide via a free radical chain reaction, nor do cobalt and lead⁵¹. Copper-catalyzed decomposition involves free radical reactions as do the ones catalyzed by titanium²²⁰ and cerium⁴⁴. Thus, the proposed theory of peroxide decomposition during brightening involving a transition metal ion-catalyzed **free radical chain reaction** is questionable. The existence of free radical chain reactions will, therefore, depend upon the concentration and type of the transition metals present in the reaction.

In summary, it seems certain that peroxide decomposition during brightening is caused by transition metal-induced reactions; some of them, probably the minority, involve a free radical chain reaction mechanism and the others occur via different routes.

3.3.4. The Solubility of Iron, Copper and Manganese Under Bleaching Conditions

The proposed mechanism for the transition metal-catalyzed peroxide decomposition (Fig. 22) assumes the existence of the metals as **free ions** in solution. However, at the pH values where brightening is usually performed (10.0-11.0), the solubility of the transition metals most commonly existing in the system is theoretically very low or non-existent (see solubility product

constants of iron, copper, and manganese hydroxides in Table A-2 - Appendix A). To demonstrate this point, a study of the solubility of iron, copper and manganese in pH 9.8, 10.8 and 11.8 solutions was carried out by ultrafiltration of the solutions. Regardless of pH or type of transition metal tested, no amounts of iron, copper or manganese above the detection limit (< 10 ppb) were found in the filtrates (Scheme 1 - section 3.2.). Moreover, the filtrates were shown to catalyze peroxide decomposition to a minor extent. The absence or near absence of soluble metals in the filtrates clearly indicates that free iron, copper, and manganese ions are not the cause of peroxide decomposition under brightening conditions. Thus, the existence of a so-called transition metal ion-catalyzed peroxide decomposition is questionable.

Another finding that negates the transition metal ion-catalyzed reaction is the variation of peroxide decomposition with pH in the presence of iron, copper or manganese (Fig. 29). Decomposition involving metal ions theoretically should be maximum at a pH value around the pKa of the hydrogen peroxide (11.5 at 50° C) where half of it is in the form of perhydroxyl anion. However, maximum peroxide decomposition in the presence of added manganese occurred at a pH (9.8) where ionization of the hydrogen peroxide is essentially zero. Iron and copper, on the other hand, catalyzed peroxide decomposition more efficiently at pH 11.8 where peroxide ionization is greater than at the pKa of hydrogen peroxide.

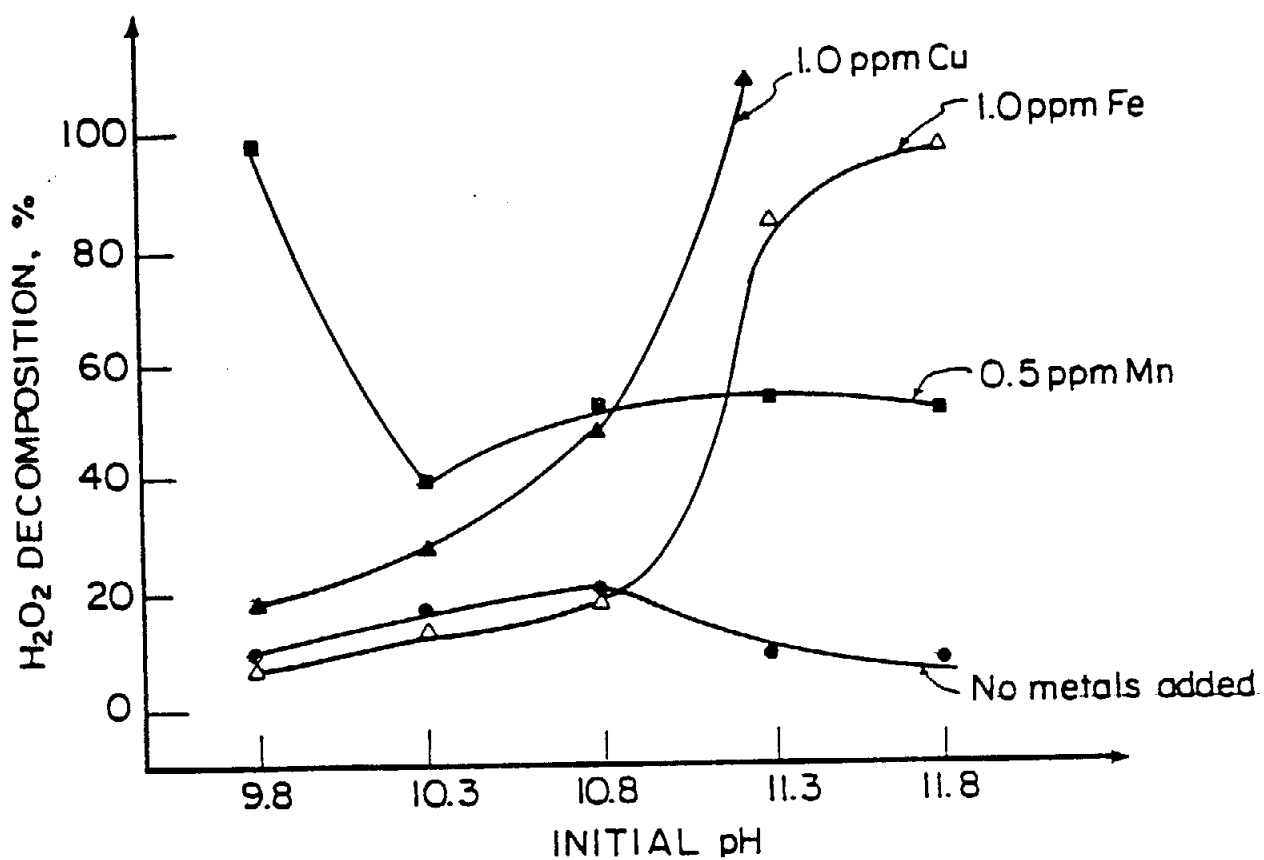
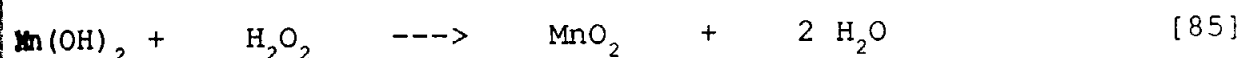
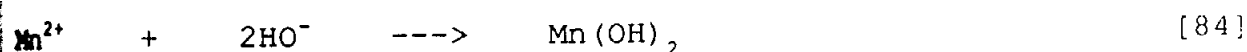
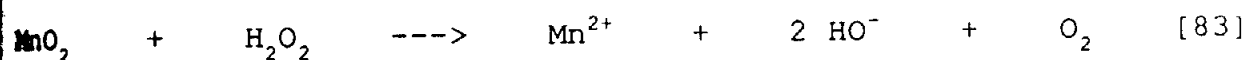


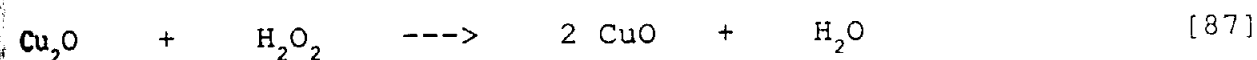
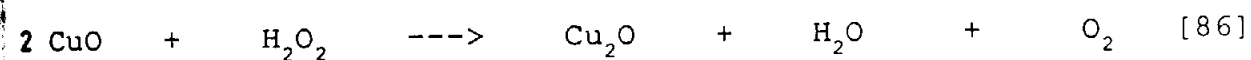
Figure 29. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of iron, copper or manganese. (50°C , 120 min).

Hydrogen peroxide decomposition under brightening conditions indeed seems to be caused by insoluble transition metal species. The exact mechanism of the decomposition reactions is very difficult to predict because the exact chemical forms of these insoluble species are not known. In the case of manganese, for instance, if one assumes that manganese dioxide is the active species, the following sequence can be written:



In the above sequence, the ionization of the hydrogen peroxide is not important because all of the reactions take place with undissociated hydrogen peroxide.

The active species in the copper-catalyzed peroxide decomposition is probably copper (II) oxide and the following sequence has been proposed⁸⁴:



In hydrogen peroxide decomposition catalyzed by insoluble iron, the active species has been postulated to be goethite (α -FeOOH)¹⁸¹. A mechanism for this reaction has not yet been proposed.

The pH of the pulp and process water present in the brightening system is usually between 5.5 and 7.0. Theoretically, in this pH range iron and copper exist in insoluble forms as

indicated by the low solubility product constants of their hydroxides. Manganese, on the other hand, exists in the ionic form in the 5.5.-7.0 pH range at the concentrations usually present in pulp brightening. However, at the pH at which brightening is performed, manganese ions are transformed into manganese dioxide. Visually, it is apparent that this reaction is very fast since a brown precipitate is immediately formed when the pH of the manganese solutions is raised above 9.0. Thus, in an actual brightening situation, iron, copper and manganese will indeed exist as insoluble hydroxides or oxides.

4. SUMMARY AND CONCLUSIONS

The theories proposed to account for hydrogen peroxide decomposition in weakly alkaline solutions were re-evaluated through a study of the effect of the following variables on peroxide stability: hydrogen peroxide concentration, pH, pH control, temperature, chemical purity, ionic strength, chelating agent type and concentration, free radical concentration, and transition metal concentration and solubility. The principal findings of this work are:

1. The decomposition of hydrogen peroxide under brightening conditions is a transition metal-induced reaction.

2. The decomposition of hydrogen peroxide under brightening conditions involves hydroxyl and superoxide anion radicals but a free radical chain reaction is not the main decomposition pathway.
3. The copper-catalyzed decomposition of hydrogen peroxide involves generation of significant amounts of hydroxyl and superoxide anion radicals but these radicals are not formed in peroxide decomposition catalyzed by iron and manganese.
4. The decomposition of hydrogen peroxide catalyzed by iron, copper and manganese under brightening conditions is caused by insoluble forms of these metals.
5. The extent of hydrogen peroxide dissociation does not affect decomposition catalyzed by iron, copper and manganese.
6. The decomposition of hydrogen peroxide is affected significantly by its initial concentration in the range of 0.040 to 0.392 M.
7. The decomposition of hydrogen peroxide reaches a maximum at a pH of approximately 11.0 in the range 9.8 to 11.8.
8. Peroxide decomposition is not significantly affected by maintaining the pH constant during the decomposition reaction.
9. The decomposition of hydrogen peroxide is completely inhibited by the addition of small amounts of Na_5DTPA in the pH range 9.8 to 11.0.

10. Triethanolamine (TEA) is a better stabilizer agent for alkaline hydrogen peroxide than Na_5DTPA at pH values higher than 11.0 but poorer at lower pH values.
11. Both Na_5DTPA and TEA react with hydrogen peroxide.
12. The decomposition of hydrogen peroxide increases with increasing pH in the presence of added iron and copper; in the presence of added manganese, hydrogen peroxide decomposition first decreases then increases with increasing pH.
13. The ionic strength has no significant influence on the decomposition of alkaline hydrogen peroxide.
14. Iron-catalyzed decomposition of peroxide is reduced significantly by aging the iron solution whereas copper- and manganese-catalyzed decomposition is not affected by this treatment.
15. Hydrogen peroxide decomposition catalyzed by iron is not affected by the anion of the iron salt.
16. Tertiary amines such as p-nitrosodimethylaniline and triethylamine are ineffective in preventing peroxide decomposition.
17. The extent of hydrogen peroxide decomposition increases more than three-fold by increasing temperature from 50° to 60° C.

FACTORS AFFECTING HYDROGEN PEROXIDE STABILITY IN THE BRIGHTENING
OF MECHANICAL AND CHEMIMECHANICAL PULPS

CHAPTER III - HYDROGEN PEROXIDE STABILITY IN THE PRESENCE OF
SODIUM SILICATE

1. INTRODUCTION

The addition of sodium silicate alone or in combination with other stabilizers to peroxide brightening liquor enhances significantly the brightening of mechanical pulps¹⁵⁴. Unfortunately, the use of silicate results in formation of deposits on the fibers and equipment, leading to decreased quality of the bleached materials (fiber harshness) and to increased lost time for equipment cleaning¹⁵². These undesirable qualities of silicate have encouraged extensive research aimed at its elimination from brightening formulations, but the fact of the matter is that silicate is still a standard and as yet irreplaceable additive in peroxide brightening of mechanical pulps¹⁴⁶.

Since sodium silicate is not at present readily replaceable in peroxide brightening formulations, an understanding of the mechanism of its action becomes very important as a means of improving its stabilizing performance. Moreover, an insight to the mechanism by which silicate acts may serve to suggest other compounds which eventually can partially or fully replace this chemical in peroxide brightening.

A large number of theories have been proposed to explain the role of sodium silicate in peroxide brightening. They can be summarized as follows: (1) stabilization of hydrogen peroxide^{14,145-153}, (2) formation of more reactive oxidizing species, e.g. peroxysilicates¹⁴³, (3) direct interaction with

lignin¹⁵⁴, (4) alteration of the mechanism of lignin oxidation through formation of new reactive species such as singlet molecular oxygen¹⁴⁶, (5) enhancement of ionic strength¹⁴⁶, (6) augmentation of alkalinity¹⁴⁶, (7) prevention of the formation of alkaline earth hydroxides which reportedly catalyze peroxide decomposition¹⁸, and (8) action as a buffering, anti-corrosion, detergent, surfactant, and flocculating agent^{23,28,146-150,154}.

Although silicate plays an important role in the peroxide brightening of mechanical pulps, it is unlikely that it can perform all of the functions listed above in any given application. In this study efforts were concentrated solely on the role of silicate as a peroxide stabilizer not only because of its generally-recognized ability to function in this manner but also because of the great controversy surrounding the mechanism of its stabilization effect.

A number of investigators^{14,119,125,150,167,221} have reported data supporting the claim that peroxide stability is enhanced in the presence of sodium silicate. Others^{143,152,158}, on the other hand, have contended that, in fact, sodium silicate destabilizes peroxide. Contrary to the foregoing conclusions, evidence has been reported indicating that silicate neither stabilizes nor destabilizes alkaline solutions of hydrogen peroxide¹⁸.

Despite the controversy, several theories have been advanced to explain the role of sodium silicate as a peroxide stabilizer, the following being the most widely accepted: (1) coating of transition metals^{147,149}, (2) passivation of transition

metals^{28,150} (3) sorption of transition metals^{14,145,151}, (4) formation of stable complexes with transition metals^{152,153}, (5) retention of transition metals in solution¹⁸, (6) termination of chain reactions by binding free radicals^{28,134}, and (7) interaction with peroxide forming peroxysilicates that are more stable than hydrogen peroxide itself^{143,152}.

With the foregoing in mind, this investigation consisted basically of a systematic re-evaluation of the proposed theories of peroxide stabilization by sodium silicate in order to clarify the mechanism of its action. This was achieved through a study of the following topics: (1) the effect of variables such as silicate concentration, peroxide concentration, pH, chemical purity, ionic strength, and $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of the silicate; (2) the reactivity of peroxide-reactive compounds with hydrogen peroxide in the presence and absence of silicate; (3) the effect of iron, copper and manganese on peroxide decomposition in the presence of silicate, including the effects of metal concentration, pH, metal "age", and metal solubility; (4) the effect of colloids such as carboxymethylcellulose, dextrin, starch, sodium polymethacrylate and gelatine on peroxide decomposition; and (5) a determination of the amounts of hydroxyl and superoxide anion radicals generated by the decomposition of hydrogen peroxide in the presence of silicate and in the presence of silicate/copper combinations.

2. MATERIALS AND METHODS

2.1. Reagents

Except when stated otherwise, the sodium silicate used throughout all the experiments was N-brand Clear ($\text{SiO}_2/\text{Na}_2\text{O} = 3.22$) supplied by Philadelphia Quartz Corporation. Additional purification of the sodium silicate was carried out according to the method developed at Philadelphia Quartz Corporation; the procedure involved the dissolution of fumed silica in 50% aqueous caustic soda solution prepared from sodium hydroxide hydrate (Alpha Chemical Co., ultrapure) and doubly-deionized water. The iron, copper and manganese contents of the silicates are presented in Table 9.

TABLE 9. Iron, Copper, and Manganese Contents of the Purified and Unpurified Silicates (0.335 M SiO_2).

Silicate	Metal Content, ppm		
	Iron	Copper	Manganese
Unpurified	1.8	0.02	<0.01
Purified	0.01	0.02	0.01

In experiments where the effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of the sodium silicate on peroxide decomposition was examined, the following sodium silicate brands were used: Starso, Star, N-Clear, and S-35. Their ratios and iron assays are presented in Table 10. To avoid any possible influence of the iron in the different silicates, the iron concentration of all four silicates was adjusted to the maximum value (37.8 ppm) by addition of

Iron (III) chloride.

TABLE 10. Iron Content and $\text{SiO}_2/\text{Na}_2\text{O}$ Ratio of Different Sodium Silicate Brands.

Silicate Brand	$\text{SiO}_2/\text{Na}_2\text{O}$ Ratio	Iron Content, ppm
Starso	1.80	31.8
Star	2.50	31.1
M-Clear	3.22	37.8
S-35	3.75	21.0

Copper silicate was prepared by reacting copper sulfate (0.05 M) and sodium metasilicate (0.05 M) according to the method proposed by Gagnon et al.²²².

All of the other chemicals used in this study were prepared and/or purified as described in section 2.1 - chapter 2. The water used throughout all of the experiments was doubly-distilled.

2.2. Peroxide Decomposition Tests

All of the decomposition tests were carried out as described in section 2.1 - chapter 2. Except when stated otherwise the order of addition of the chemicals was standardized as follows: water, transition metal salt, sodium silicate, sodium hydroxide, and hydrogen peroxide, with stirring between additions.

2.3. pH Measurement and Control

See section 2.3 - chapter 2

2.4. Determination of Hydroxyl and Superoxide Anion Radicals

See section 2.4 - chapter 2

2.5. Ultrafiltration of Transition Metal Solutions

Samples (200 mL) of 0.34 mM solutions of iron, copper and manganese were prepared at pH 10.3, 10.8 or 11.8 from "aged" solutions of these metals (prepared by dissolving the metal salts in water at pH 6.5 and boiling the resultant solution for 3 h). In the preparation of these solutions the order of addition of the chemicals was as follows: water, transition metal salt, sodium silicate (0.08 M SiO_2), and sodium hydroxide, with stirring between additions. In all cases, there was a 10min lag between the additions of sodium silicate and sodium hydroxide. The solutions were then heated to 50° C and allowed to stand for 2 h. Subsequently, they were ultrafiltered using the procedure described in section 2.5 - chapter 2.

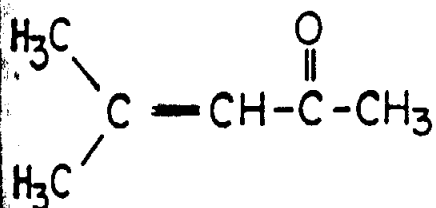
2.6. Determination of the Metal Content of the Solutions

See section 2.6 - chapter 2

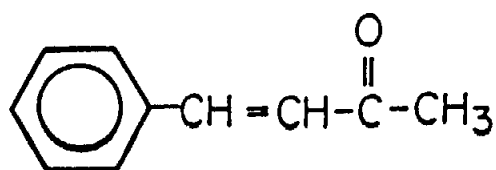
2.7. Reaction of Hydrogen Peroxide with Peroxide-Reactive Compounds

The peroxide-reactive compounds (Table 11) were supplied by Aldrich Chemical Co. The consumption of these compounds by hydrogen peroxide was monitored by high pressure liquid chromatography (HPLC) using a 10 cm/8 mm C_{18} cartridge column

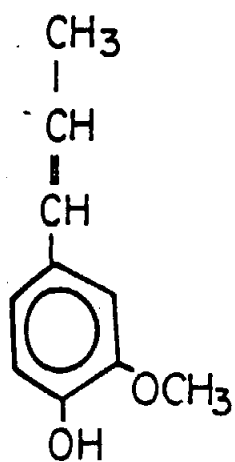
TABLE 11. Hydrogen Peroxide-Reactive Compounds



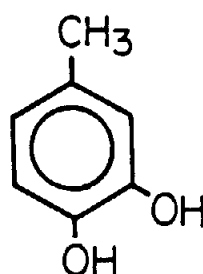
Mesityl Oxide



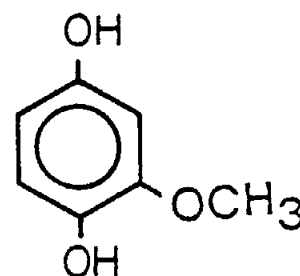
Benzal Acetone



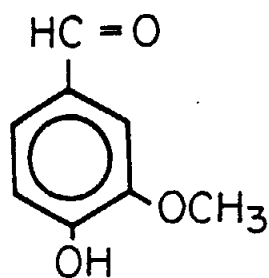
Isoeugenol



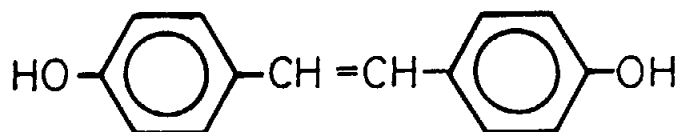
4-Methylcatechol



Methoxyhydroquinone



Vanillin



4,4'-Di hydroxystilbene

(Waters Assoc.) as the stationary phase and a mixture of 60% methanol and 40% water (2 mL/min) as the mobile phase. The HPLC unit was manufactured by Waters Associates and was composed of the following components: automatic gradient controller model 680, pumps model 510, absorbance detector series 440, universal liquid chromatography injector model U6K, and data module model 740.

2.8. Ionic Strength Variation

Ionic strength adjustment was accomplished by adding the appropriate amounts of sodium chloride to the reaction mixtures. The ionic strength of the sodium silicate solution at the concentration studied was indirectly determined by conductometric measurements. Conductometric measurements were performed with a Beckman conductivity meter model RA5.

2.9. Order of Addition of Sodium Silicate and Sodium Hydroxide

These experiments were conducted using "aged" and "fresh" transition metal species. "Fresh" metals were prepared by dissolving the appropriate metal salts in 0.1 N HCl solution. "Aged" metals were prepared by dissolving the salts in water at pH 6.5 and boiling the resulting solution for 3 h. There was always a 10-min interval between the additions of sodium hydroxide and sodium silicate to the solutions containing the transition metal species and vice versa. Hydrogen peroxide was always added last.

3. RESULTS AND DISCUSSION

3.1. Effect of Reaction Variables on Peroxide Decomposition

3.1.1. Effect of Hydrogen Peroxide Concentration

Concentrations of hydrogen peroxide in the range 0.040 to 0.39 M were chosen in order to bracket the concentration range typically encountered in commercial brightening. Concentrations of 0.040 and 0.39 M correspond, respectively, to 0.41 and 4.0% hydrogen peroxide on o.d. pulp at 25% consistency. The effect of hydrogen peroxide concentrations of 0.040 M and 0.098 M on its extent of decomposition at 50° C in the presence of sodium silicate in the pH range 10.3 to 11.8 is shown by the plots in Figures 30-33. A slightly increased extent of hydrogen peroxide decomposition was observed at the higher initial peroxide concentration for all four pH values.

In order to establish whether the reaction extent differences were real, a broader range of concentrations (0.040 - 0.39 M) was investigated. The results presented in Table 12 show that peroxide decomposition in the presence of silicate is not influenced by peroxide concentration in the range 0.098 to 0.39 M. These results differ from those obtained in the absence of silicate (section 3.1.1 - chapter 2) which show that peroxide decomposition is significantly affected by concentration in this range.

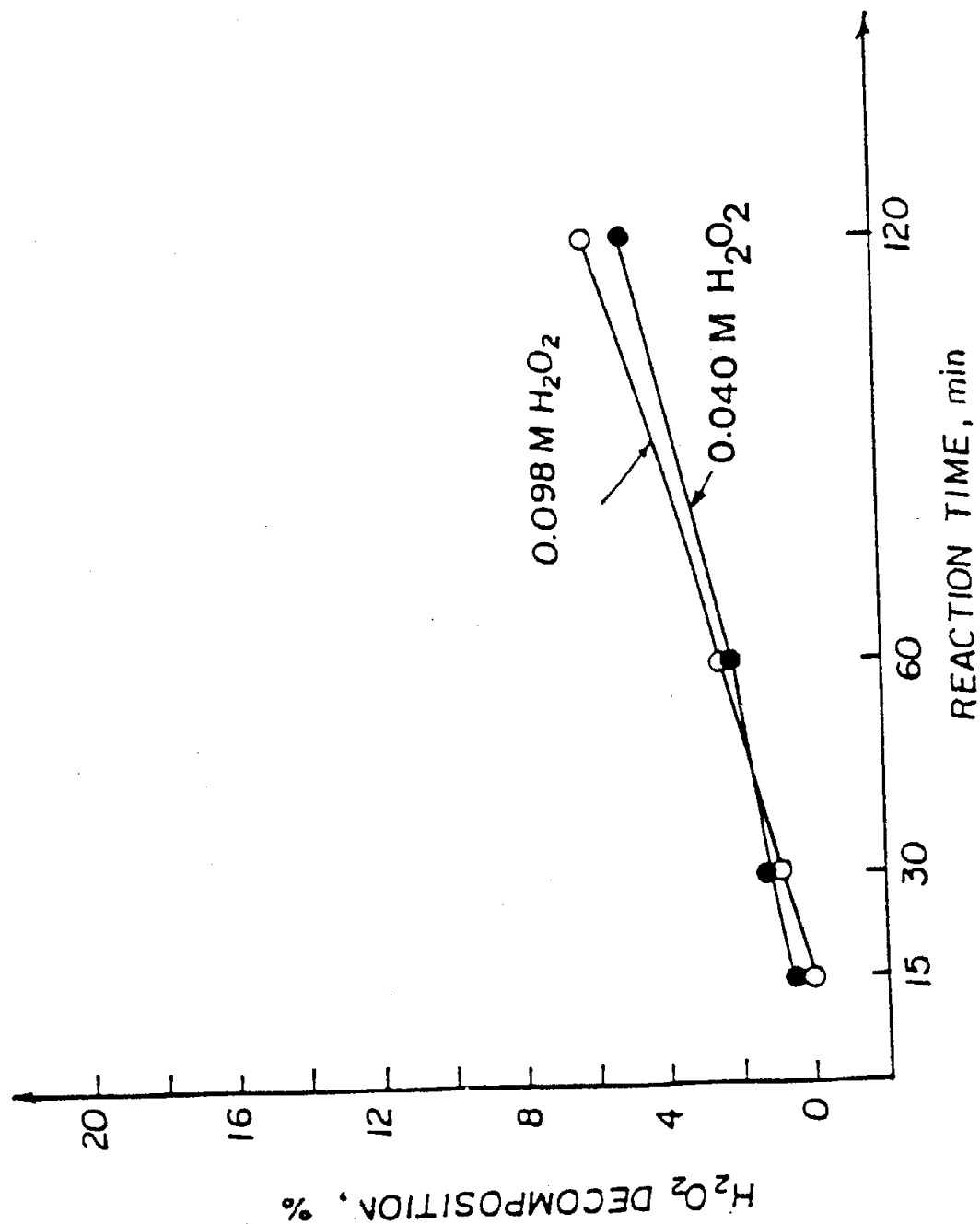


Figure 30. Effect of concentration on the extent of hydrogen peroxide decomposition in the presence of sodium silicate. ($\text{SiO}_2 = 0.08 \text{ M}$, initial pH 10.3, 50°C).

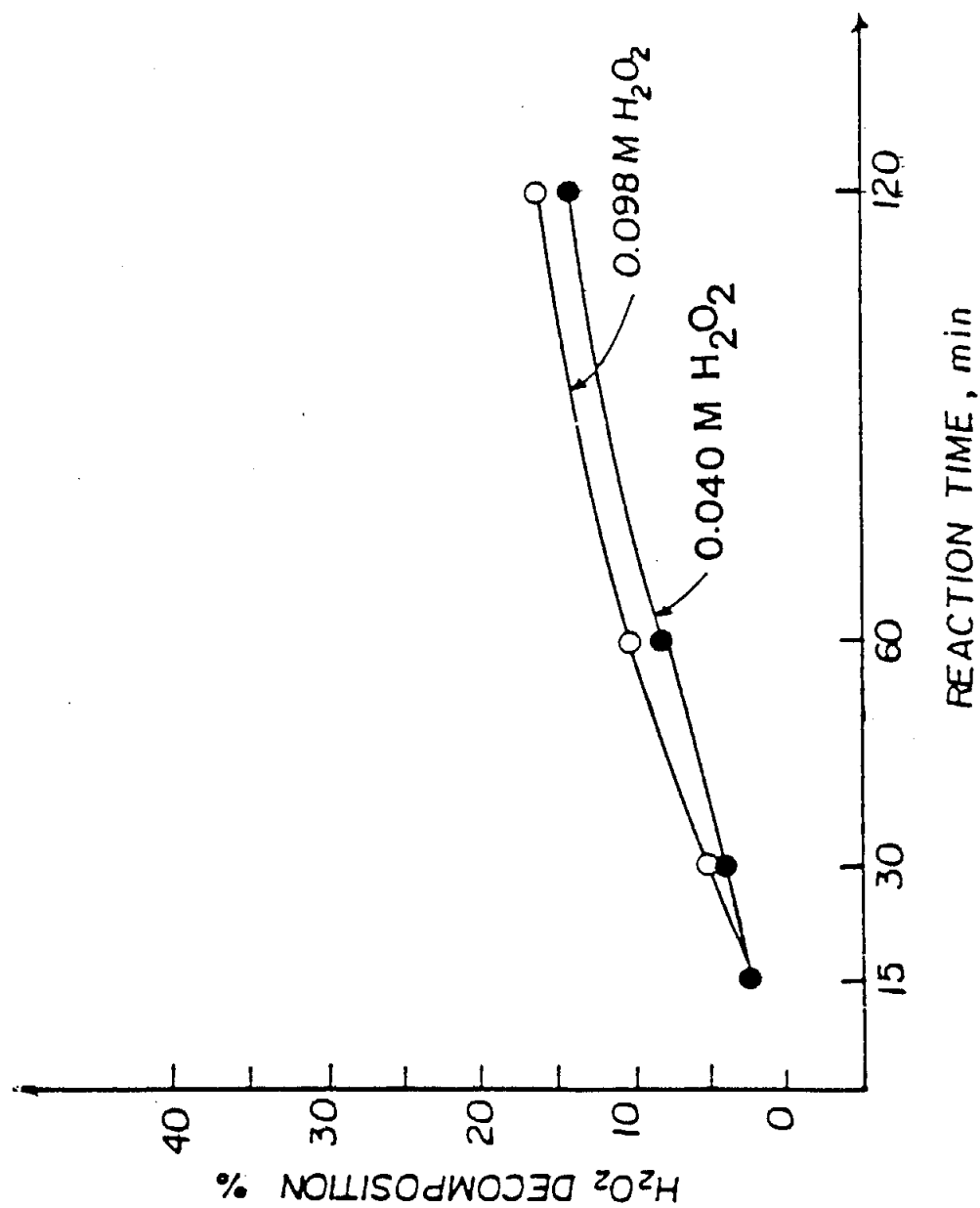


Figure 31. Effect of concentration on the extent of hydrogen peroxide decomposition in the presence of sodium silicate. ($\text{SiO}_2 = 0.08 \text{ M}$, initial pH 10.8, 50°C).

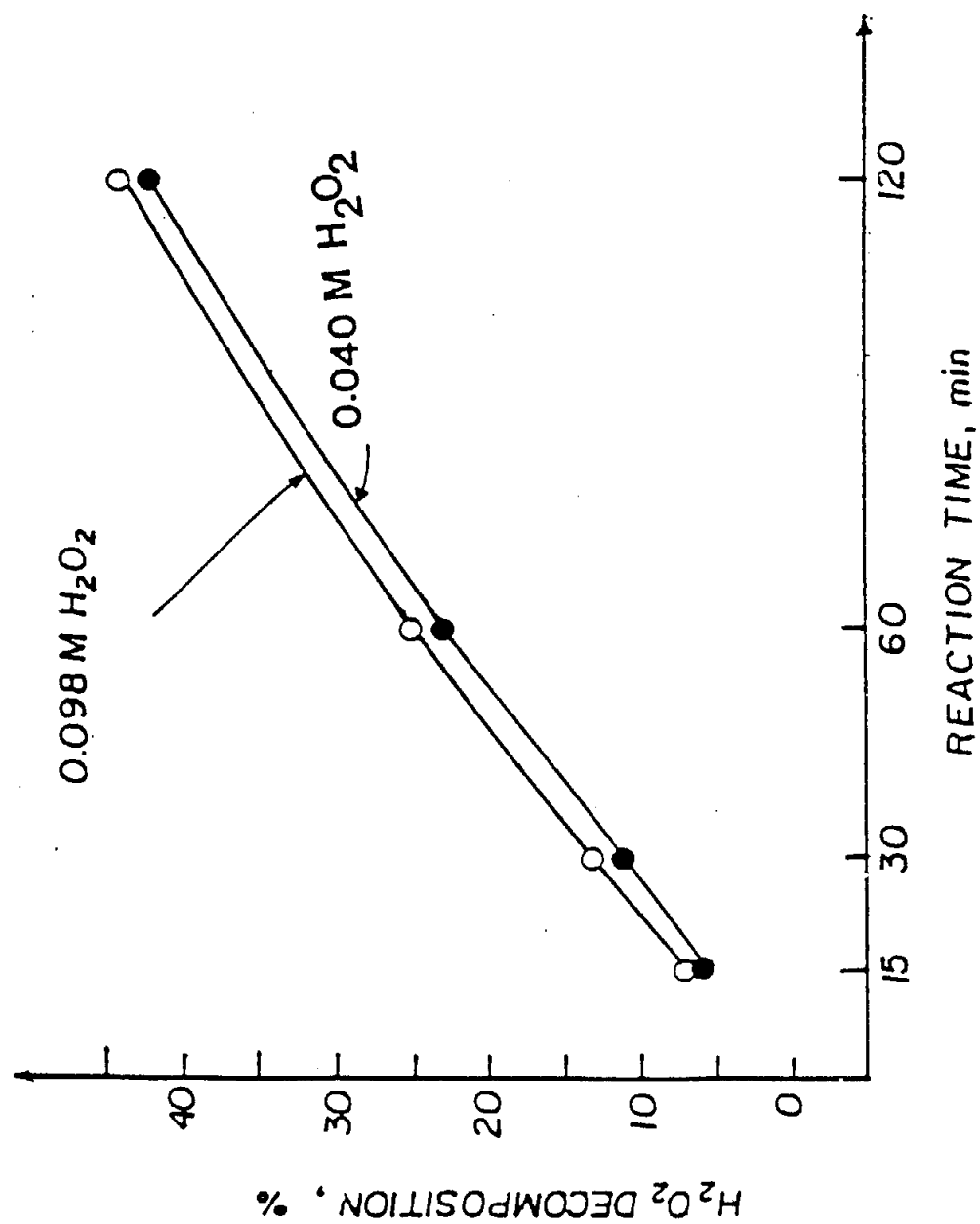


Figure 32. Effect of concentration on the extent of hydrogen peroxide decomposition in the presence of sodium silicate. ($SiO_2 = 0.08$ M, initial pH 11.3, $50^\circ C$).

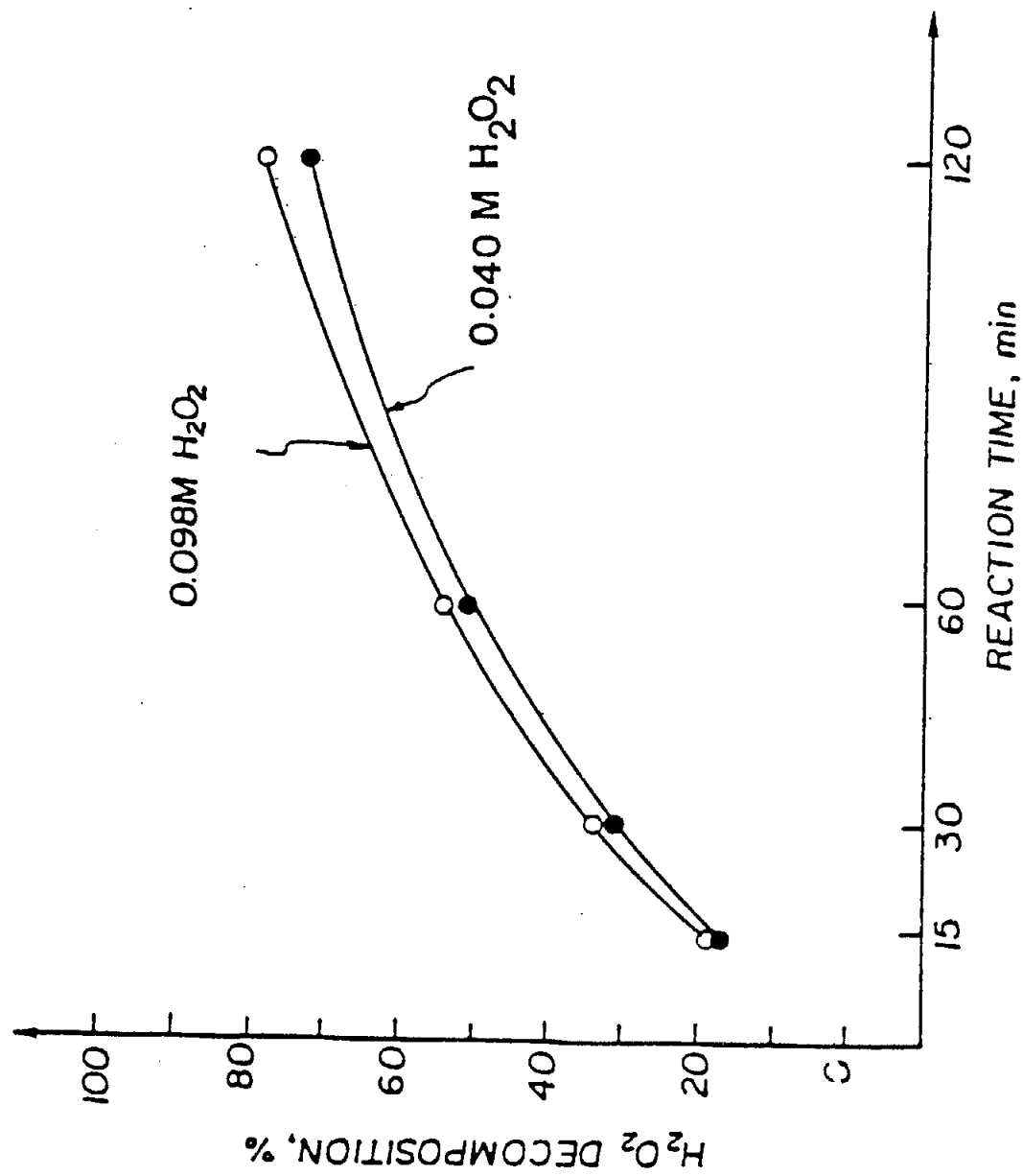


Figure 33. Effect of concentration on the extent of hydrogen peroxide decomposition in the presence of sodium silicate. ($\text{SiO}_2 = 0.08 \text{ M}$, initial pH 11.8, 50°C).

TABLE 12. The Effect of Concentration on the Decomposition of Hydrogen Peroxide in the Presence of Silicate (0.08 M SiO_2 , initial pH 10.8, 50° C, 120 min).

H_2O_2 Conc., M	H_2O_2 Decomposition, %	Final pH
0.040	14.9	10.85
0.098	18.9	10.90
0.196	19.8	10.90
0.294	18.9	10.90
0.392	19.5	10.90

3.1.2. Effect of Sodium Silicate Concentration

The effect of sodium silicate concentration on the extent of peroxide decomposition in the pH range 10.3 to 11.8 is illustrated in Figures 34-37. The concentrations chosen (0.04, 0.08, and 0.16 M SiO_2), which are equivalent, respectively, to 2.5, 5.0, and 10.0% sodium silicate on o. d. pulp at 25% consistency encompass the range most commonly used in the commercial brightening of mechanical pulps. An increase in sodium silicate concentration results in a decreased peroxide decomposition extent for each of the four solutions adjusted to different pH values. This same trend has been found by other researchers^{143,221} and attributed to sodium silicate's capacity to stabilize hydrogen peroxide.

Furthermore, increasing pH results in an enhanced extent of peroxide decomposition at all three concentrations. This behavior can be explained by the enhancement of the catalytic activity of

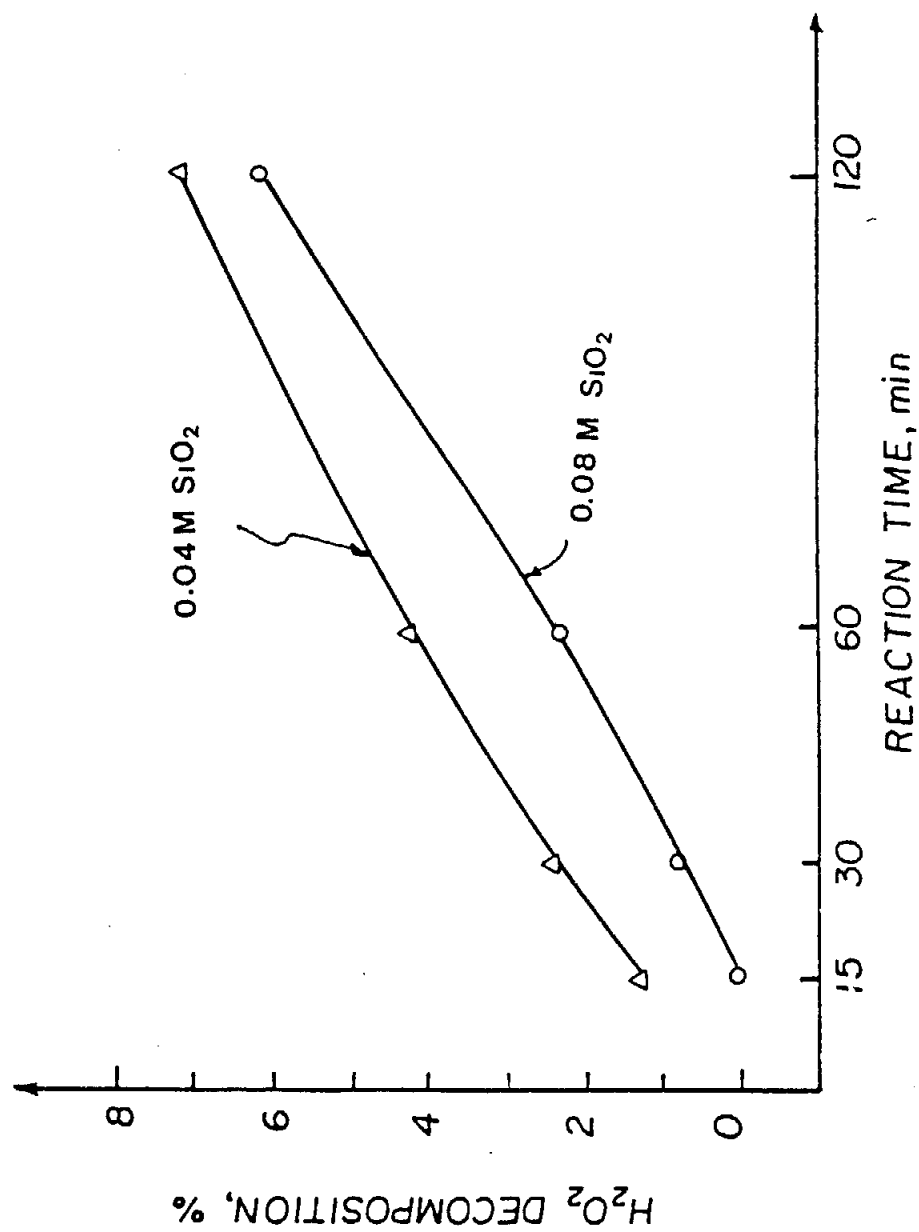


Figure 34. Effect of the sodium silicate concentration on the extent of decomposition of 0.098 M H₂O₂. (initial pH 10.3, 50° C).

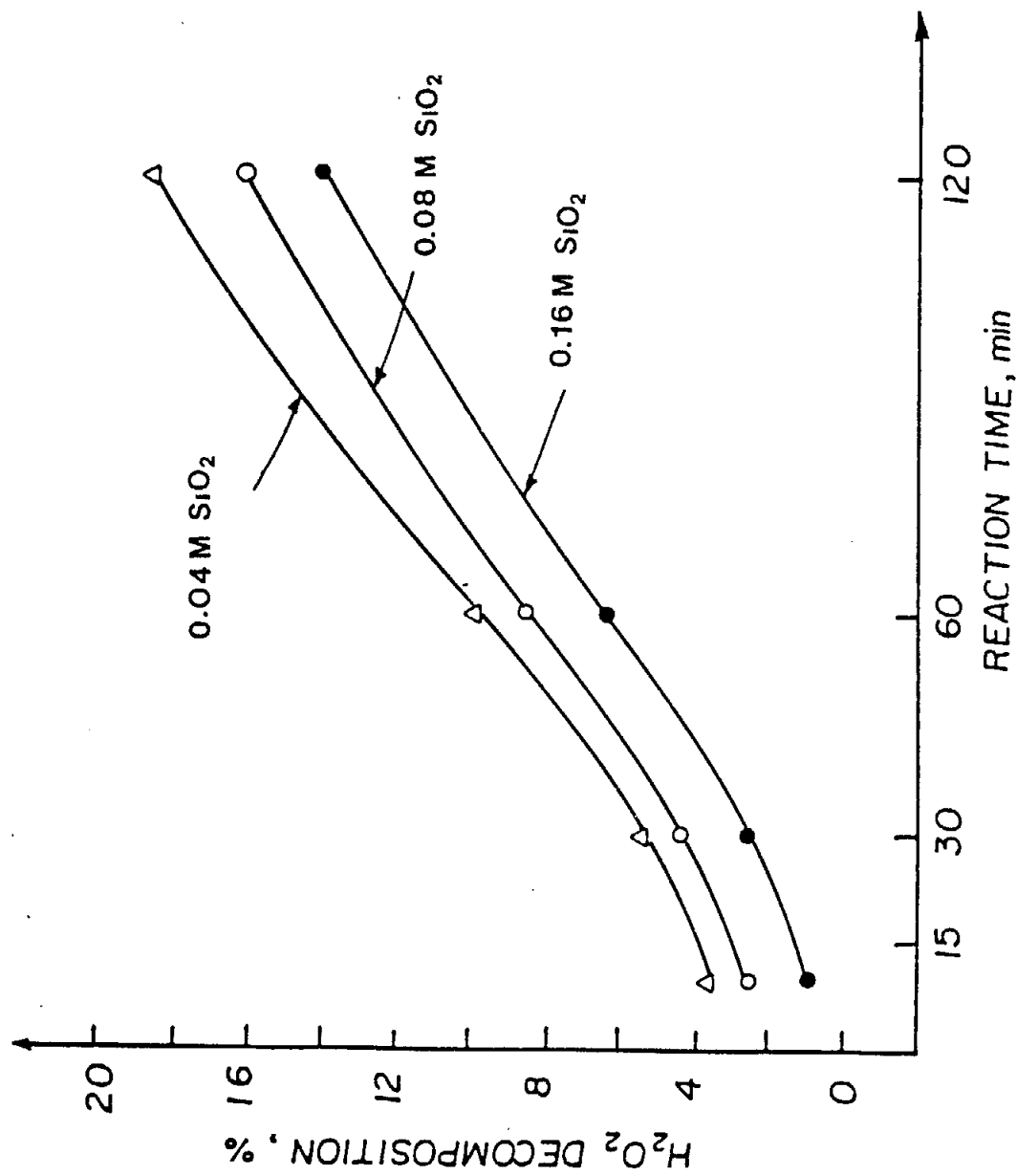


Figure 35. Effect of the sodium silicate concentration on the extent of decomposition of 0.098 M H_2O_2 . (initial pH 10.8, 50° C).

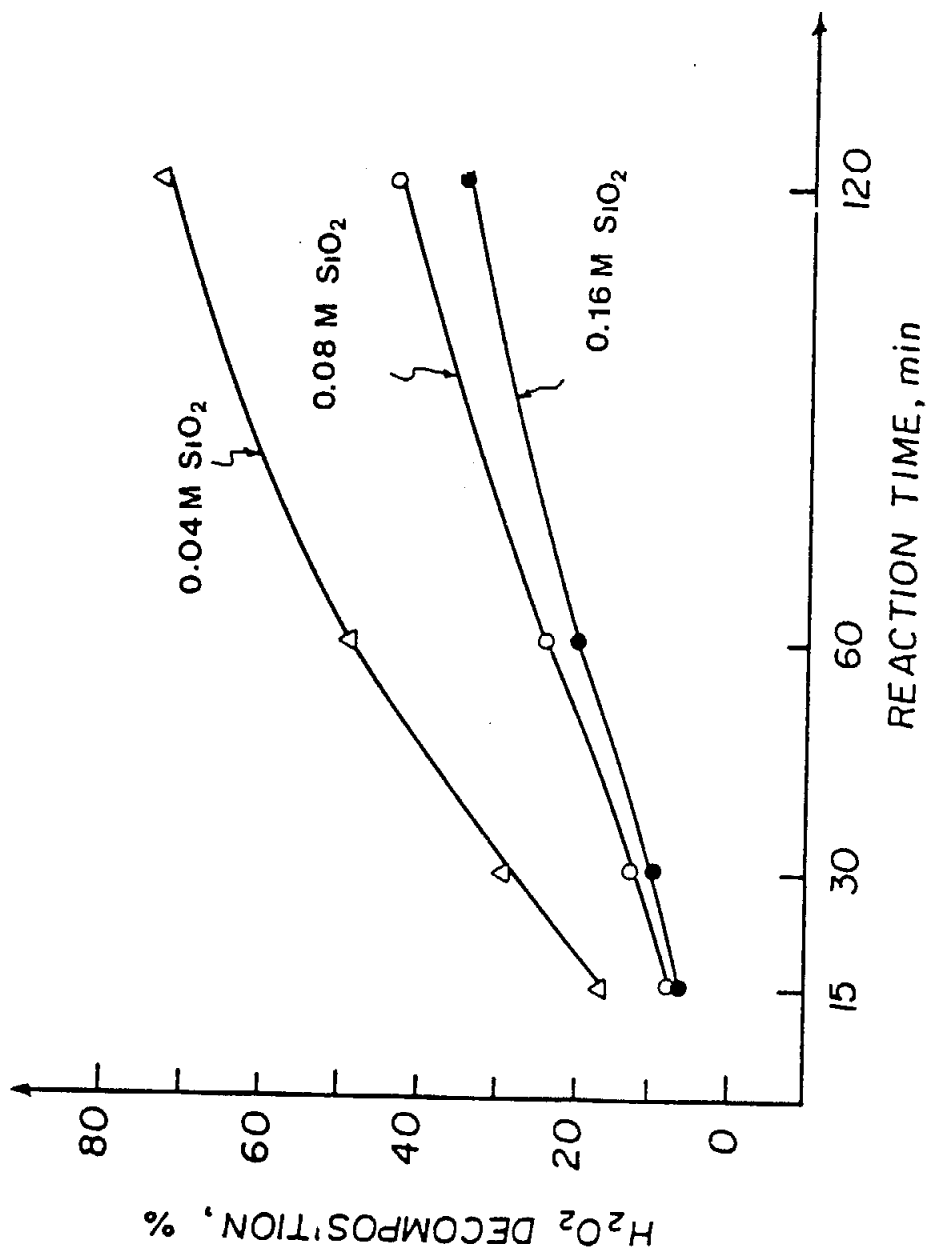


Figure 36. Effect of the sodium silicate concentration on the extent of decomposition of 0.098 M H_2O_2 . (initial pH 11.3, 50° C).

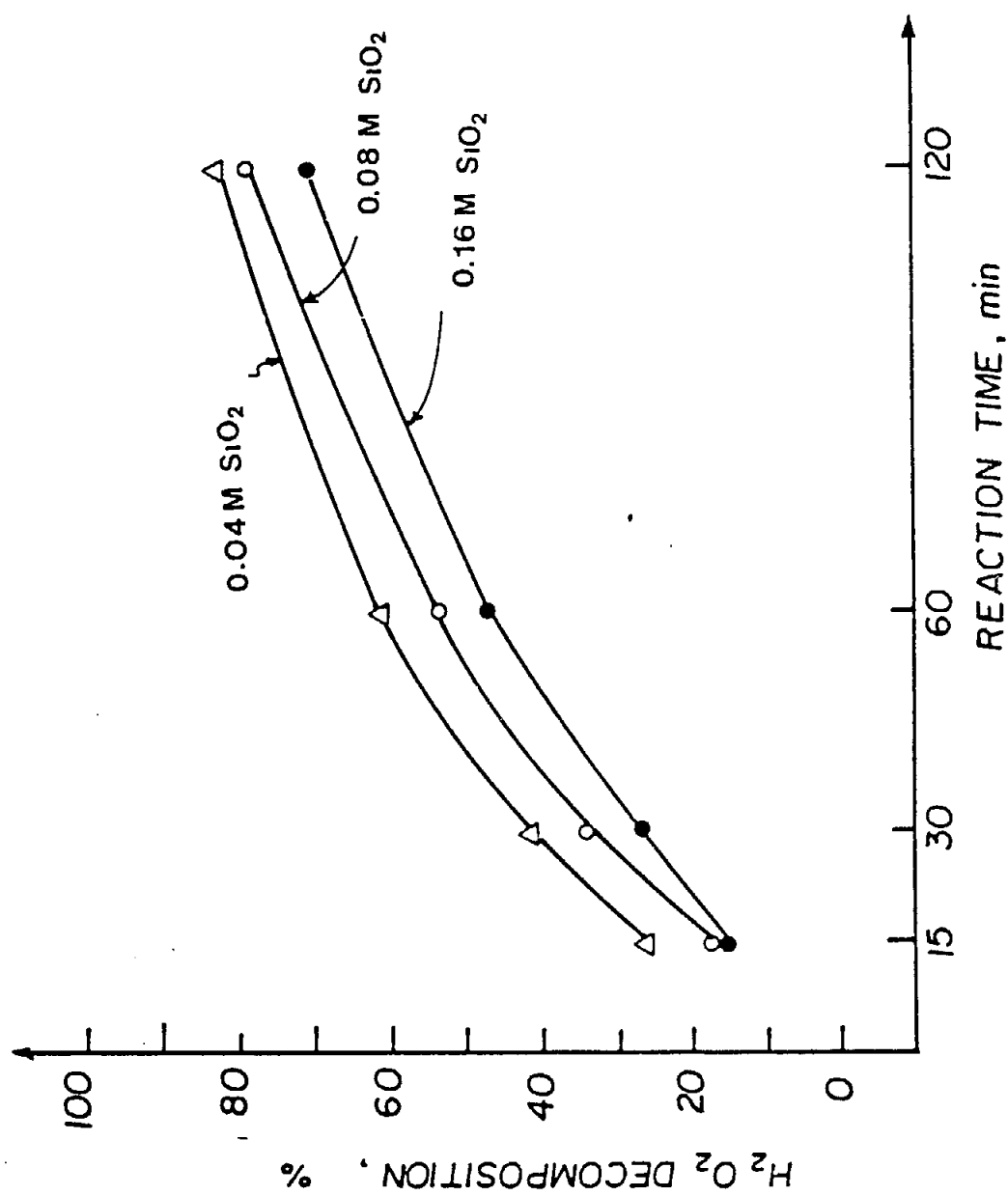


Figure 37. Effect of the sodium silicate concentration on the extent of decomposition of 0.098 M H_2O_2 . (initial pH 11.8, 50° C).

certain transition metal impurities (e.g. Fe, Cu, and Mn) present in the commercial silicate, particularly at pH values above 10.8.

3.1.3. pH Control

To investigate the theory that hydroxyl ions enhance peroxide decomposition^{139,150}, a study was undertaken in which the pH of the solutions was kept constant over the entire course of the reaction without using buffers. This was accomplished by automatic titration of decomposition-generated hydroxyl ions with hydrochloric acid.

The results of these tests show that control of pH decreased peroxide decomposition over the whole pH range investigated (Fig. 38). The decrease in decomposition caused by maintaining the pH can probably be attributed to the decreased availability of hydroxyl ions which are responsible for the activation of the transition metal impurities present in the sodium silicate, especially at pH values above 10.8. The extents of peroxide decomposition under pH controlled conditions in the pH range 10.3 to 11.8 are presented in Figure B-1 (Appendix B).

3.1.4. Ionic Strength

The effect of ionic strength on peroxide decomposition in the presence of silicate is portrayed in Figure 39. In contrast to what has been found by other workers¹⁴⁸, increasing ionic strength up to 1.0 M is shown to have an insignificant effect on peroxide decomposition. The ionic strength of solutions containing silicate was indirectly measured by conductometric

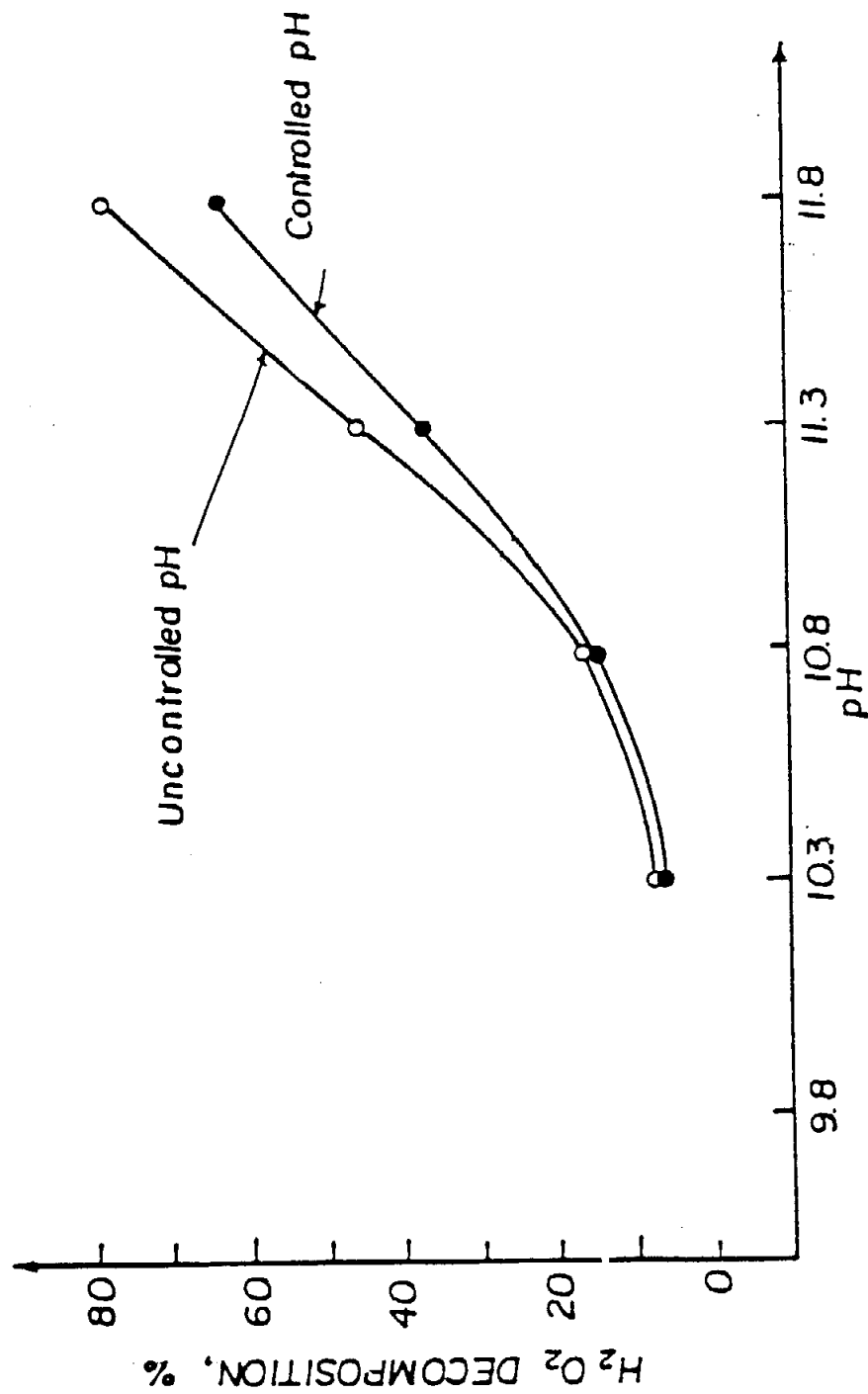


Figure 38. Decomposition of 0.098 M H_2O_2 in the presence of sodium silicate under pH-controlled and pH-uncontrolled conditions. ($SiO_2 = 0.08$ M, 50° C, 120 min).

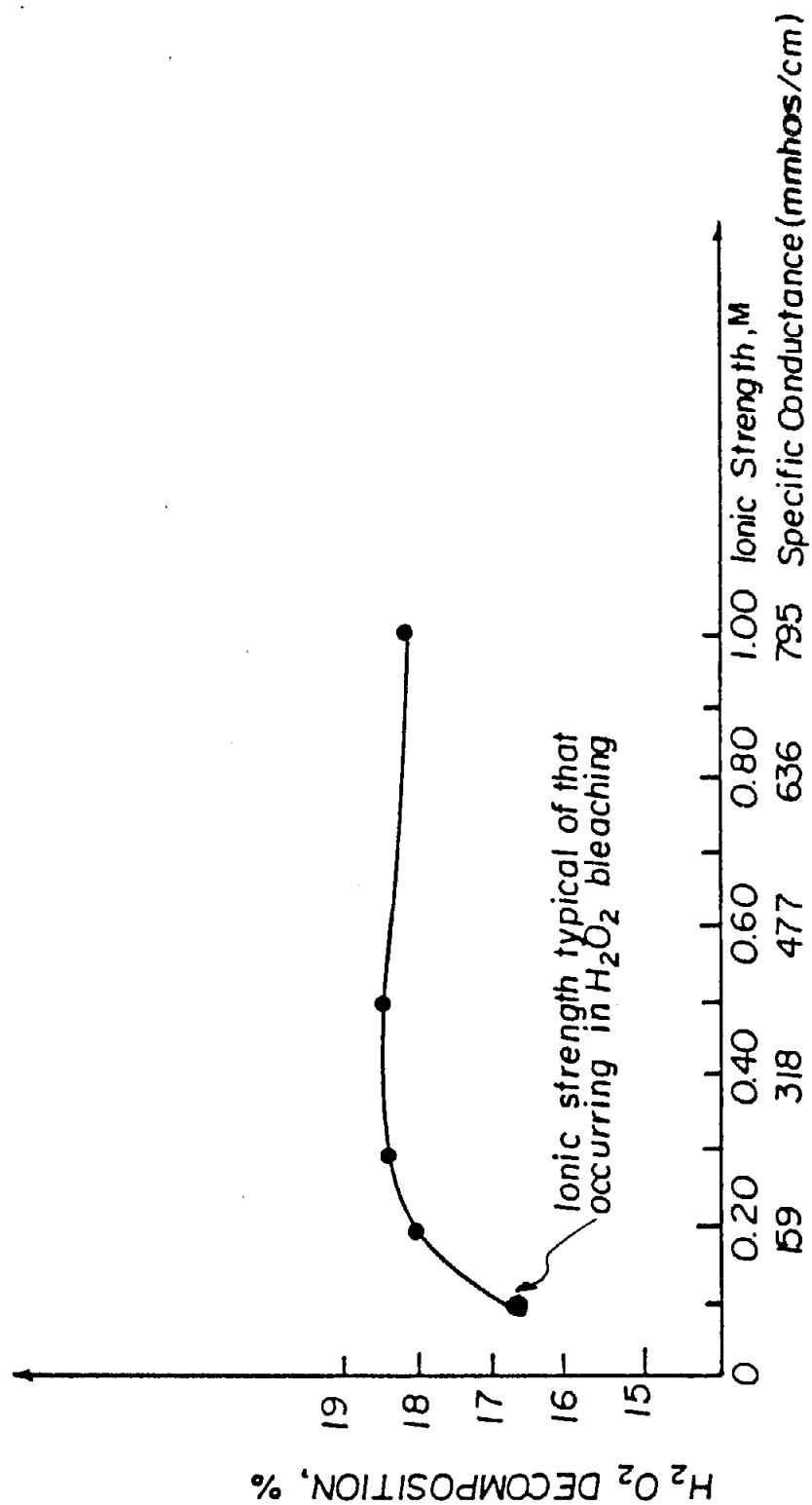


Figure 39. Effect of ionic strength on the decomposition of 0.098 M H_2O_2 in the presence of sodium silicate. ($SiO_2 = 0.008$ M, initial pH 10.8, 50° C, 120 min).

analysis because the ion concentrations of silicate solutions can not be determined simply by calculation.

3.1.5. Temperature

Temperatures of 50° and 60° C were chosen for this study because they are typical of those most generally used in commercial pulp brightening. The results in Figure 40 show that decomposition was enhanced approximately three-fold after 120-min by increasing the temperature from 50° to 60° C. The enhanced extent of peroxide decomposition with increasing temperature was also observed in the presence of iron, copper, and manganese (Figs. 41-43).

3.1.6. Effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ Ratio of Sodium Silicate

Results showing the effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio on peroxide decomposition (Fig. 44) indicate no distinct and understandable trend. The least effective stabilizer is the sodium silicate with the lowest $\text{SiO}_2/\text{Na}_2\text{O}$ ratio but, on the other hand, the most effective stabilizer did not have the highest $\text{SiO}_2/\text{Na}_2\text{O}$ ratio. Theoretically, silicates with higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratios should be more effective stabilizers since they are more extensively polymerized²⁸. The rather irregular results obtained in these experiments probably arose from the different purities of the various silicates studied. Although the iron concentrations of the four silicates were adjusted to the same value, the concentrations of other transition metal impurities such as copper and manganese may have been different, thus

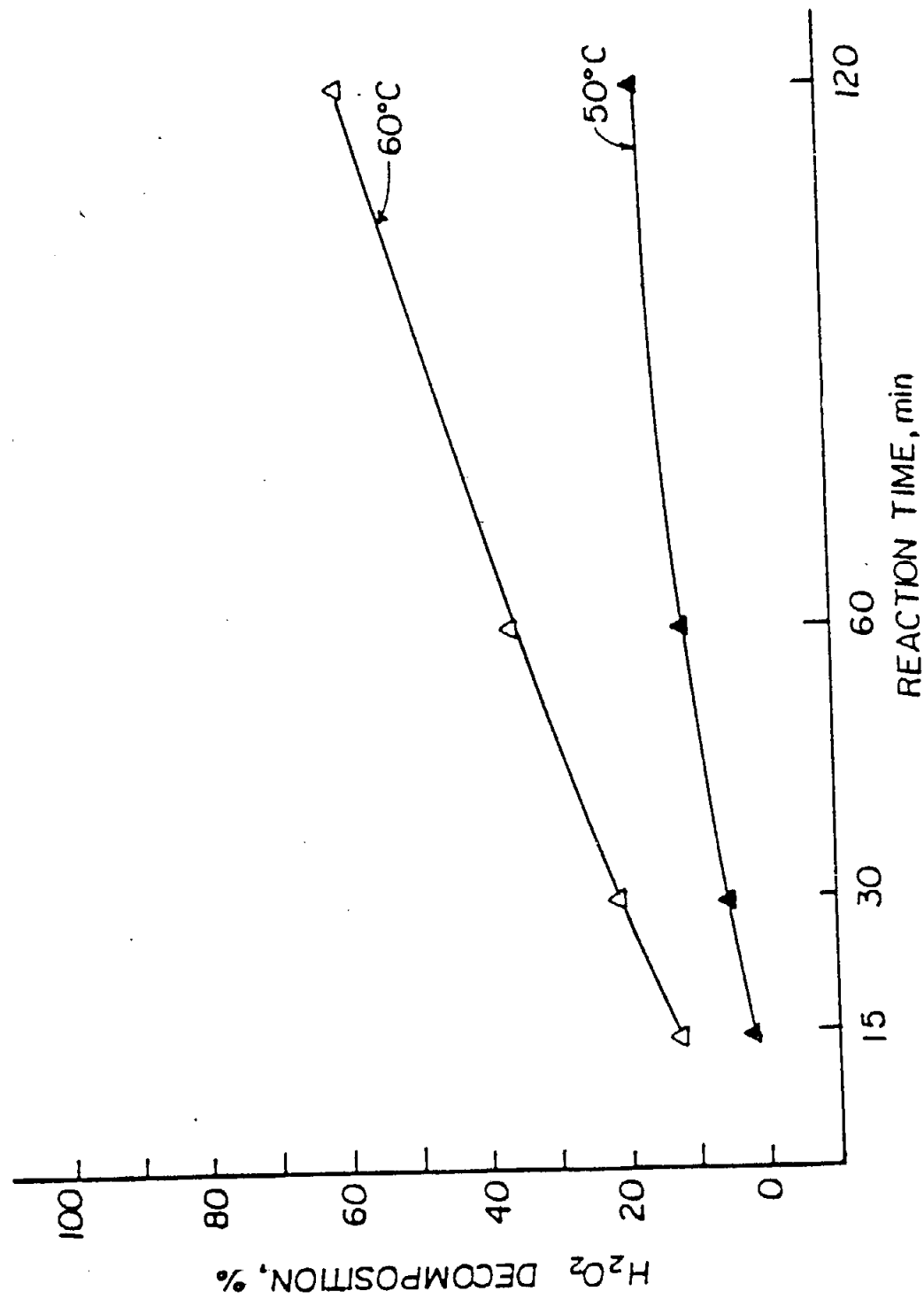


Figure 40. Effect of temperature on the extent of decomposition of 0.098 M H_2O_2 in the presence of sodium silicate. ($\text{SiO}_2 = 0.08 \text{ M}$, initial pH 10.8).

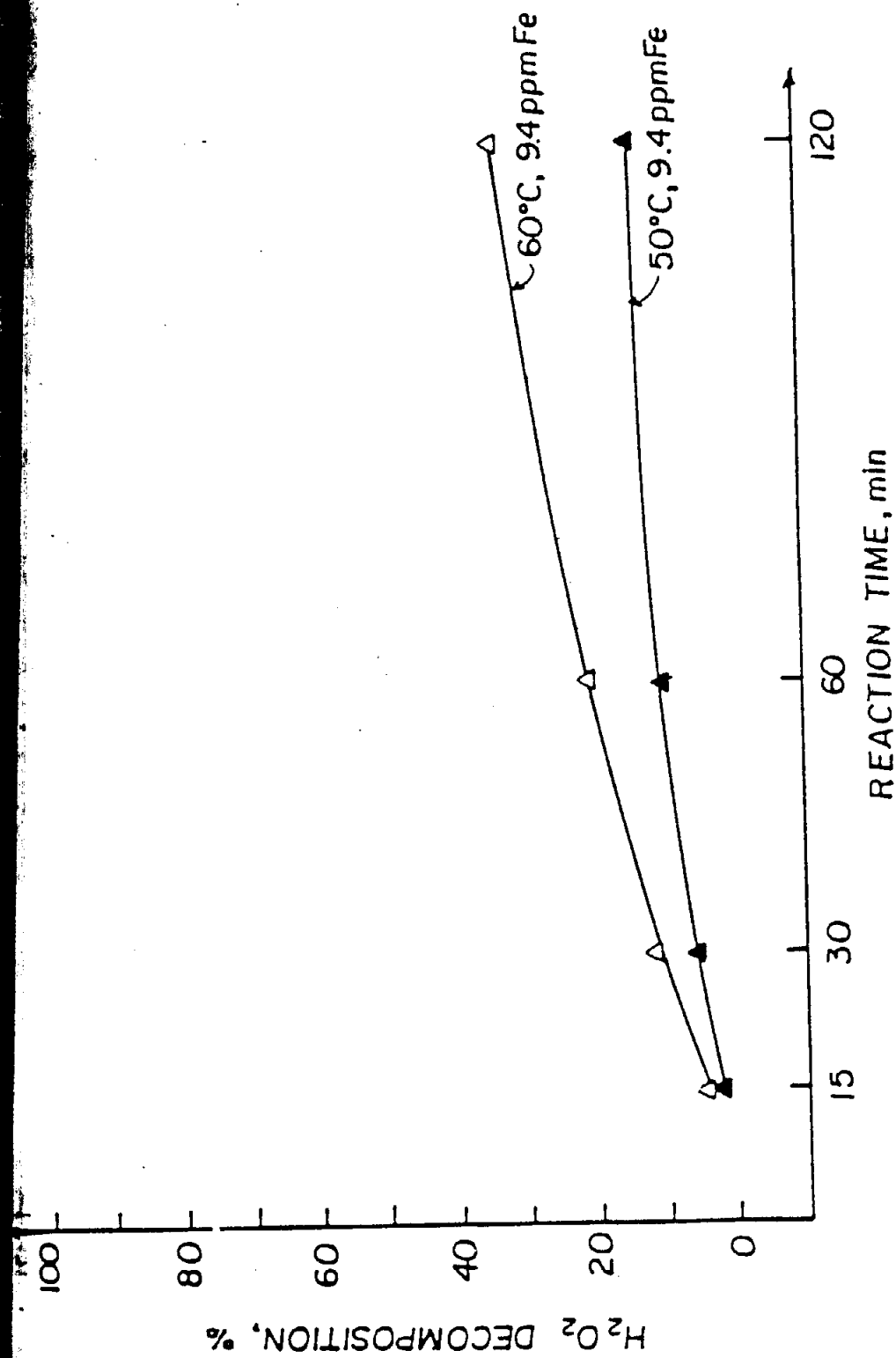


Figure 41. Effect of temperature on the extent of decomposition of 0.098 M H_2O_2 in the presence of sodium silicate and iron. ($\text{SiO}_2 = 0.08$ M, initial pH 10.8).

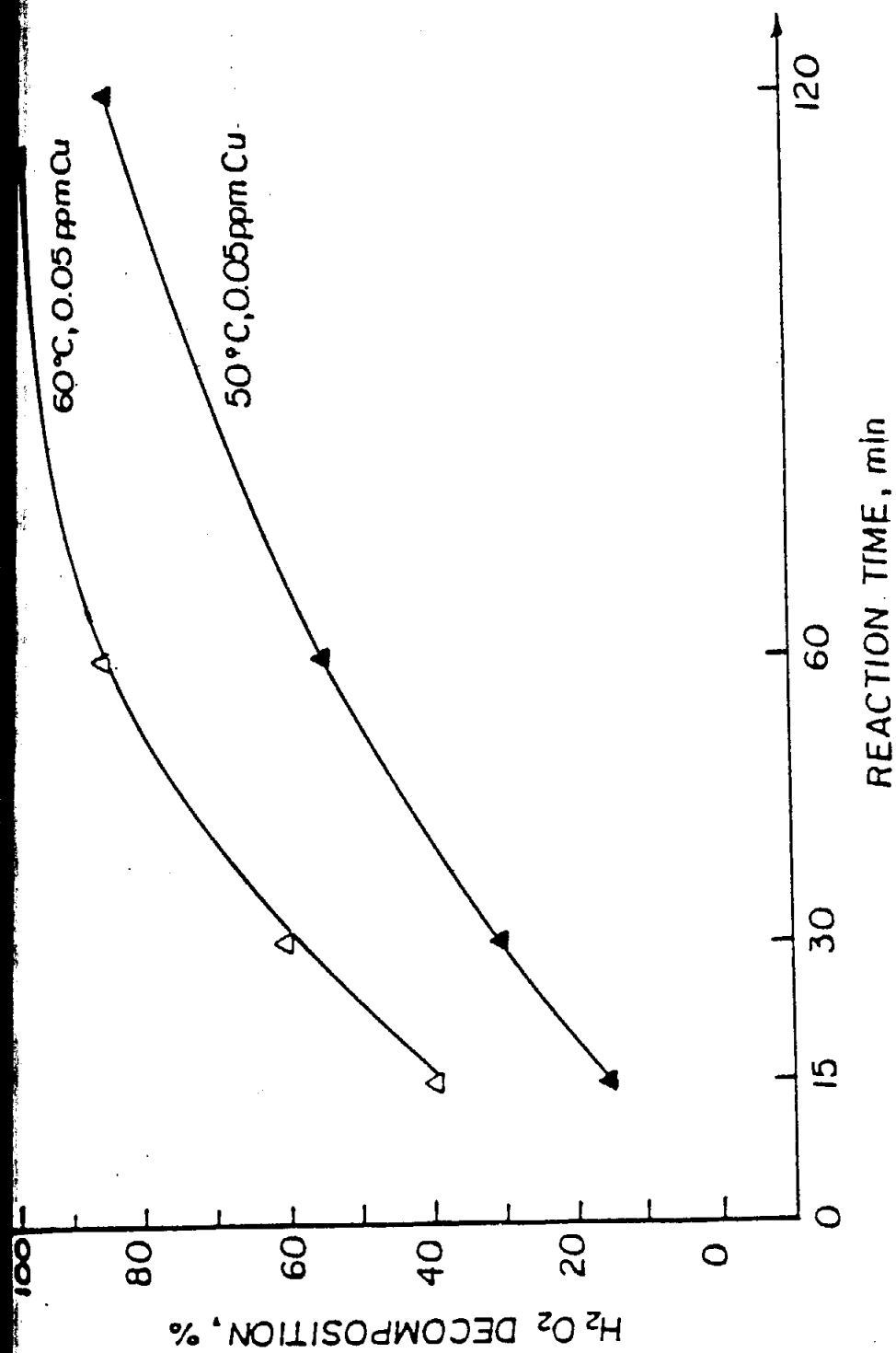


Figure 42. Effect of temperature on the extent of decomposition of 0.098 M H₂O₂ in the presence of sodium silicate and copper. (SiO₂ = 0.08 M, initial pH 10.8).

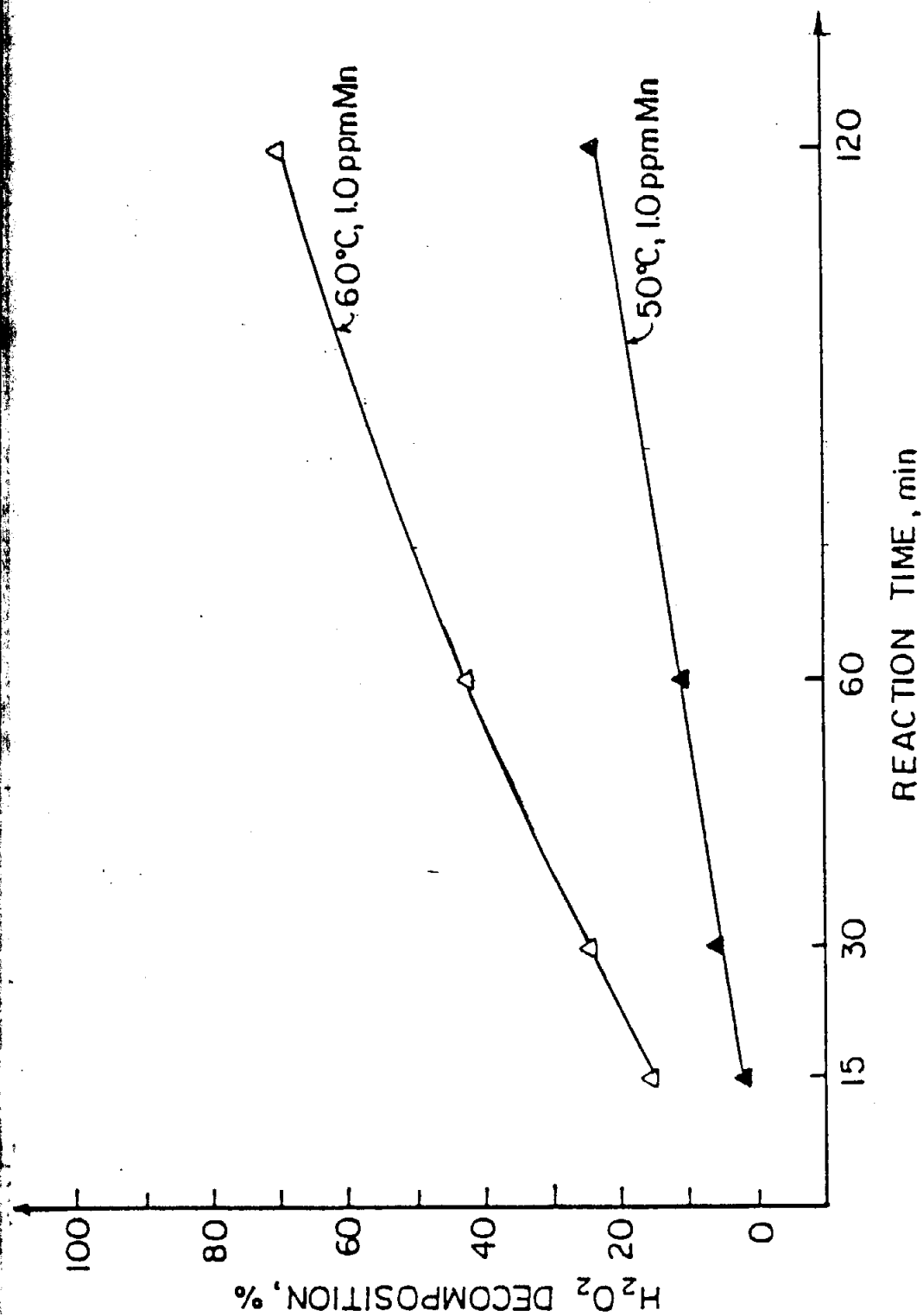


Figure 43. Effect of temperature on the extent of decomposition of 0.098 M H_2O_2 in the presence of sodium silicate and manganese. ($SiO_2 = 0.08$ M, initial pH 10.8).

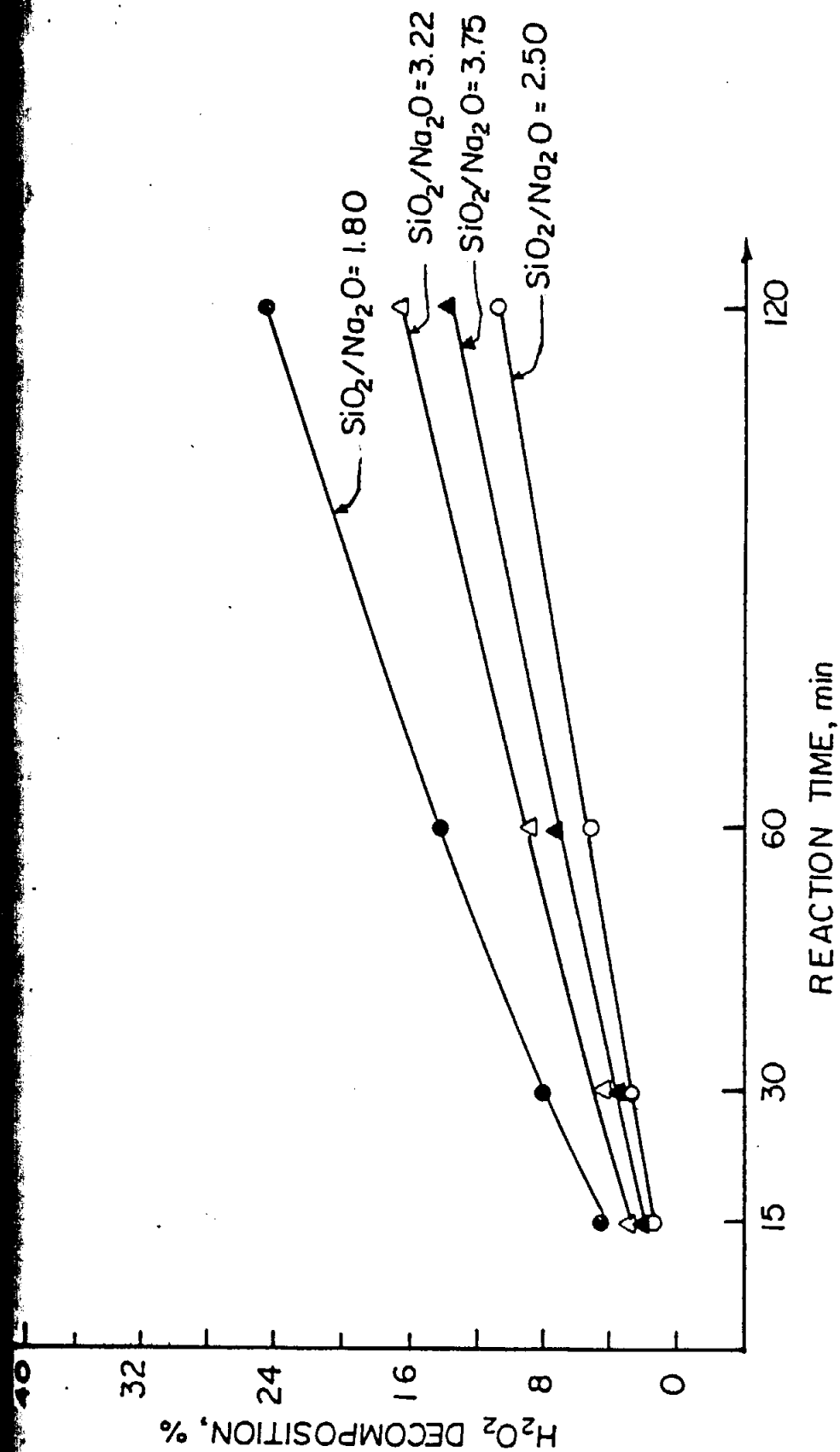


Figure 44. Effect of sodium silicate composition on the extent of decomposition of 0.098 M H_2O_2 . ($\text{SiO}_2 = 0.08 \text{ M}$, initial pH 10.8, 50°C).

causing unpredictable decomposition values.

3.2. Effect of Transition Metals on Peroxide Decomposition

The iron concentrations were chosen so as to bracket the concentrations normally encountered during pulp brightening. Concentrations of manganese and copper lower than those prevailing in pulp brightening systems were used in order to avoid total consumption of the hydrogen peroxide during the test.

3.2.1. Iron

Under certain conditions sodium silicate is an effective stabilizer for hydrogen peroxide in the presence of iron. For example, at pH values below 10.8, iron in concentrations of up to 9 ppm acts as a peroxide stabilizer rather than as a catalyst whereas at very high concentration it catalyzes peroxide decomposition (Fig. 45). With increasing pH values above 10.8, the iron-catalyzed reaction takes place and sodium silicate becomes a poor peroxide stabilizer regardless of iron concentration. It should be pointed out, nevertheless, that hydrogen peroxide brightening is usually conducted at pH values of 11 or below, hence the benefits of sodium silicate in this particular situation are substantial. The reason why sodium silicate is a more effective peroxide stabilizer in the presence of low concentrations of iron than in its absence is as yet unknown. Also, it is not known why sodium silicate becomes ineffective as a peroxide stabilizer at pH values above 10.8.

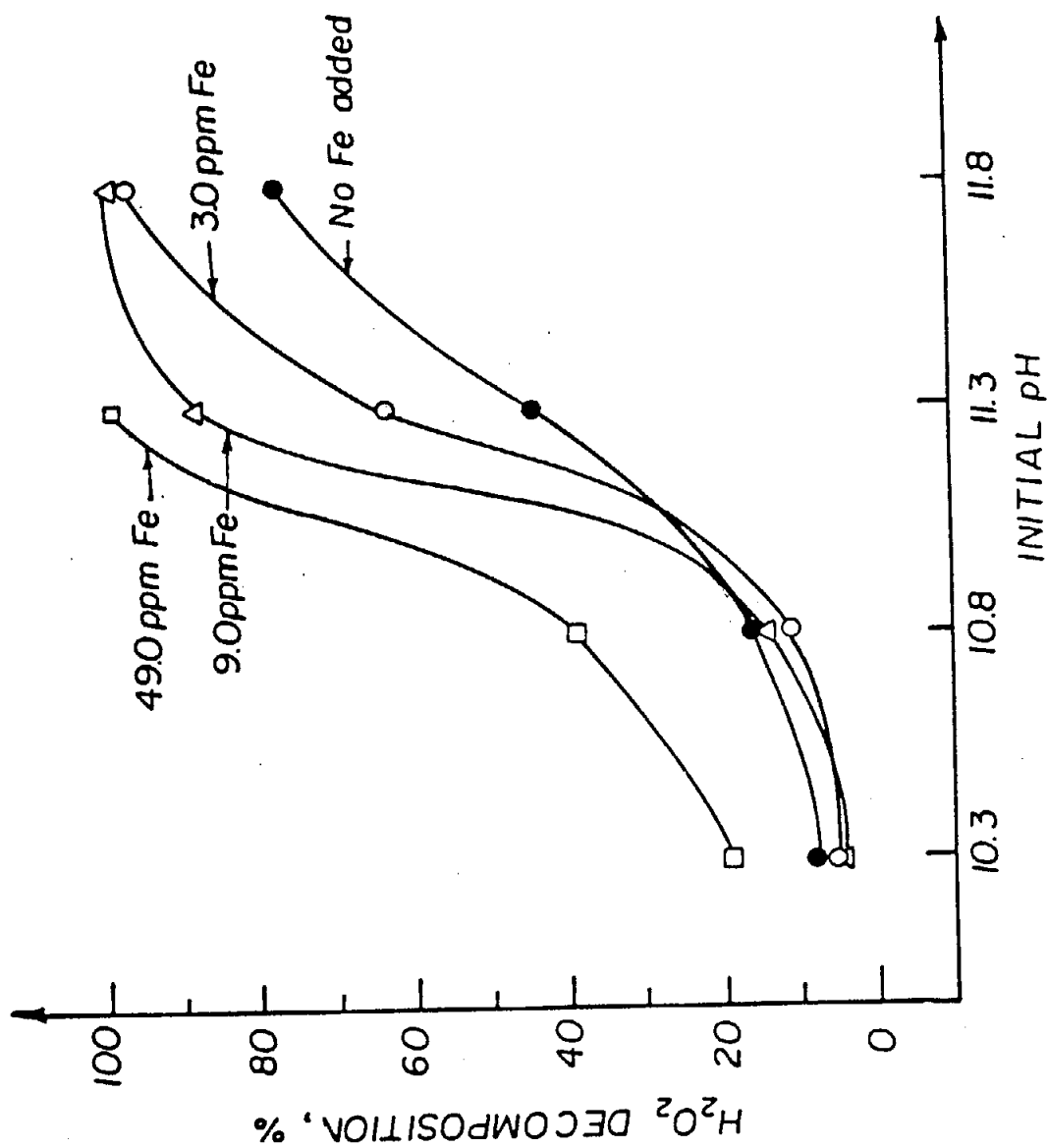


Figure 45. Effect of iron concentration on the decomposition of 0.098 M H_2O_2 in the presence of sodium silicate. ($SiO_2 = 0.08$ M, $50^\circ C$, 120 min).

3.2.2. Copper

In the presence of copper, sodium silicate is a strong catalyst for peroxide decomposition regardless of pH (Fig. 46). Copper concentrations as low as 0.01 ppm, which are innocuous in the absence of sodium silicate, caused significant decomposition of hydrogen peroxide even at lower pH values. It is interesting to note that the synergistic effect of copper-silicate combinations on peroxide decomposition is not observed when the copper is present in high (>50 ppm) concentrations. The results compiled in Table 13 demonstrate that at a copper concentration of 100 ppm, silicate is indeed a stabilizer for hydrogen peroxide. Under normal brightening conditions, however, the copper concentration rarely exceeds 10 ppm, therefore the synergistic effect of copper and silicate is bound to exist. It should be pointed out that the experiments with high copper concentrations were conducted at 6° C to avoid the total consumption of peroxide during the test.

The catalytic effect of sodium silicate in the presence of copper has been found by other workers^{18,61} but no plausible explanation for this observation has yet been given. However, it is reasonable to assume that this synergistic effect is caused by some type of interaction between sodium silicate and hydrous copper oxide (the most likely copper species under weakly alkaline conditions) which results in formation of copper silicate.

In an effort to determine whether copper silicate is a more

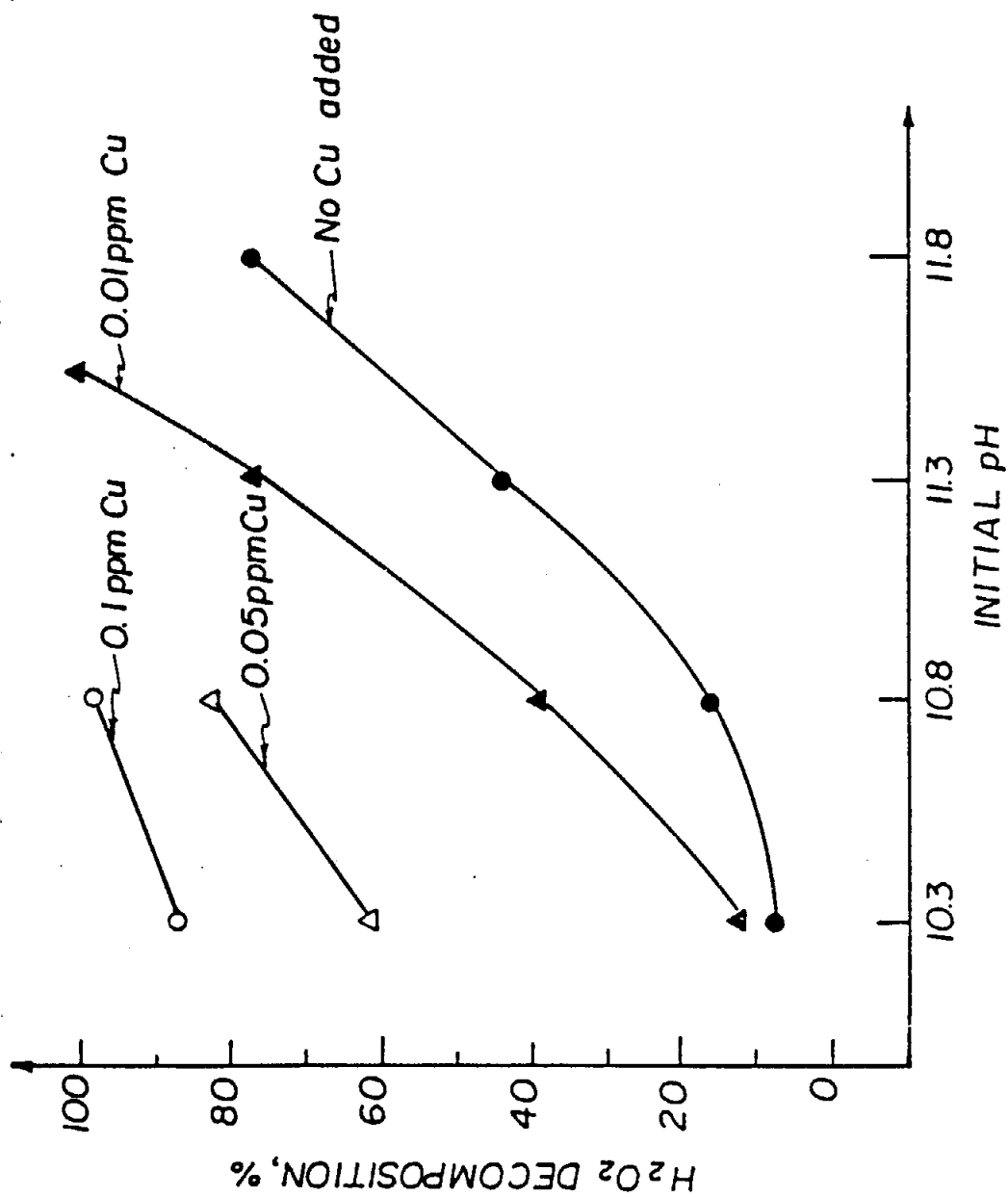


Figure 46. Effect of copper concentration on the decomposition of 0.098 M H_2O_2 in the presence of sodium silicate. ($\text{SiO}_2 = 0.08 \text{ M}$, 50°C , 120 min).

severe catalyst for peroxide decomposition than hydrous copper oxide itself, the former was synthesized from sodium silicate and copper sulfate and reacted with hydrogen peroxide.

TABLE 13. The Effect of Copper Concentration on the Decomposition of 0.098 M H_2O_2 in the Presence and Absence of Silicate. (0.08 M SiO_2 , initial pH 10.8, 6° C, 120 min).

Copper Conc., ppm	H_2O_2 Decomposition, %	
	Without Silicate	With Silicate
0.5	1.6	28.8
2.5	2.4	32.3
10.0	9.2	37.6
50.0	32.8	38.6
100.0	78.9	43.3

The results in Table 14 show that peroxide decomposition in the H_2O_2 - $CuSiO_3$ system is similar to that occurring in the H_2O_2 - $CuSO_4$ system. Thus, copper silicate is not a more effective catalyst for peroxide decomposition than hydrous copper oxide itself. Besides, if only the relatively small amount of sodium silicate which is chemically combined with copper is responsible for the synergistic effect, peroxide decomposition in the H_2O_2 - $CuSiO_3$ and H_2O_2 - $CuSO_4$ - Na_2SiO_3 systems should have been similar but such was not the case (Table 14). Therefore, the excess silicate that does not react with copper plays an important role in the observed synergistic effect. Changes in the SiO_2/Cu_2O ratio of the copper silicate occur when excess silicate

is present in the reaction²²² and these changes may explain the enhanced synergistic effect caused by the addition of silicate in excess of that which reacts with the copper.

TABLE 14. The Effect of Copper Silicate on the Decomposition of 0.098 M H_2O_2 in the Presence and absence of Sodium Silicate (0.08 M SiO_2). ($CuSO_4 = CuSiO_3 = 10$ ppm as Cu, initial pH 10.8, 6° C, 120 min).

System	H_2O_2 Decomposition, %
$H_2O_2 - CuSO_4$	9.2
$H_2O_2 - CuSiO_3$	10.1
$H_2O_2 - CuSO_4 - Na_2SiO_3$	37.6
$H_2O_2 - CuSiO_3 - Na_2SiO_3$	48.8

The reason why decomposition is lower in the H_2O_2 - $CuSO_4$ - Na_2SiO_3 system than it was in the H_2O_2 - $CuSiO_3$ - Na_2SiO_3 system is not apparent.

3.2.3. Manganese

The effect of pH and manganese concentration on hydrogen peroxide decomposition in the presence of silicate is illustrated in Figure 47. Similar to the cases of iron and copper, peroxide decomposition catalyzed by manganese increases rather sharply with increasing pH above 10.8. Manganese-catalyzed peroxide decomposition in the presence of silicate under varying pH conditions differs substantially from that observed in the absence of silicate. In the latter situation, decomposition

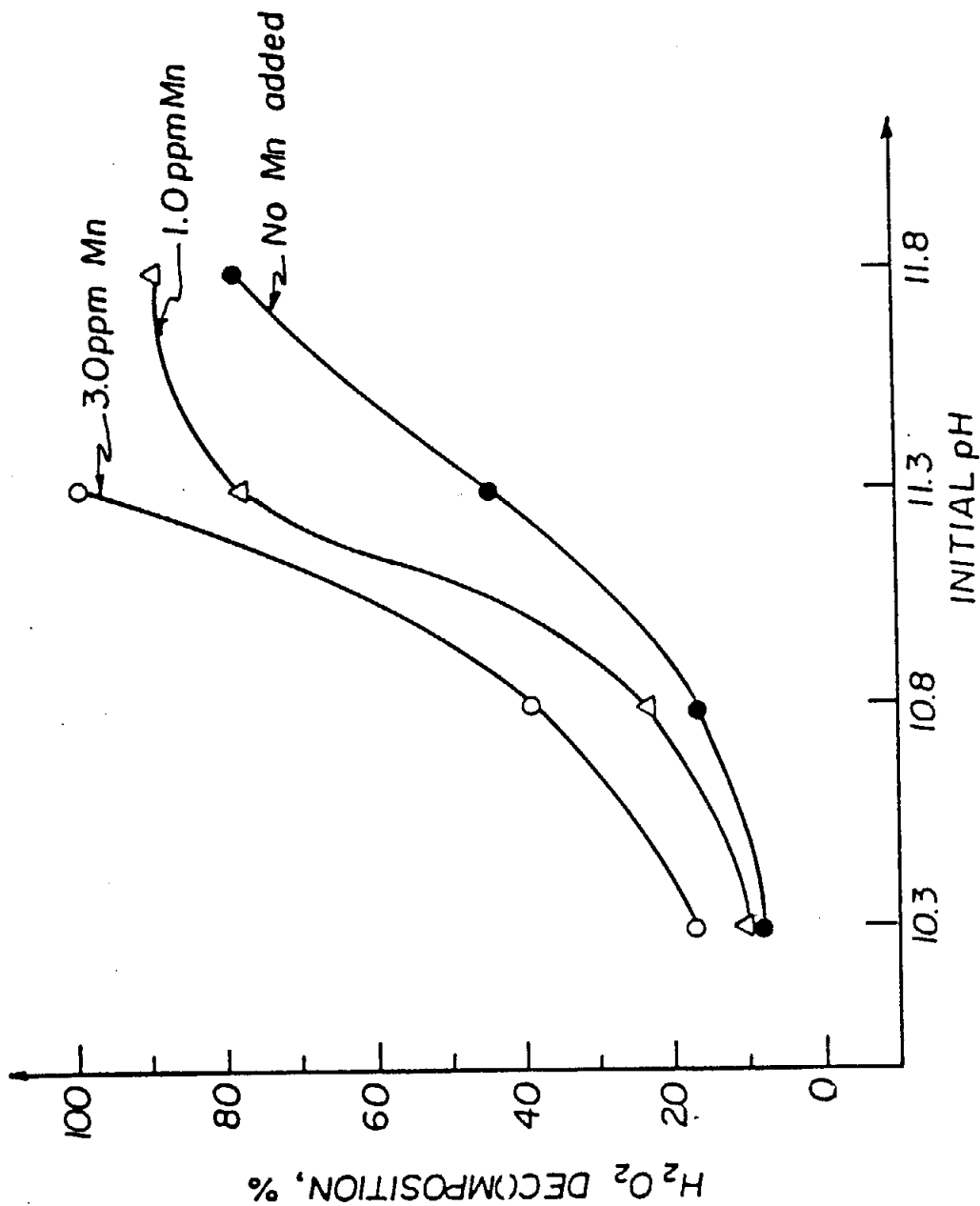


Figure 47. Effect of manganese concentration on the decomposition of 0.098 M H_2O_2 in the presence of sodium silicate. ($SiO_2 = 0.08$ M, 50° C, 120 min).

correlated very irregularly with pH reaching a maximum value at pH 9.8 and a minimum value at pH 10.3 (section 3.2.3 - chapter 2). In the presence of silicate, the lower decomposition values obtained in the pH range 10.3 to 10.8 are probably attributable to the formation of stable manganese silicate. However, with increasing pH, formation of manganese hydroxide and manganese dioxide is more favored thus preventing or retarding the formation of stable manganese silicate. Consequently, peroxide decomposition increases sharply because of the strong catalytic effect of manganese dioxide.

3.2.4. Metal Combinations

The effect of sodium silicate on peroxide stability in the presence of various combinations of iron, copper, and manganese is illustrated by the data in Table 15. Although the results are interesting a more thorough investigation of this subject is needed in order to draw any valid conclusion.

3.2.5. Aging of the Metals

"Aged" transition metals were prepared by boiling 0.005 M solutions of the metal salts for three hours at pH 6.5. A pH of 6.5 was selected in order to reproduce the pH conditions normally prevailing in wood pulp and process water which are the main sources of most of the transition metals encountered in pulp brightening systems. Metal solutions designated of "fresh" were prepared by dissolving the transition metal salts in 0.1 M HCl.

Of the metals studied, iron was the only one whose catalytic activity was changed significantly by the aging treatment (Table 16). The decrease in the catalytic activity of iron resulting from aging probably can be traced to the formation of hydrous iron oxides which are effectively inactivated by sodium silicate. When silicate was added to "fresh" iron solutions, formation of iron silicate took place but, apparently, the latter is a more effective peroxide decomposition catalyst than hydrous iron oxides deactivated with sodium silicate.

The aging of manganese and copper solutions did not result in any significant changes in the catalytic activities of these metals in the presence of silicate. Similar results were obtained in the absence of silicate (ref. section 3.2.5 - chapter 2). It should be pointed out, however, that in the case of manganese, the solution was not changed to any extent by the aging treatment, i.e., no insoluble manganese hydroxide or oxide was formed as indicated by the clarity of the solution. Therefore, no alteration in the catalytic activity of manganese towards peroxide was expected to result from aging. In the case of copper, on the other hand, the aging presumably resulted in formation of hydrous copper oxide but even so, no difference in peroxide decomposition was observed. This result can be explained if one assumes that the catalytic activity of the copper silicate formed by interaction between "fresh" copper and sodium silicate is similar to the catalytic activity of the copper hydroxide formed during the aging of the solutions.

TABLE 15. Individual and Combined Effects of Transition Metals (Fe, Cu and Mn) on the Decomposition of 0.098 M H_2O_2 in the Presence of Sodium Silicate. (0.08 M SiO_2 , Initial pH 10.8, 50° C, 120 min).

Metal Combination	H ₂ O ₂ Decomposition, %					Combined Effect
	Individual Effect					
	No Added Metal	Fe ¹	Cu ¹	Mn ¹	Total	
Fe + Cu + Mn	16.0	-3.0	22.0	8.0	43.0	59.0
Fe + Cu	16.0	-3.0	22.0	-	35.0	15.0
Fe + Mn	16.0	-3.0	-	8.0	21.0	54.0
Cu + Mn	16.0	-	22.0	8.0	46.0	38.0

¹ Fe = 9.4 ppm, Cu = 0.01 ppm, Mn = 1.0 ppm

TABLE 16. Decomposition of 0.098 M H_2O_2 by "Fresh" and "Aged" Solutions of Iron, Copper, and Manganese in the Presence of Silicate. (0.08 M SiO_2 , initial pH 10.8).

Transition Metal	H_2O_2 Decomposition, %	
	Fresh Metal	Aged Metal
Iron (20 ppm) ¹	29.5	11.8
Copper (0.1 ppm) ²	23.4	20.6
Manganese (5 ppm) ³	19.5	18.3

¹ 50° C, 2 h; ² RT, 30 min; ³ 50° C, 30 min

Under the nearly neutral conditions prevailing in biological systems, iron and copper certainly exist as "aged" metals, i.e., as hydroxides or hydrous oxides. Manganese, on the other hand,

exists in the "fresh" or ionic form. Therefore, the interactions of iron and manganese with silicate, which result in peroxide stabilization, probably occur via different routes.

3.3. Effect of Chelating Agents on Peroxide Decomposition

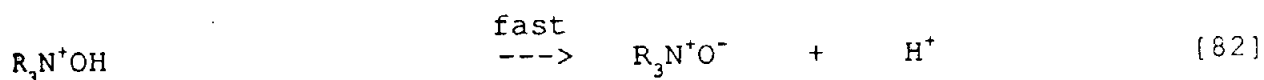
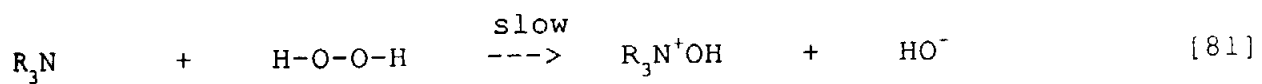
The two chelating agents chosen were the pentasodium salt of diethylenetriaminepentaacetic acid (Na_5DTPA) and triethanolamine (TEA). The former is frequently used commercially as a chemical pretreatment prior to mechanical pulp brightening the latter, on the other hand, is regarded as a very effective chelating agent at pH values above 10.0²¹⁴. The effect of chelating agent concentration on peroxide decomposition in the presence of sodium silicate is shown by the data compiled in Table 17.

TABLE 17. The Effect of Chelating Agent Concentration on the Decomposition of 0.098 M H_2O_2 in the Presence of Silicate. (0.08 M SiO_2 , initial pH 10.8, 50° C, 120 min).

Chelating Agent, g/L	H_2O_2 Decomposition, %	
	Na_5DTPA	TEA
1.700	8.8	12.9
0.340	2.4	9.4
0.170	1.0	4.8
0.034	0.5	5.5
0.000	16.0	16.0

Concentrations of Na_5DTPA as low as 0.034 g/L, which corresponds to 0.01 % Na_5DTPA on o. d. pulp at 25% consistency,

stabilized hydrogen peroxide solutions almost completely. Higher concentrations of Na_5DTPA resulted in small losses of hydrogen peroxide. These losses have been previously reported¹¹⁹, and probably are the result of peroxide consumption in reactions with Na_5DTPA . The reaction of tertiary amines with hydrogen peroxide is well-documented in the literature²¹⁵, reactions [81] and [82].



TEA, on the other hand, was unable to completely prevent the decomposition of hydrogen peroxide. Similar to Na_5DTPA , TEA consumes hydrogen peroxide. As seen in Table 17, none of TEA concentrations tested was able to completely stabilize peroxide without consuming it.

The effect of pH on peroxide stability in the presence of Na_5DTPA and TEA is presented in Figure 48. It is seen that both compounds were effective peroxide stabilizers in the pH range 10.3 to 11.8, Na_5DTPA being slightly superior. The fact that Na_5DTPA was an effective peroxide stabilizer at a pH above 11.0 in the presence of silicate contrasts with the results obtained in the absence of silicate. It was shown in the latter case that the stabilization capacity of Na_5DTPA is significantly reduced by increasing pH above 11 (section 3.3.2 - chapter 2 - page 103).

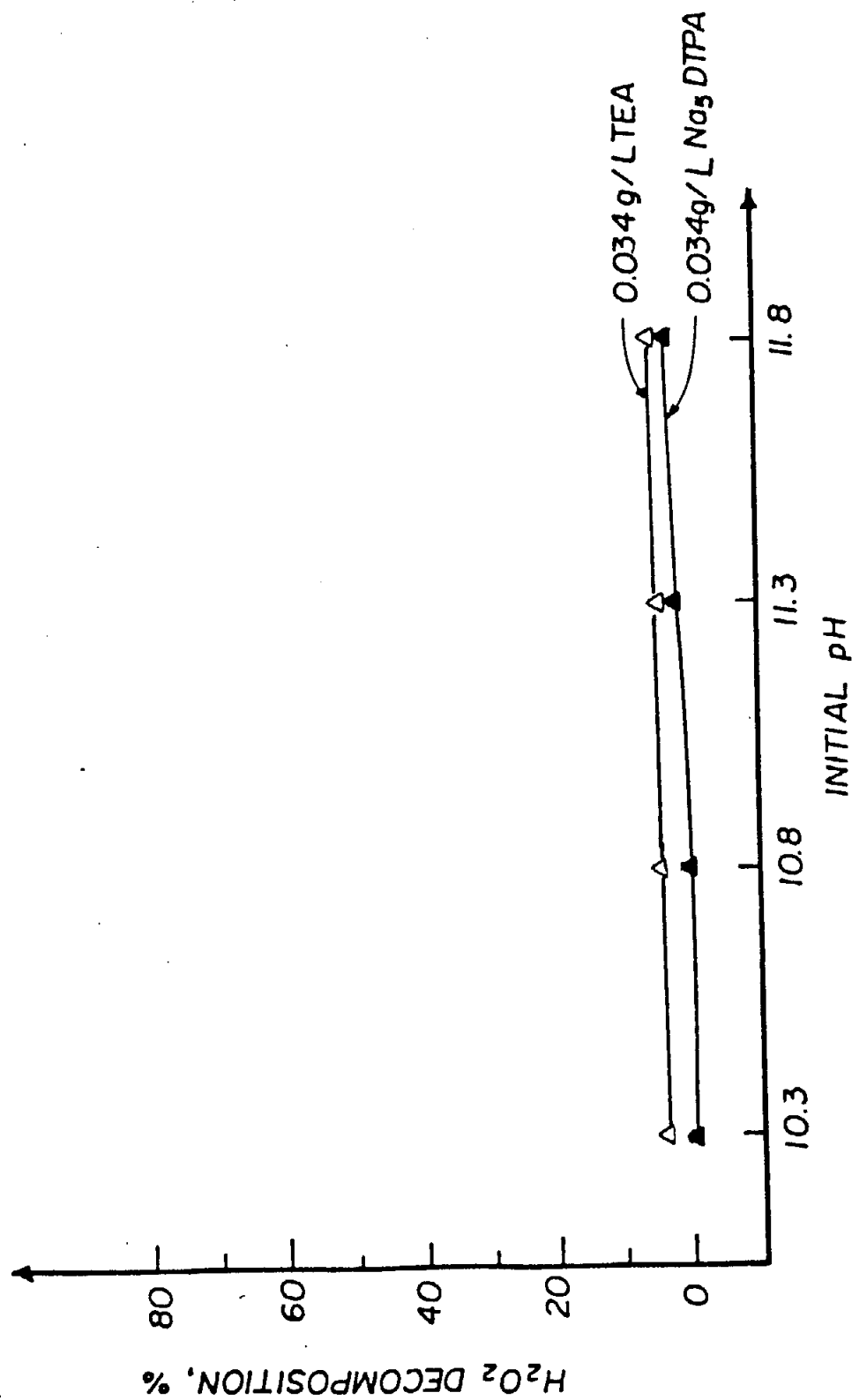


Figure 48. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of silicate and chelating agents. ($SiO_2 = 0.08$ M, $50^\circ C$, 120 min).

3.4. Mechanistic Considerations

In this section the most widely-accepted theories for peroxide stabilization by sodium silicate are considered in detail. In addition, the proposed formation of more reactive peroxysilicates is also discussed.

3.4.1. Formation of Peroxysilicates

The formation of a more reactive brightening agent, peroxysilicate, has been suggested as being the reason for improved peroxide brightening in the presence of sodium silicate¹⁴³. In an effort to find supporting evidence for this claim, the reactivities of alkaline hydrogen peroxide towards some peroxide-reactive compounds in the presence and absence of sodium silicate were compared under conditions where peroxide decomposition was negligible (in the presence of 0.034 g/L of Na_5DTPA). The reasoning was that any change in the reactivity of hydrogen peroxide caused by reaction with the silicate would indicate the existence of some other form of hydrogen peroxide which could very well be regarded as evidence for peroxysilicate formation.

The results in Table 18 show that the reactivity of hydrogen peroxide towards seven peroxide-reactive compounds (containing phenol, enone, ethylenic, and carbonyl functionalities) was not increased to any extent in the presence of sodium silicate. Since peroxide reactivity towards these compounds was not enhanced in the presence of silicate, it is also very unlikely that, if

present, peroxysilicates would have any extraordinary effect on lignin chromophores. Thus, based on the results in Table 18, the proposed theory which claims formation of more reactive peroxysilicates when silicate is added to alkaline solutions of peroxide is likely incorrect.

TABLE 18. Consumption of Peroxide-Reactive Compounds by 0.049 M H_2O_2 in the Presence and Absence of Sodium Silicate (0.04 M SiO_2 , initial pH 10.8, 120 min).

Compound	Consumption, %	
	Without Silicate	With Silicate
Mesityl Oxide (0.049M) ¹	84.1	85.3
Benzal Acetone (0.0049M) ¹	75.3	74.0
Isoeugenol (0.0049M) ²	15.3	15.8
4,4'-Dihydroxystilbene (0.0049M) ²	38.4	37.3
4-Methylcatechol (0.049M) ²	25.8	24.7
Methoxyhydroquinone (0.0049M) ¹	81.1	82.8
Vanillin (0.049M) ²	37.5	38.0

¹ RT, ² 50° C.

3.4.2. Stabilization of Hydrogen Peroxide

Most of the theories proposed to account for peroxide stabilization by sodium silicate involve deactivation of transition metals by the former. However, it has also been proposed that silicate stabilizes peroxide by forming stable peroxysilicates¹⁴³ with it or by disrupting free radical

decomposition reactions^{28,134}.

3.4.2.1. Disruption of Free Radical Chain Reactions

It has been suggested that silicate terminates reactions of hydrogen peroxide decomposition by binding free radical intermediates while simultaneously undergoing polymerization in the process^{28,134}. The free radicals that most likely exist under the weakly alkaline conditions used in brightening are hydroxyl and superoxide anion. Therefore, assuming the integrity of the proposed mechanism, the addition of sodium silicate to alkaline solutions of peroxide should decrease the concentration of these radicals.

The results presented in Table 19 show that the concentrations of hydroxyl and superoxide anion radicals are not changed significantly when silicate is added to a peroxide solution at pH 10.8. To further confirm this finding, copper was added to the reaction system in order to catalyze peroxide decomposition and thereby increase the amounts of free radicals in the system. In this case as well, silicate caused no reduction in the concentration of the radicals. Indeed, under the same reaction conditions, the amounts of radicals measured are higher in the system containing silicate. The higher concentration of radicals observed when copper and silicate are combined is attributable to the previously reported synergistic effect which causes enhanced peroxide decomposition (see results in brackets - Table 19).

The fact that silicate did not cause any significant

decrease in the concentration of hydroxyl and superoxide anion radicals is a clear indication that it does not function as a free radical scavenger. Therefore, the theory that silicate causes disruption of free radical chain reactions is also invalid.

A comparison of the extents of formation of superoxide anion radicals when peroxide is decomposed in the presence and absence of sodium silicate is illustrated in Figure B-2 (Appendix B). The effects of silicate concentration and pH on the generation of superoxide anion radical are shown, respectively, in Figures B-3 and B-4 (Appendix B).

TABLE 19. The Amounts of Hydroxyl and Superoxide Anion Radicals Detected when Hydrogen Peroxide is Decomposed in the Presence and Absence of Silicate and/or Copper. (initial pH 10.8, 50° C).

System	Radical Concentration, M . 10 ⁴		
	Hydroxyl ¹	Superoxide Anion ²	
No Silicate or Copper	9.4 (1.43) ³	1.4 ± 0.6	(5.0)
Silicate	9.2 (13.8)	1.5 ± 0.6	(4.5)
Copper	34.3 (28.0)	8.9 ± 2.8	(7.2)
Silicate - Copper	54.7 (95.7)	9.1 ± 3.1	(23.5)

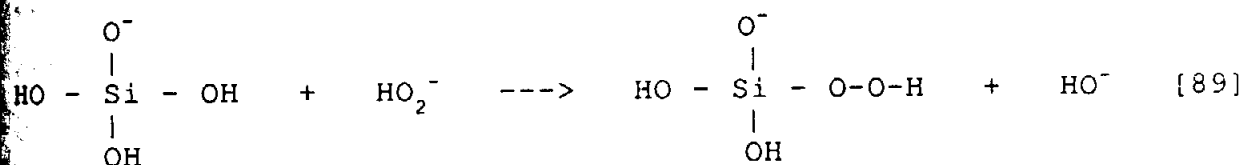
¹ Determined by measurement of the amounts of phenol generated during peroxide decomposition in the presence of benzene for 2 h. (H₂O₂ = 0.098 M, SiO₂ = 0.08 M, Fe = 18.8, Cu = 0.7, Mn = 0.3 ppm).

² Determined by EPR spectrometry after 10-min reaction (H₂O₂ = 0.49 M, SiO₂ = 0.08 M, Fe = 94, Cu = 3.5, Mn = 1.5 ppm).

³ Values in parentheses indicate % of peroxide decomposition

3.4.2.2. Formation of Stable Peroxysilicates

The peroxide stabilization effected by sodium silicate during brightening has been attributed to the formation of stable peroxysilicates¹⁴³. The proposed mechanism of peroxysilicate formation suggests a nucleophilic attack of perhydroxyl anion (a very powerful nucleophile) on a silanol group of the silicic acid resulting in the replacement of one of the hydroxyl groups, eq. [89].



If this reaction does in fact occur, formation of larger amounts of peroxysilicate should occur at higher alkalinities where a greater concentration of perhydroxyl anions is present and, consequently, better peroxide stability should be expected. The results presented in Figure 49 show, however, that peroxide stability is not influenced by pH if purified chemicals are used. Therefore, formation of more stable peroxysilicates, if it occurs, does not appear to be responsible for improved peroxide stabilization in the presence of sodium silicate.

3.4.2.3. Deactivation of Transition Metals

Before undertaking a thorough discussion of the proposed theories for silicate deactivation of transition metal impurities

during brightening, it is useful to first interpret the stability characteristics of peroxide when pH is varied in the presence and near absence of transition metals in solutions containing silicate. As is shown in Figure 49, peroxide decomposition in the presence of unpurified chemicals increases sharply with increasing pH, particularly above 10.8. On the other hand, decomposition in the presence of purified chemicals is not affected significantly by increasing pH in the range 10.3 to 11.8. The rather high decomposition values obtained at pH values above 11 in the presence of unpurified chemicals may be attributed to the enhancement of the catalytic activity of certain transition metal impurities present in the chemicals (Table 1 - page 65 and Table 9 - page 128). The enhancement of the catalytic activities of iron, copper, and manganese with increasing pH is clearly demonstrated in Figure 50. It is important to note that iron functions as a peroxide stabilizer at pH values lower than 10.8; this fact explains why peroxide decomposition in this pH range is slightly lower in the presence of the unpurified chemicals which contain iron as the major impurity (Fig. 49).

The fact that metal impurities, especially iron, present in commercial silicate increase peroxide decomposition at pH values above 11 explains why some researchers^{152,158} have contended that silicate actually destabilizes peroxide. Furthermore, the enhanced catalytic activity provided by the metals also explains why peroxide brightening of mechanical pulps is highly inefficient at pH values above 11. If transition metal-free

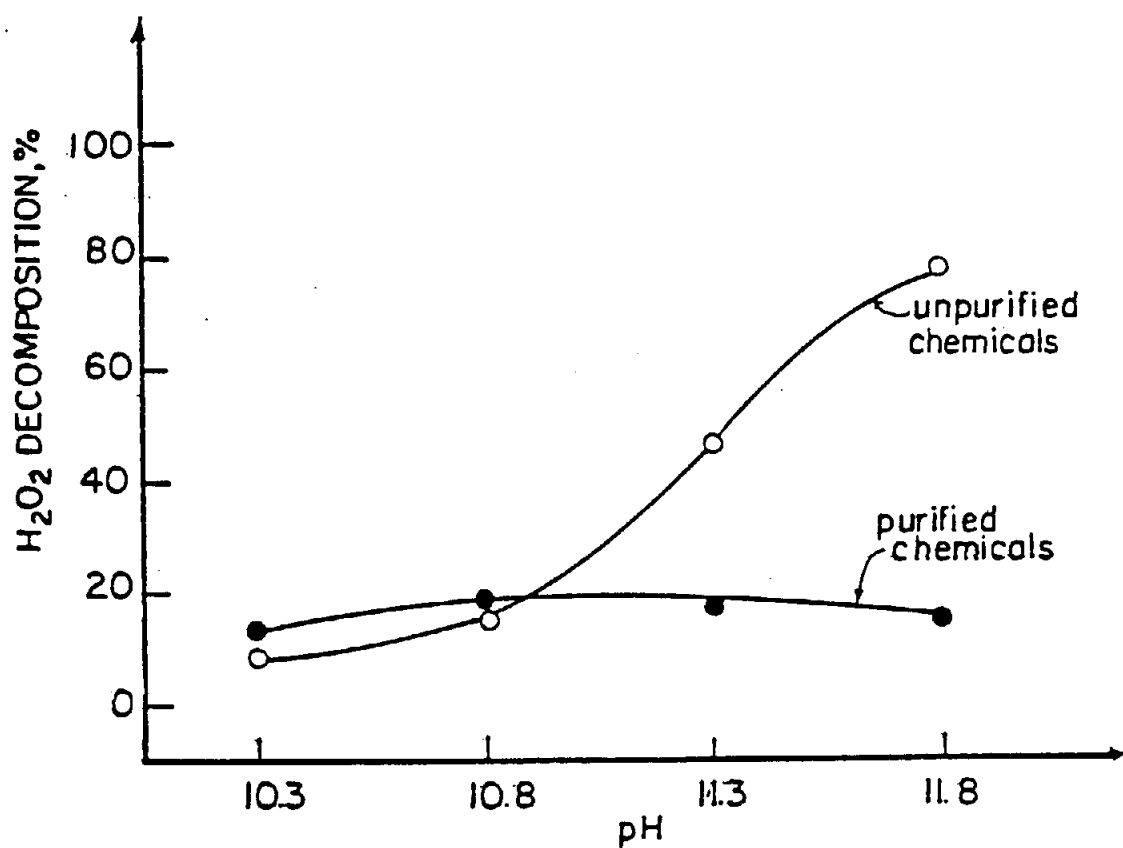


Figure 49. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of sodium silicate in purified and unpurified chemicals. ($\text{SiO}_2 = 0.08 \text{ M}$, 50°C , 120 min).

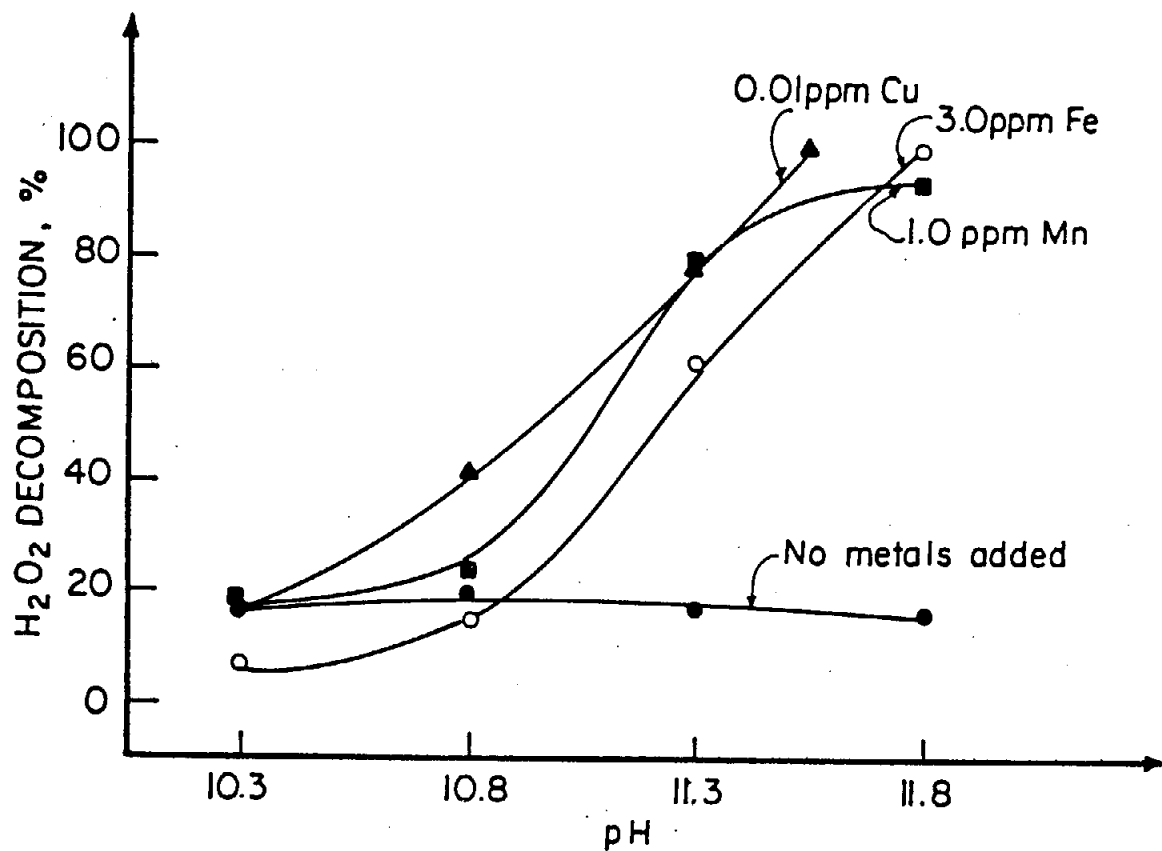


Figure 50. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of purified sodium silicate, iron, copper, and manganese. ($SiO_2 = 0.08$ M, 50° C, 120 min).

brightening systems existed, peroxide brightening should be more efficient at pH values above 11 where decomposition would not occur and where hydrogen peroxide would be mostly dissociated to perhydroxyl anion which is the active brightening species.

Comparing the results of peroxide decomposition in the presence and absence of silicate when purified chemicals are used, it is observed that silicate is not by itself a peroxide stabilizer (Fig. 51). However, in the presence of added iron and manganese, the positive effect of sodium silicate as a peroxide stabilizer is quite evident (Table 20). In the presence of added copper, on the other hand, silicate is an active peroxide catalyst.

TABLE 20. Concentrations of Iron, Copper, and Manganese Causing 50% Decomposition of 0.098 M H_2O_2 in the Presence and Absence of Sodium Silicate. (0.08 M SiO_2 , initial pH 10.8, 50° C, 120 min).

H_2O_2 Solution	Transition Metal Conc., ppm		
	Iron	Copper	Manganese
Without Silicate	18.8	1.0	0.32
With Silicate	>50	0.015	4.60

In pulp brightening, iron and manganese are the principal impurities whereas copper and other metals are usually present in much lower concentration. Therefore, at least one role of silicate in peroxide stabilization must be the deactivation of iron and manganese. An important question to be answered is how

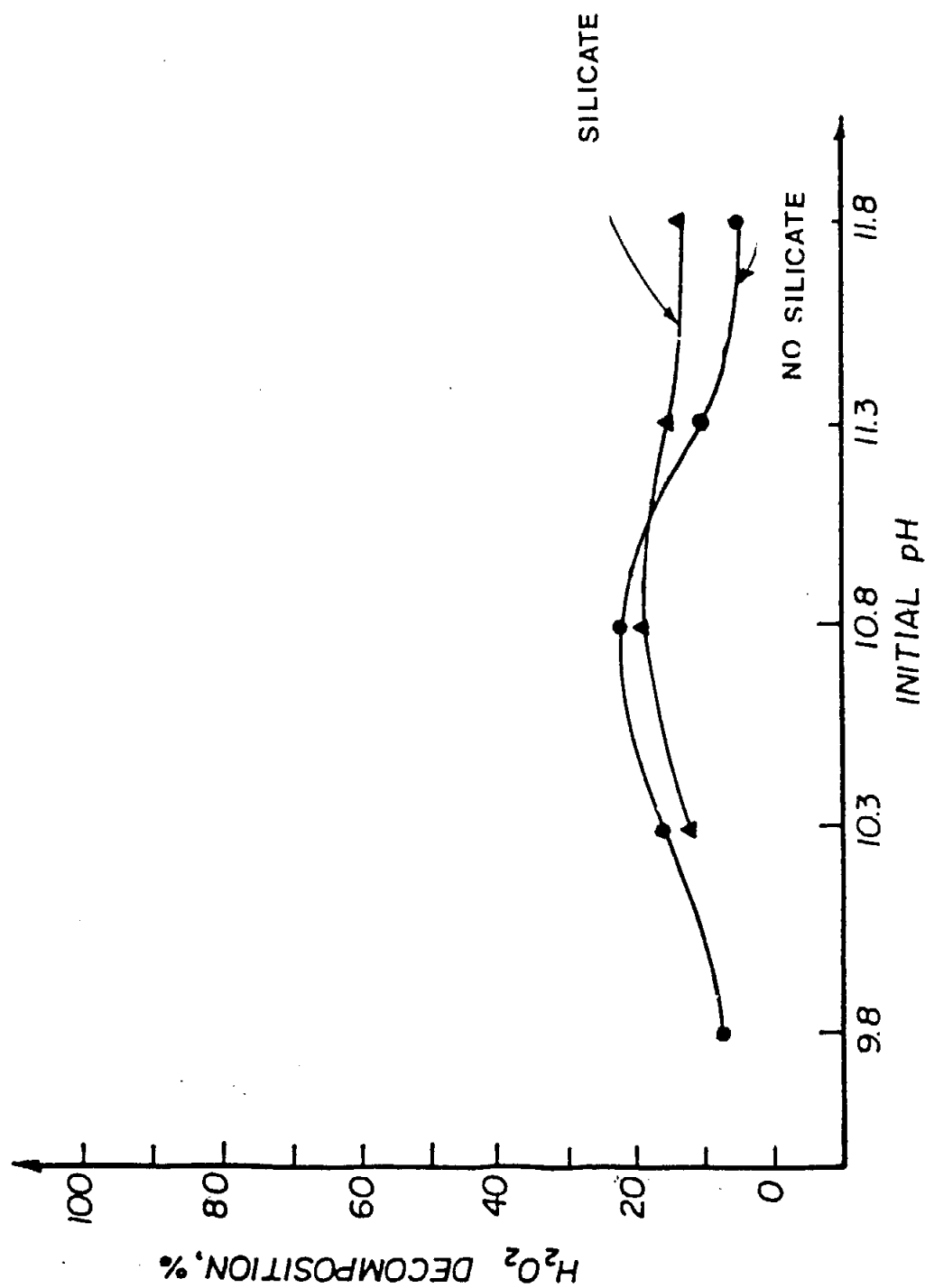


Figure 51. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence and absence of sodium silicate in purified chemicals. ($SiO_2 = 0.08$ M, 50° C, 120 min).

silicate deactivates these metals. It has been suggested that silicate deactivates metals by forming stable complexes with them^{152,153}, by maintaining the metals in solution thus avoiding formation of insoluble metal oxides/hydroxides¹⁸, and by coating the metals so that surface-catalyzed reactions are retarded or suppressed^{147,149}.

3.4.2.3.1. Coating of Transition Metals

The claim has been made that sodium silicate coats transition metal oxide solids with a protective layer so that the heterogeneous surface catalysis of hydrogen peroxide is either retarded or prevented^{147,149}. In an effort to verify the validity of this theory, the effectiveness of various organic colloids as peroxide stabilizers in the presence of insoluble iron, copper and manganese was examined. This approach was chosen because the ability of sodium silicate to coat surfaces reportedly stems from its colloidal properties¹⁸.

The results presented in Table 21 show that organic colloids such as carboxymethylcellulose (CMC), starch, dextrin, sodium polymethacrylate and gelatine have no significant positive effect on peroxide stability regardless of the transition metal involved. Moreover, CMC and starch actually caused an increase in peroxide decomposition. In these experiments, the transition metal solutions were aged for two hours at pH 10.8 and 50° C prior to the addition of organic colloids and hydrogen peroxide. This aging was performed in order to produce solid metal oxide surfaces that could be coated by the organic colloids.

TABLE 21. The Effect of Organic Colloids on the Decomposition of 0.098 M H_2O_2 in the Presence of Iron, Copper, and Manganese. ($Fe = 20$ ppm, $Cu = Mn = 5$ ppm, initial pH 10.8).

Organic Colloid, g/L	H_2O_2 Decomposition, %		
	Iron ¹	Copper ²	Manganese ²
Blank (no additive)	31.8	9.8	23.6
Sodium Silicate, 16.7	11.8	97.8	11.3
Carboxymethylcellulose, 2.0	57.8	48.3	55.2
Starch, 1.0	48.3	40.3	46.2
Dextrin, 1.0	33.5	9.3	22.5
Sodium Polymethacrylate, 0.5	29.7	8.2	21.3
Gelatine, 1.0	33.1	10.5	31.3

¹ 50° C, 120 min.

² RT, 30 min.

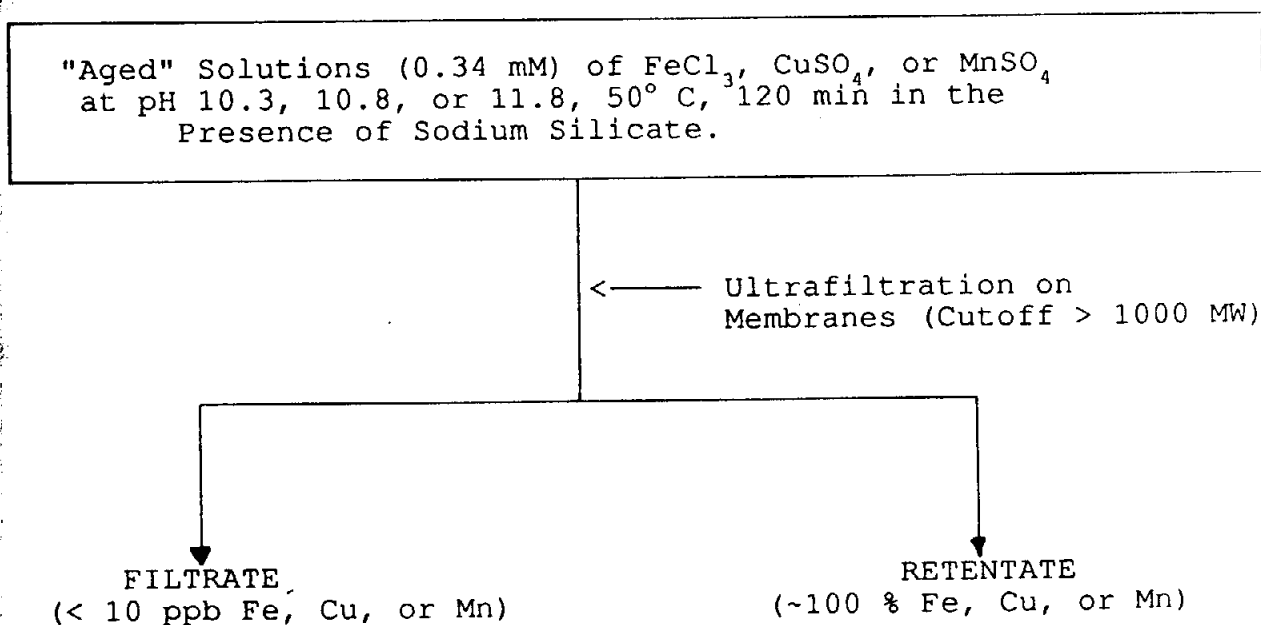
The ineffectiveness of the organic colloids in stabilizing peroxide indicate that the coating of transition metal surfaces is very unlikely to be the reason for peroxide stabilization in the presence of silicate unless the latter has very unique colloidal properties.

3.4.2.3.2. Retention of Transition Metals in Solution

It has been claimed that sodium silicate retains transition metals in solution thus preventing the formation of insoluble hydroxides/oxides which are reportedly more efficient catalysts for peroxide decomposition than soluble metals¹⁸. If this is so, the solubility of the metals under weakly alkaline conditions

should increase when sodium silicate is added. Scheme 2 shows the schematic representation and results of an experiment in which the solubility of iron, copper, and manganese solutions at pH 10.3, 10.8, and 11.8 was investigated by ultrafiltration. It is observed (Scheme 2) that undetectable (< 10 ppb) amounts of these metals are in the filtrates of the solutions. This provides an indication that sodium silicate does not solubilize the metals to any extent. Therefore, the proposed theory that silicate retains transition metals in solution is incorrect.

In principle, the proposed theory is already questionable on the grounds that the reaction of sodium silicate with transition metals can only form metal silicates which are by nature relatively insoluble compounds.



Scheme 2. The solubility of iron, copper, and manganese solutions in the presence of sodium silicate.

3.4.2.3.3. Formation of Stable Complexes with Transition Metals

It is difficult to prove the existence of silicate-transition metal complexes since their identification in solution is rather intricate. On the other hand, the isolation of such compounds under brightening conditions is also difficult because of their low concentration. Although the existence of these complexes in pulp brightening has never been demonstrated, it has been claimed that their formation during brightening results in inactivation of the transition metals with consequent peroxide stabilization^{152,153}.

In an effort to determine the possible influence of metal silicates on peroxide stability under brightening conditions, the effect of the order of addition of sodium silicate and sodium hydroxide to "fresh" and "aged" solutions of iron, copper and manganese on peroxide decomposition was investigated. The rationale behind this study was that the addition of silicate to "fresh" solutions of the metals prior to the addition of the sodium hydroxide should favor the formation of metal silicates because the metals are initially present in the form of free ions. On the other hand, the addition of sodium hydroxide prior to the addition of silicate results in the immediate formation of insoluble metal oxides/hydroxides which do not react as readily with silicate to form metal silicates.

The results presented in Table 22 show that peroxide decomposition catalyzed by "fresh" iron was higher when silicate was added to the solution prior to the addition of sodium

hydroxide (Fe/Silicate/NaOH) than in the opposite case (Fe/NaOH/Silicate). By visual observation, it was inferred that iron silicate was formed in the system Fe/Silicate/NaOH since a precipitate of hydrous iron oxides was observed upon addition of sodium hydroxide. On the other hand, when sodium hydroxide was added to the "fresh" solutions of iron prior to sodium silicate, the immediate formation of a brown precipitate of hydrous iron oxide was observed which did not dissolve significantly upon addition of sodium silicate. Thus, it was concluded that less iron silicate was formed in the Fe/NaOH/Silicate system. The fact that better peroxide stabilization is observed in the Fe/NaOH/Silicate system than in the Fe/Silicate/NaOH system (Table 22) indicates that silicate is more effective when inactivating insoluble hydrous iron oxide than when forming iron silicate with the iron ions. It is important to note, however, that the presence of silicate resulted in decreased peroxide decomposition regardless of order of addition.

TABLE 22. The Effect of Order of Addition of Sodium Silicate and Sodium Hydroxide on the Decomposition of 0.098 M H_2O_2 Catalyzed by "Fresh" and "Aged" Iron Solutions. ($SiO_2 = 0.08$ M, Fe = 20 ppm, initial pH 10.8, 50° C, 120 min).

Order of Addition	H ₂ O ₂ Decomposition, %	
	"Fresh" Iron	"Aged" Iron
Fe/Silicate/NaOH	29.5	11.8
Fe/NaOH/Silicate	9.6	10.4
Fe/NaOH	85.9	31.8

The results obtained for "aged" iron solutions are quite different from those shown for "fresh" solutions. It is observed that the order of addition of sodium silicate and sodium hydroxide does not affect peroxide decomposition. This is because in both cases iron is present in the form of insoluble hydrous oxide from the outset hence the formation of iron silicate is very low. Apparently, the reaction of insoluble hydrous oxides with sodium silicate to form iron silicate occurs at a very low rate.

The experiments performed with "aged" solutions simulate brightening conditions more realistically since the iron present in the pulp and process water very likely exists in the "aged" form, i.e., as insoluble hydrous iron oxides. Therefore, it can be postulated that formation of iron silicate does not contribute decisively to the stabilization of peroxide against iron-catalyzed decomposition during brightening.

The effect of order of addition of sodium silicate and sodium hydroxide on peroxide decomposition presents an entirely different pattern in the presence of manganese. The results in Table 23 show that better peroxide stabilization is obtained when sodium silicate is added to the "fresh" solution of manganese prior to the sodium hydroxide than when the order is reversed. The addition of silicate prior to sodium hydroxide resulted in formation of manganese silicate as was indicated by the clarity of the solutions even following addition of sodium hydroxide. On the other hand, the prior addition of sodium hydroxide caused the

immediate formation of a dark brown precipitate of manganese dioxide which did not dissolve upon the addition of sodium silicate. The formation of manganese silicate is very beneficial because it prevents the generation of manganese dioxide which is a severe catalyst for peroxide decomposition. It should be pointed out, however, that silicate retarded peroxide decomposition quite significantly even after manganese dioxide was formed.

TABLE 23. The Effect of Order of Addition of Sodium Silicate and Sodium Hydroxide on the Decomposition of 0.098 M H_2O_2 Catalyzed by "Fresh" and "Aged" Manganese Solutions. (SiO_2 = 0.08 M, Mn = 5 ppm, initial pH 10.8, 50° C, 30 min).

Order of Addition	H ₂ O ₂ Decomposition, %	
	"Fresh" Manganese	"Aged" Manganese
Mn/Silicate/NaOH	19.5	18.3
Mn/NaOH/Silicate	43.2	41.0
Mn/NaOH	85.9	83.6

There were no significant differences between peroxide decomposition catalyzed by "fresh" or "aged" manganese solutions because the solutions were not changed during the aging treatment, i.e., manganese was not precipitated as manganese dioxide when boiled at pH 6.5 for 3 hours. Therefore, the "aged" and "fresh" manganese solutions were essentially identical.

In a brightening system, manganese exists in the form of

free ions since the pH of the pulp and process water are not high enough to cause its precipitation as manganese dioxide. Thus, formation of manganese silicate must play an important role in the stabilization of peroxide by sodium silicate during brightening by preventing the formation of manganese dioxide. If silicate is not present, formation of manganese dioxide will occur immediately after the pulp slurry is made alkaline in the peroxide brightening stage.

A more practical piece of evidence for the benefits accompanying manganese silicate formation was obtained in experiments where the order of addition of sodium silicate and sodium hydroxide was studied in connection with the brightening of TMP. The TMP contained 78 ppm of iron, 97 ppm of manganese, and 19.5 ppm of copper. The iron and copper present in the pulp were disregarded in this particular study since the majority of these metals exists in an insoluble form and is therefore unaffected by the order of chemical addition.

The bleachability of the TMP when sodium silicate and sodium hydroxide were added as a mixture (Silicate + NaOH) was first determined. This was done in order to produce a basis for comparison since the prior mixing addition of chemicals is common practice in industry.

The results in Table 24 show that the final brightness value for the system where silicate was added to the pulp slurry prior to the sodium hydroxide was similar to the one where they were added as a mixture. This was to be expected since formation of

manganese silicate took place in both cases (visual observation). A lower final brightness value was obtained when sodium hydroxide was added to the pulp slurry prior to sodium silicate but the difference was very insignificant compared to the standard (Silicate + NaOH). To establish whether the decrease in brightness observed when sodium hydroxide was added prior to silicate was real, 100 ppm of manganese on o.d. pulp was added to the pulp slurry and the experiment repeated. The results show that the final brightness when sodium silicate was added prior to the sodium hydroxide is 1.6 % higher than in the opposite case (Table 24).

TABLE 24. The Effect of Order of Addition of Sodium Silicate and Sodium Hydroxide on the Brightening of TMP in the Presence and Absence of Added Manganese. (H_2O_2 = 1 % on o. d. pulp, Silicate = 5 % on o. d. Pulp, Consistency = 12 %, initial pH 10.8, 50° C, 120 min, unbleached brightness = 58.2 %).

Order of Addition	Brightness %	H_2O_2 Cons., %	Final pH
Silicate + NaOH	73.4	80.9	9.3
Silicate/NaOH	73.3	80.5	9.4
NaOH/Silicate	72.7	81.2	9.4
Mn (100 ppm)/Silicate/NaOH	72.1	92.5	9.6
Mn (100 ppm)/NaOH/Silicate	70.5	96.0	9.7

The above results indicate that formation of manganese silicate has a very important role in the stabilization of hydrogen peroxide during brightening. When silicate is added to

the pulp slurry prior to the sodium hydroxide or as a mixture with sodium hydroxide, formation of manganese silicate takes place thus preventing formation of the powerful peroxide catalyst, manganese dioxide. When sodium hydroxide is added first, manganese dioxide is immediately formed and lower brightness values are obtained as a result of enhanced peroxide decomposition. The higher values of peroxide consumption and final pH (Table 24) support the fact that more peroxide decomposition occurred when sodium hydroxide was added to the pulp prior to the sodium silicate.

In the case of the copper-catalyzed reaction, the order of addition of sodium silicate and sodium hydroxide had no significant effect on peroxide decomposition (Table 25). In this situation formation of copper silicate probably takes place when sodium silicate is added to the "fresh" solutions of copper prior to the sodium hydroxide. However, the catalytic activity of copper silicate is probably similar to that of the hydrous copper oxide which is formed when sodium hydroxide is added prior to the sodium silicate. Because the catalytic activities of copper silicate and hydrous copper oxide are similar, the decomposition of peroxide is approximately the same in "aged" and "fresh" copper solutions. The fact that silicate interacts synergistically with copper to decompose hydrogen peroxide (section 3.2.2) severely complicates the interpretation of these results.

TABLE 25. The Effect of Order of Addition of Sodium Silicate and Sodium Hydroxide on the Decomposition of 0.098 M H_2O_2 Catalyzed by "Fresh" and "Aged" Copper Solutions. ($SiO_2 = 0.08$ M, Cu = 0.1 ppm, initial pH 10.8, RT, 30 min).

Order of Addition	H ₂ O ₂ Decomposition, %	
	"Fresh" Copper	"Aged" Copper
Cu/Silicate/NaOH	23.4	20.6
Cu/NaOH/Silicate	26.1	25.8
Cu/NaOH	1.6	1.5

The results discussed above indicate that formation of iron, manganese, and copper silicates under brightening conditions is relevant only in the case of manganese because only the latter exists as free ions which are readily available for reaction with sodium silicate. The formation of manganese silicate prevents the generation of the insoluble manganese dioxide which is a severe peroxide decomposition catalyst. The other two metals exist in the form of insoluble hydroxide/oxides which do not react promptly with silicate to form metal complexes. The mechanism of the inactivation of insoluble hydrous iron oxides by sodium silicate is far from being understood at this point.

4. SUMMARY AND CONCLUSIONS

The theories proposed to account for peroxide stabilization by sodium silicate were re-evaluated through a study of

effect of: (1) sodium silicate on the generation of hydroxyl and superoxide anion radicals during peroxide decomposition, (2) sodium silicate on the solubility of transition metals such as iron, copper, and manganese, (3) organic colloids on peroxide decomposition in the presence of iron, copper, and manganese, (4) the order of addition of sodium silicate and sodium hydroxide on peroxide decomposition in the presence of iron, copper, and manganese, and (5) pH and chemical purity on peroxide decomposition in the presence of silicate. Also assessed was the influence of reaction variables such as chemical concentration (peroxide, silicate, chelating agents, iron, copper, and manganese), pH control, temperature, ionic strength, and $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of the silicate on hydrogen peroxide decomposition in the presence of sodium silicate. Finally, the effect of addition of sodium silicate on the reactivity of alkaline hydrogen peroxide towards peroxide-reactive compounds was also determined. The principal findings of this work are as follows:

1. Silicate does not stabilize peroxide by itself but it may inactivate certain transition metals that catalyze peroxide decomposition during brightening.
2. Silicate stabilizes peroxide under brightening conditions by inactivating hydrous iron oxides and manganese ions.
3. Silicate inactivates manganese ions through the presumed formation of manganese silicate.

4. The reactivity of hydrogen peroxide towards peroxide-reactive compounds is not affected by sodium silicate.
5. Formation of copper silicate is not the cause of the synergistic effect of copper and silicate on peroxide decomposition.
6. The concentrations of hydroxyl and superoxide anion radicals in alkaline peroxide solutions are not reduced to any extent when silicate is added to the reaction system.
7. The concentrations of hydroxyl and superoxide anion radicals are increased significantly when copper is added to alkaline peroxide solutions containing sodium silicate.
8. The stability of alkaline solutions of hydrogen peroxide is not affected by the addition of organic colloids such as gelatine, sodium polymethacrylate, and dextrin to the reaction system and was actually decreased by the addition of carboxymethylcellulose and starch.
9. Sodium silicate does not increase the solubility of iron, copper, and manganese in alkaline media.
10. Iron-catalyzed peroxide decomposition is greater when sodium silicate is added to the reaction prior to the addition of sodium hydroxide. The opposite trend is observed for manganese-catalyzed peroxide decomposition.

11. Peroxide decomposition is not significantly affected by the initial peroxide concentration in the range 0.098 to 0.39 M which is equivalent to 1.0 to 4.0 % H_2O_2 on o. d. pulp at 25% consistency.
12. Peroxide decomposition is significantly decreased by increasing silicate concentration in the range 0.04 to 0.08 M which is equivalent to 2.5 to 10 % Silicate on o. d. pulp at 25% consistency.
13. Maintenance of constant pH during the course of the decomposition reaction reduces slightly peroxide decomposition.
14. Peroxide decomposition is completely inhibited by the addition of small amounts of Na_5DTPA in the pH range 10.3 to 11.8.
15. Triethanolamine (TEA) stabilizes peroxide in the presence of silicate but does not completely eliminate decomposition in the pH range 10.3 to 11.8.
16. Significant amounts of hydrogen peroxide are consumed in reactions with TEA and Na_5DTPA if too high a concentration of the chelating agent is used.
17. Peroxide decomposition increases sharply with increasing pH above 11 when iron, copper or manganese is added to the reaction system.

18. At pH values lower than 11, sodium silicate is an effective peroxide stabilizer in the presence of iron and manganese but a peroxide decomposition catalyst in the presence of copper.
19. In the presence of unpurified chemicals, silicate stabilizes peroxide insignificantly at pH values lower than 11 but destabilizes it extensively at higher pH values. In the presence of purified chemicals, silicate does not affect peroxide stability significantly in the pH range 10.3 to 11.8.
20. Ionic strength has no significant effect on peroxide decomposition.
21. Iron-catalyzed decomposition of peroxide is reduced significantly by "aging" solutions of the metal whereas copper- and manganese-catalyzed decomposition is not affected by this treatment.
22. Peroxide decomposition increased more than three-fold when the temperature was increased from 50° to 60° C.

FACTORS AFFECTING PEROXIDE STABILITY IN THE BRIGHTENING OF
MECHANICAL AND CHEMIMECHANICAL PULPS

CHAPTER 4 - HYDROGEN PEROXIDE STABILITY IN THE PRESENCE OF
MAGNESIUM AND COMBINATIONS OF STABILIZERS

1. INTRODUCTION

It is well-known that compounds such as sodium silicate, magnesium sulfate, and chelating agents play important roles in the peroxide brightening of mechanical pulps, the most commonly accepted of which is the stabilization of hydrogen peroxide solutions^{18,96}.

Magnesium has been shown to stabilize alkaline hydrogen peroxide solutions quite effectively^{128,223,224}. Under actual brightening conditions, however, it does not function efficiently, especially in systems containing significant amounts of transition metals¹²⁸.

The term "magnesium" used throughout this text designates a weakly alkaline solution of a magnesium salt, usually magnesium sulfate. It is difficult to predict accurately the composition of the magnesium species under the various conditions cited but it is reasonable to postulate that a large proportion of it exists as magnesium hydroxide in equilibrium with magnesium ions since the solubility product of this hydroxide is relatively low ($5.66 \cdot 10^{-12}$ at 25° C)²²⁵.

The mechanism by which magnesium stabilizes alkaline hydrogen peroxide is very controversial. Of the several mechanisms proposed to explain this process, the following two are most widely accepted: (1) deactivation of transition metal catalysts either by sorbing them^{110,129-131} or by forming stable, not readily oxidizable, complexes with them¹²⁷ and (2) stabilization of superoxide anion radicals thereby retarding the

propagation of the free radical chain decomposition reaction^{18,133,134}. The best performance of magnesium in peroxide brightening is achieved when it is added in combination with sodium silicate¹¹⁹. Thus, the brightness gain attained when sodium silicate and magnesium are added in combination to the brightening liquor is higher than the sum of the individual gains obtained when each of the chemicals is applied separately¹⁶¹. The reason for the apparent synergistic effect of the two stabilizers is not clear. The formation of a stable colloidal suspension of magnesium silicate which absorbs transition metal catalysts has been suggested²²⁶ as a possible cause for the observed synergistic effect but the large imbalance in stoichiometry existing between the two stabilizers under typical brightening conditions makes this theory very questionable.

The role of chelating agents in peroxide brightening is basically to inactivate traces of transition metals which catalyze peroxide decomposition. These compounds are usually used in the pretreatment of the pulp slurry so that the chelated metals are removed from the brightening system in the subsequent dewatering operation. The removal of the metal-chelate complexes is believed to be important because some metal cations in a high valence state (e.g. Fe^{3+} and Mn^{4+}), though complexed with the chelating agent, reportedly induce peroxide decomposition¹⁷⁴. On the other hand, the use of the chelating agents in combination with other stabilizers in the brightening formulation may be advantageous because it simplifies the brightening operation by eliminating the pulp pretreatment step in addition to reducing

the amount of chelating agent required.

The application of chelating agents in combination with sodium silicate and magnesium sulfate in the brightening formulation has not yet been thoroughly explored. Preliminary laboratory studies and mill trials¹⁰² have indicated that concentrations of Na₅DTPA significantly lower than those commonly used in pulp pretreatments provide efficient peroxide brightening when applied to bleaching liquors stabilized with sodium silicate and magnesium sulfate. Moreover, the use of Na₅DTPA in the brightening formulation permits the use of lower-than-usual concentrations of sodium silicate¹⁰².

A full understanding of the effect of chelating agents on the stabilization of peroxide bleaching liquors, especially in the presence of transition metals such as iron, copper, and manganese, is of fundamental importance in order to assess their potential in this particular application mode.

The objectives of this investigation were to: (1) clarify the mechanism of alkaline hydrogen peroxide stabilization by magnesium, (2) clarify the individual and combined roles of Na₅DTPA, magnesium, and sodium silicate as stabilizers for alkaline hydrogen peroxide in the absence and presence of varying amounts of iron, copper, and manganese under conventional hydrogen peroxide brightening conditions, and (3) evaluate the effect of hydrogen peroxide decomposition inhibitors such as sodium citrate, sodium tartrate, and sodium pyrophosphate.

2. MATERIALS AND METHODS

2.1. Reagents

The sodium silicate used throughout these experiments was N-brand clear ($\text{SiO}_2/\text{Na}_2\text{O} = 3.22$) supplied by the Philadelphia Quartz Corporation. All of the other chemicals used were c.p. reagent grade supplied by Fisher Scientific and Aldrich Chemical Companies. The purified sodium hydroxide and sodium silicate solutions used in all of the experiments were prepared according to procedures described in section 2.1 - chapter 2 and section 2.1 - chapter 3, respectively. In the experiments involving magnesium, borax, pyrophosphate, citrate, and tartrate, the following salts were used: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$, and $\text{Na}_4\text{KC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

2.2. Peroxide Decomposition Tests

See section 2.2. - chapter 2

2.3. pH Measurement and Control

See section 2.3. - chapter 2

2.4. Determination of Superoxide Anion Radicals

See section 2.4. - chapter 2

3. RESULTS AND DISCUSSION

3.1. Peroxide Decomposition in the Presence of Magnesium

3.1.1. In the Near Absence of Transition Metals

Magnesium was added in the form of Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) at a concentration of 0.17 g/L which is equivalent to 0.05% of Epsom salt on o.d. pulp at 25% consistency. The pH adjustments were made with highly purified sodium hydroxide.

The results presented in Table 26 show that the addition of magnesium to alkaline hydrogen peroxide solutions prevents decomposition almost completely regardless of pH in the range 9.8 to 11.8 in agreement with results of other workers^{125,223}. Due to its high efficiency in stabilizing alkaline peroxide solutions, magnesium is usually added to peroxide bleaching liquors in order to avoid decomposition during storage.

TABLE 26. Decomposition of 0.098 M H_2O_2 in the Absence and Presence of Magnesium. ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ = 0.17 g/L, 50° C, 120 min).

pH	H_2O_2 Decomposition, %	
	With $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Without $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
9.8	0.0	7.5
10.3	0.5	16.0
10.8	1.5	20.5
11.3	1.0	10.5
11.8	0.0	8.0

3.1.2. In the Presence of Iron, Copper, and Manganese

The results presented in Figures 52, 53, and 54 show the decomposition of alkaline hydrogen peroxide solutions stabilized by magnesium in the presence of increasing amounts of iron, copper, and manganese, respectively. It is noted that magnesium does not effectively stabilize peroxide in the presence of any of the three metals. In the case of iron, peroxide decomposition increases rapidly at a molar ratio above 0.167 Fe/Mg which corresponds to a concentration of 6.3 ppm iron in the solution under the conditions used in this experiment. Iron concentrations much higher than this value are found in typical brightening systems¹⁸¹. Under the same conditions, sodium silicate can inactivate iron in concentrations greater than 35 ppm.

Magnesium is also inefficient in preventing copper-catalyzed peroxide decomposition especially at Cu/Mg molar ratios above 0.041 which is equivalent to 1.8 ppm Cu in the solution used in this experiment. Similar results have been found by other workers¹²⁷.

Alkaline hydrogen peroxide solutions containing manganese and magnesium decompose at a extent directly proportional to the concentration of manganese in the solution. It should be pointed out that the manganese-catalyzed peroxide decomposition is higher in the presence of magnesium than in its absence, i.e, manganese interacts synergistically with magnesium to decompose hydrogen peroxide. At a molar ratio of 0.0066 Mn/Mg, which corresponds to

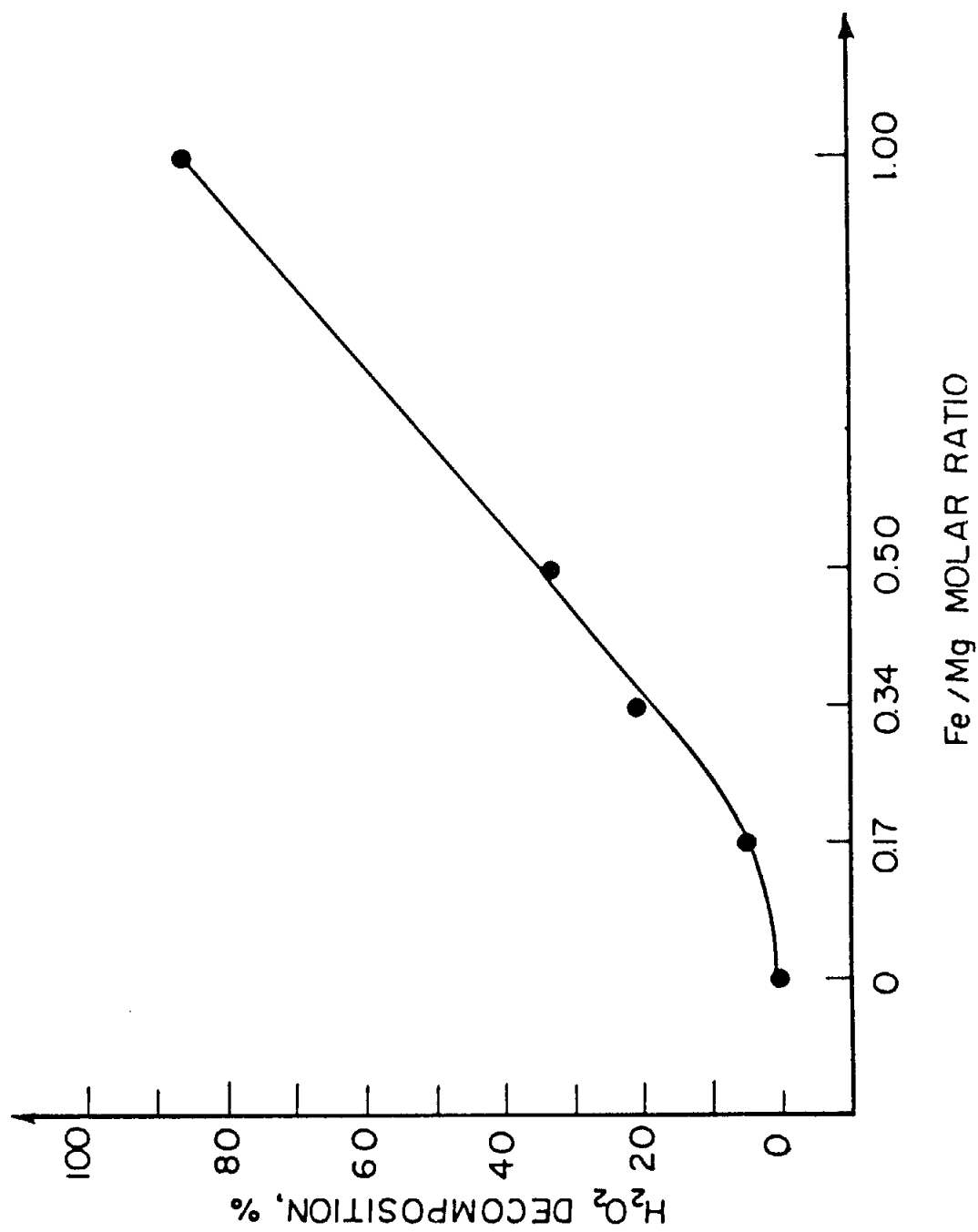


Figure 52. Effect of the iron/magnesium ratio on the decomposition of 0.098 M H_2O_2 . (initial pH 10.8, 50° C, 120 min).

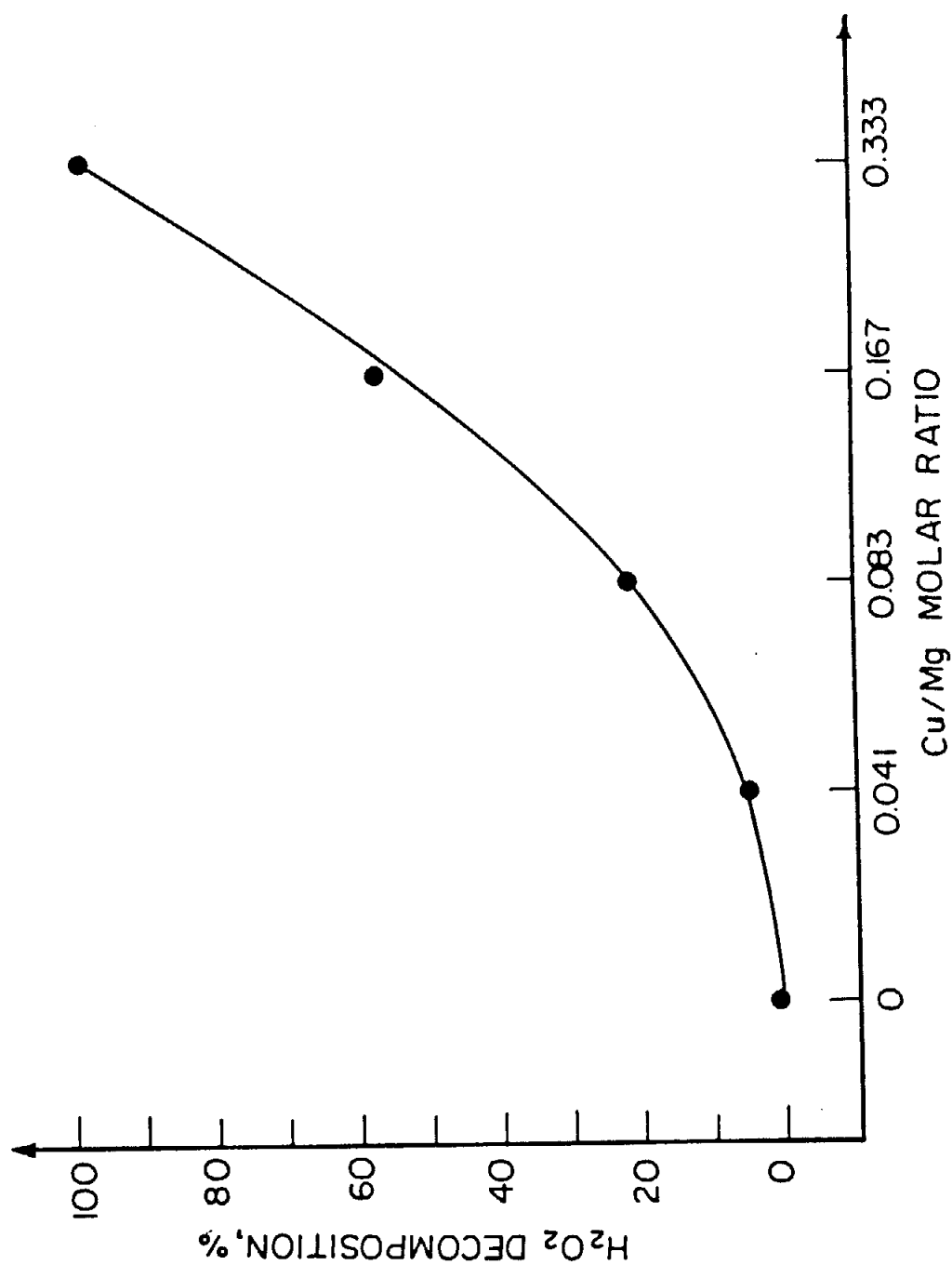


Figure 53. Effect of the copper/magnesium ratio on the decomposition of 0.098 M H_2O_2 . (initial pH 10.8, 50° C, 120 min).

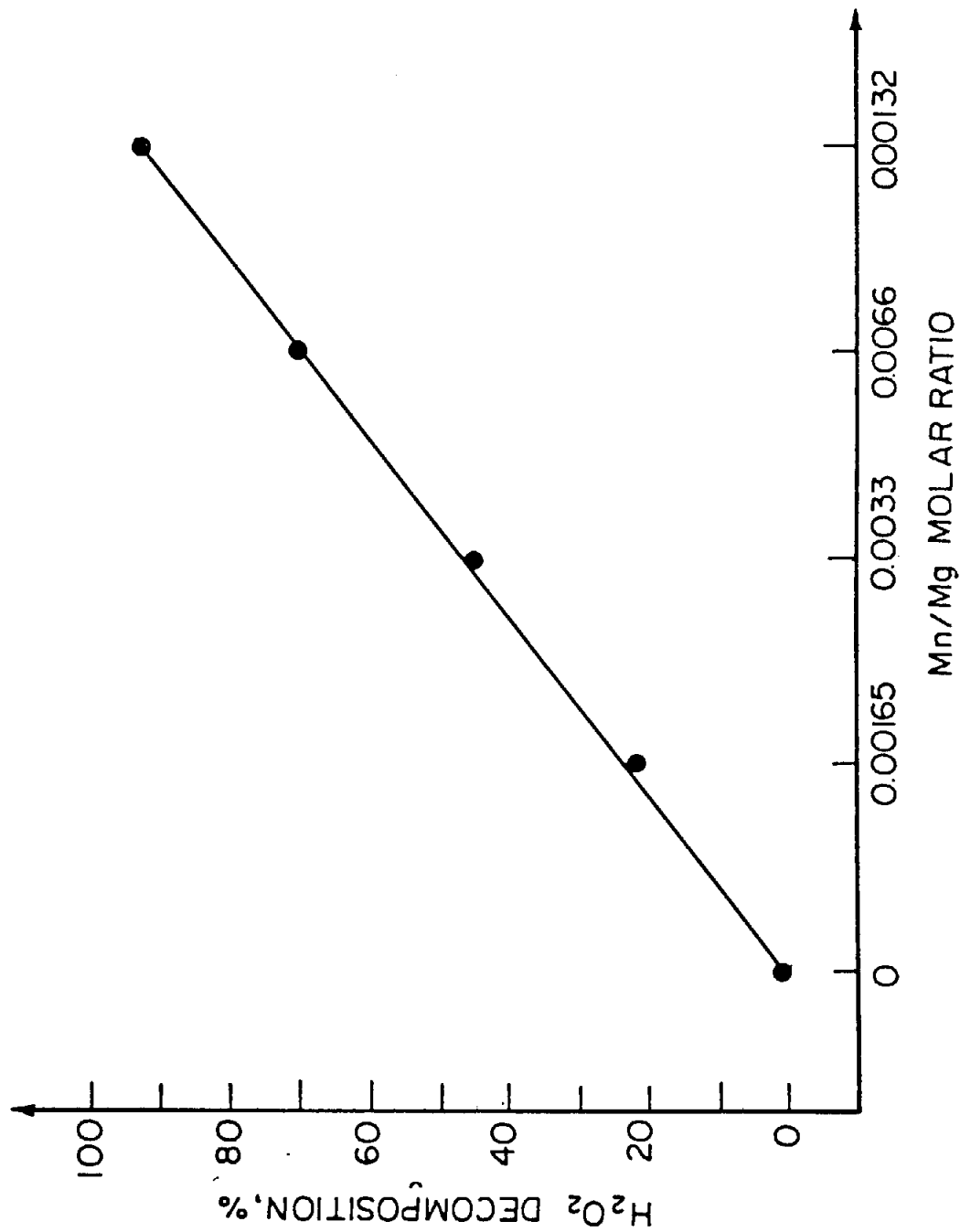


Figure 54. Effect of the manganese/magnesium ratio on the decomposition of 0.098 M H_2O_2 . (initial pH 10.8, 50° C, 120 min).

a manganese concentration of 0.25 ppm in the solution used in this experiment, decomposition is ~70% in 2 hours at 50° C, and pH 10.8 (Fig. 54). Under the same conditions, decomposition is ~28% in the absence of magnesium. The acceleration of peroxide decomposition by magnesium in the presence of manganese has been reported²⁹ but no explanation for this finding has been offered.

Results showing the effect of pH in the range 9.8 to 10.3 on the decomposition of peroxide solutions catalyzed by iron, copper, and manganese in the presence of magnesium are presented in Figures C-1, C-2, and C-3 (Appendix C), respectively. Copper- and manganese-catalyzed reactions are significantly affected by changes in pH whereas the iron-catalyzed reaction is not.

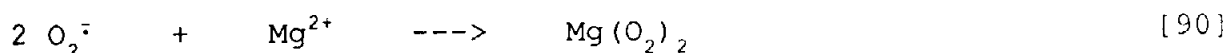
The effect of magnesium on the decomposition of peroxide solutions containing various combinations of iron, copper, and manganese is shown in Table C-1 (Appendix C).

3.1.3. Mechanistic Considerations

Magnesium compounds have been claimed to stabilize alkaline hydrogen peroxide solutions by: (1) inactivating transition metals^{110,127,129-131} and (2) stabilizing superoxide anion radicals thereby disrupting the free radical chain decomposition reaction^{133,134}. The first mechanism may be disregarded because it has been shown that magnesium stabilizes peroxide very inefficiently in the presence of transition metals such as iron,

copper, and manganese (section 3.1.2). Thus, it is unlikely that the nearly complete peroxide stabilization by magnesium in the absence of added metals results from inactivation of metal impurities.

The second proposed mechanism of peroxide stabilization, which involves the disruption of free radical chain reactions by the magnesium, was investigated by measuring the concentrations of superoxide anion radicals in alkaline solutions of peroxide in the presence and absence of magnesium. The results in Figure 55 indicate that larger amounts of superoxide anion radical are detected in the system containing magnesium. It is seen that the amounts of superoxide anion radical measured in the presence of magnesium increase sharply in the beginning of the reaction, reach a maximum at approximately 30 min and then decrease slowly. Although very small amounts of peroxide were decomposed in the presence of magnesium, sizable amounts of superoxide anion radical were detected. This finding is consistent with the postulated¹³³ reaction of magnesium with these radicals forming stable magnesium superperoxide (eq. [90]) which is detectable by EPR spectrometry.



The slight decrease in the measured amounts of superoxide anion observed at the later stages of the reaction may be

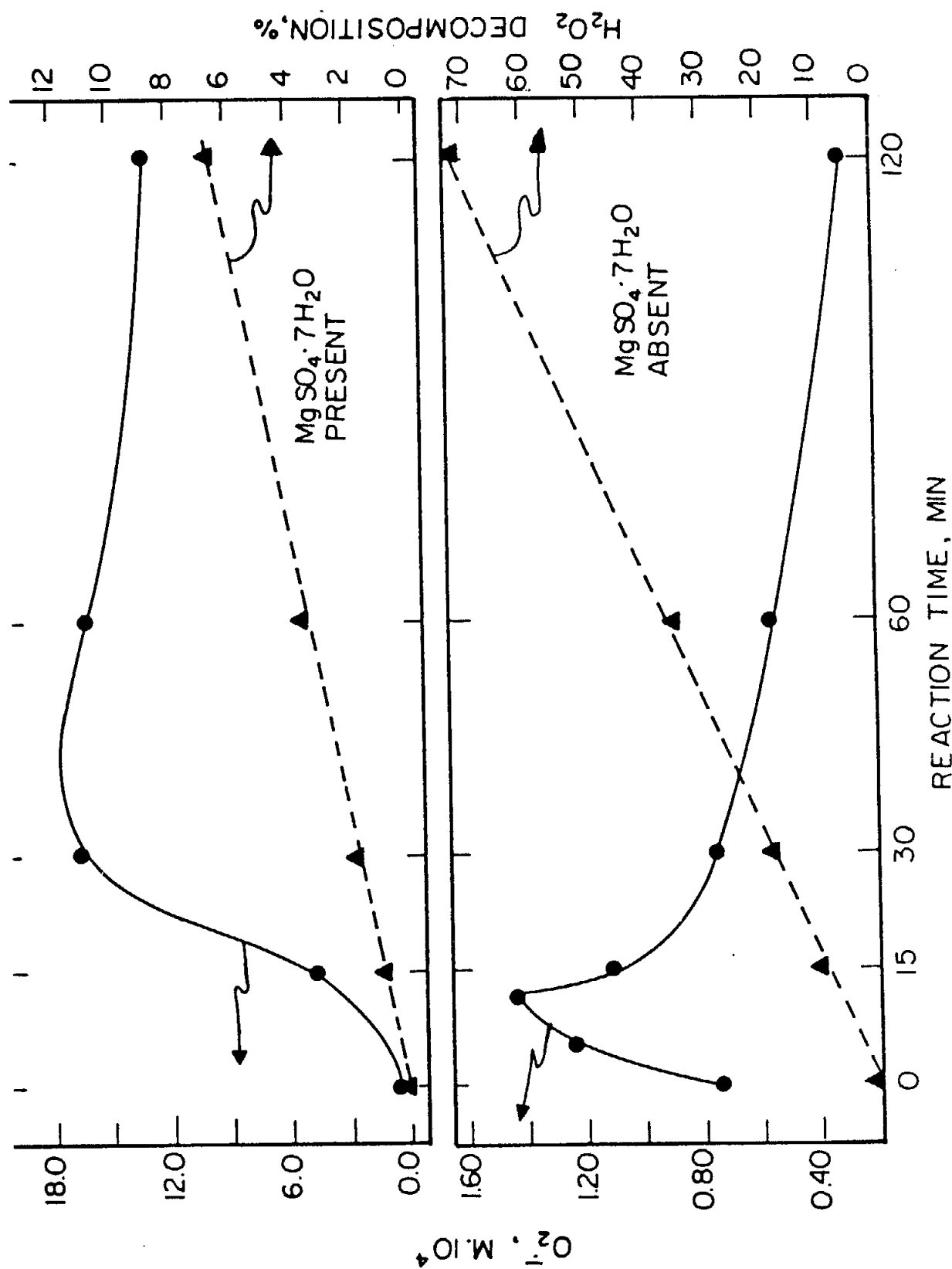
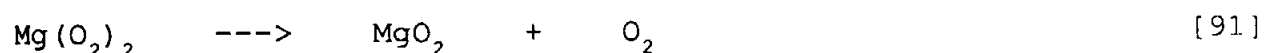


Figure 55. Concentration of superoxide anion radicals in peroxide solutions in the presence and absence of magnesium. ($H_2O_2 = 0.49$ M, $MgSO_4 \cdot 7H_2O = 0.85$ g/L, initial pH 10.8, $50^\circ C$).

attributed to the decomposition of the magnesium superperoxide formed in eq. [90] to produce oxygen and magnesium dioxide, according to eq. [91]:



In alkaline peroxide solutions not containing magnesium, the maximum measured amount of superoxide occurs at 10 minutes' reaction and then decreases significantly thereafter. This decrease in superoxide anion radical concentration results from the fact that these radicals are consumed by side reactions which produce oxygen, eq. [7], or new radicals, eq. [12]:



The steady state concentration of superoxide anion radical is probably greater in the system where magnesium is absent because peroxide decomposition is higher in this case. However, larger amounts of radical are detected in the system containing magnesium because they are stabilized by the latter and therefore accumulate.

The decomposition of alkaline hydrogen peroxide solutions has been shown to be caused by traces of transition metal impurities introduced with the reagents, especially sodium hydroxide (section 3.3.2 - chapter 2). It has also been demonstrated that, in contrast to copper-catalyzed decomposition, peroxide decomposition catalyzed by transition metal impurities

such as iron and manganese does not involve free radical reactions (section 3.3.3 - chapter 2). Cobalt and lead reportedly do not induce formation of free radicals on decomposing peroxide⁵¹ whereas titanium does²²⁰. Therefore, the proposed function of magnesium as a superoxide anion radical stabilizer is applicable only if it is assumed that most of the peroxide decomposition in alkali is caused by metals that induce formation of free radicals. In fact, it has been suggested that peroxide decomposition under alkaline conditions is caused mainly by copper impurities originating from the sodium hydroxide solution²³.

A fact that in part supports the concept that magnesium functions by disrupting free radical chain reactions is the low efficiency of the magnesium in stabilizing peroxide under actual brightening conditions where large concentrations of transition metals are present. The bulk of the peroxide decomposition occurring under brightening conditions probably does not occur **via** a free radical chain reaction since the transition metal impurities present in largest concentrations under those conditions are iron and manganese which do not induce formation of radicals on decomposing peroxide. Therefore, the role of magnesium under actual brightening conditions becomes minor since it cannot prevent peroxide decomposition attributable to mechanisms other than those involving free radical chain reactions. The only benefit of magnesium in this case is to prevent or retard decomposition reactions caused by copper and other free radical-inducing transition metals which occur **via** a

free radical chain reaction. However, such reactions are apparently of minor importance.

If magnesium prevents or retards only free radical decomposition reactions, it is understandable why increasing its concentration above a certain value during brightening does not result in any improvement in the peroxide brightening action. Obviously, the free radical reactions are limited and no demand for larger concentrations of magnesium exists.

3.2. Peroxide Stabilization by Combinations of Stabilizers in the Presence of Transition Metals

This set of experiments was designed to determine the maximum amounts of iron, copper and manganese that could be individually added to alkaline hydrogen peroxide solutions in the absence and presence of stabilizers and combinations of stabilizers without seriously affecting peroxide stability. In order to simulate brightening conditions more realistically, "aged" metals were used throughout the experiments. To minimize the introduction of transition metal impurities into the system, the sodium silicate and sodium hydroxide used in all experiments were purified prior to use. The concentrations of sodium silicate (0.08 M SiO_2) and Epsom salt (0.17 g/L) used in these particular experiments are similar to those commonly used in commercial brightening applications and are equivalent to 5.0% silicate and

0.05% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ on o.d. pulp at 25% consistency, respectively. The concentration of Na_5DTPA was fixed at 0.34 g/L, which is equivalent to 0.1% Na_5DTPA on o.d. pulp at 25% consistency, and was selected based on the results of laboratory studies reported by other workers¹⁰².

The effect of pH in the range 10.3 to 10.8 on peroxide decomposition in the combined presence of magnesium and sodium silicate at varying iron, copper, and manganese concentrations is illustrated in Figures C-4, C-5, and C-6 (Appendix C). Also shown is the effect of pH on peroxide decomposition in the combined presence of sodium silicate, magnesium, and Na_5DTPA in solutions containing iron, copper, and manganese (Fig. C-7 - Appendix C). No significant differences in peroxide decomposition with pH are observed in this pH range in any of the cases examined. Therefore, all of the experiments were performed at an initial pH of 10.8 which is a value commonly used in peroxide brightening.

A temperature of 50° C was used in this study because it is typical of temperatures used in pulp brightening. The effect of temperature on peroxide decomposition in the presence of magnesium/sodium silicate combinations in solutions containing iron, copper, or manganese is shown in Figures C-8, C-9 and C-10 (Appendix C), respectively.

Although the main objective in this work was to determine the effect of stabilizer combinations on peroxide decomposition in the presence of individual transition metals, the effect of various combinations of iron, copper, and manganese on peroxide

stability in the presence of sodium silicate and magnesium sulfate was also determined. The results presented in Table C-2 (Appendix C) show that the metals acted synergistically in all cases, the most pronounced effect being exhibited by the combination of iron and manganese.

3.2.1. Iron

The effect of iron solutions on peroxide decomposition in the absence and presence of various stabilizers and combinations of stabilizers is shown in Figure 56. It is observed that iron in low concentrations stabilizes hydrogen peroxide rather than catalyzing its decomposition. In the complete absence of stabilizers, the addition of 1.2 ppm of iron to the peroxide solution decreases decomposition from 20 to 14%. Magnesium is an ineffective peroxide stabilizer in the presence of iron being unable to completely prevent decomposition in the presence of more than 1.0 ppm of this transition metal. A fairly stable system is obtained in the presence of sodium silicate where the addition of iron in concentrations as high as 37.6 ppm to the peroxide solution causes only ~8% decomposition. In the combined presence of magnesium and sodium silicate, peroxide stability is even greater, being nearly complete regardless of iron concentration. Since iron concentrations above 30 ppm are seldom present during pulp brightening, it seems that the addition of

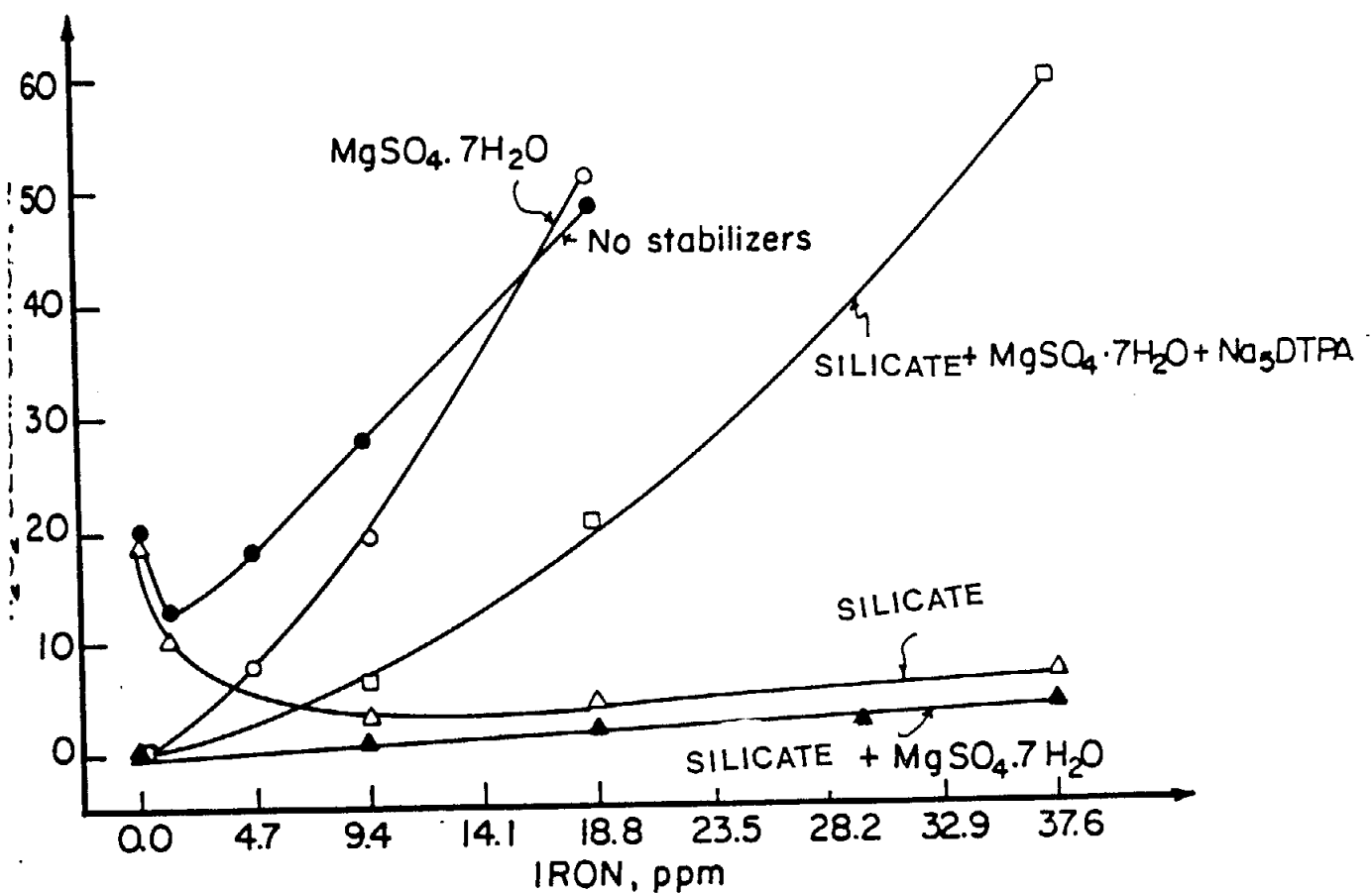


Figure 56. Effect of iron on the decomposition of 0.098 M H_2O_2 in the presence of various stabilizers and combinations of stabilizers. (SiO_2 = 0.08 M, $MgSO_4 \cdot 7H_2O$ = 0.17 g/L, Na_5DTPA = 0.34 g/L, initial pH 10.8, 50° C, 120 min).

sodium silicate alone to the brightening liquor results in iron being an unimportant factor as far as peroxide stability is concerned.

The addition of Na_5DTPA to a combination of magnesium and silicate decreases peroxide stability in the presence of iron. At an iron concentration of 18.8 ppm, the addition of 0.34 g/L Na_5DTPA to an alkaline peroxide solution containing magnesium and silicate increases peroxide decomposition by approximately 15%. The enhancement of peroxide decomposition caused by the addition of chelating agents to alkaline hydrogen peroxide solutions containing iron has been observed by other workers¹¹⁵⁻¹¹⁷. In the case of Na_4EDTA , this type of behavior has been explained by the formation of an unstable purple complex identified as $\text{Fe(III)[EDTA]O}_2^{3-}$ which decomposes readily releasing oxygen⁶⁶. The formation of a purple color was also observed in the experiments with Na_5DTPA which suggests the formation of a similar complex. It is important to point out that the purple complex was formed despite the fact that iron was present as an insoluble hydrous oxide ("aged solution"). This indicates the existence of a reversible equilibrium between hydrous iron oxide and chelatable iron.

The addition of Na_5DTPA in combination with magnesium and silicate in the brightening formulation is not recommended if a significant concentration of iron is present in the brightening system because of the resulting enhanced peroxide decomposition. Fortunately, the use of stabilizers other than magnesium and silicate seems unnecessary for the prevention of iron-catalyzed

peroxide decomposition since a very stable system is obtained with these two stabilizers alone even at high iron concentrations.

3.2.2. Copper

The results in Figure 57 show the effect of copper on peroxide decomposition in the absence and presence of stabilizers and combinations of stabilizers. In the absence of any stabilizer, peroxide decomposition is approximately 30% in solutions containing 0.05 ppm of copper. Decomposition is much greater in the presence of sodium silicate, reaching 100% in solutions containing less than 0.05 ppm of copper. Magnesium stabilizes peroxide up to a copper concentration of 0.2 ppm. A combination of magnesium and sodium silicate showed a synergistic effect in improving hydrogen peroxide stabilization. In this case, a copper concentration of 3 ppm caused insignificant decomposition. The synergistic effect of magnesium in combination with silicate seems to be quite large since magnesium alone has a very small positive effect and silicate has a deleterious effect on peroxide stability in the presence of copper.

A combination of Na_5DTPA , magnesium, and sodium silicate stabilized peroxide over a wide range of high copper concentrations. It is interesting to point out that Na_5DTPA interacts synergistically with magnesium and silicate in stabilizing peroxide against the copper-catalyzed decomposition. Under optimum conditions, i.e., assuming all the copper is present in a chelatable form, the amount of chelating agent added

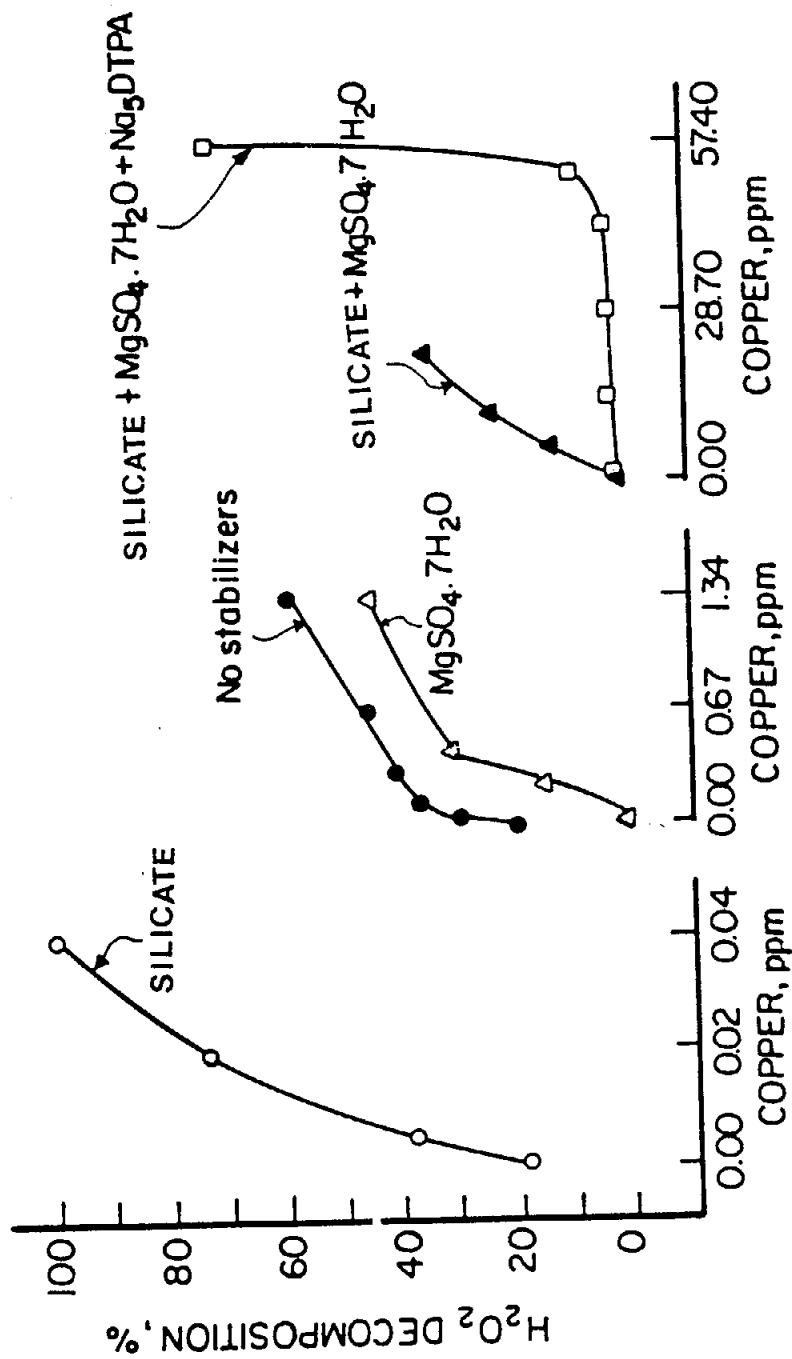


Figure 57. Effect of copper on the decomposition of 0.098 M H_2O_2 in the presence of various stabilizers and combinations of stabilizers. ($\text{SiO}_2 = 0.08 \text{ M}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 0.17 \text{ g/L}$, $\text{Na}_5\text{DTPA} = 0.34 \text{ g/L}$, initial pH 10.8, 50°C , 120 min).

(0.34 g/L) is sufficient to chelate only 17 ppm of copper²¹⁴. However, the combination Na₅DTPA/magnesium/silicate stabilized peroxide nearly completely in the presence of 40 ppm of copper. Moreover, optimum conditions for chelation cannot be assumed under the conditions of the experiment because copper was added in the "aged" form, i.e., as insoluble hydrous copper oxides which probably are not readily chelatable.

The cause of the aforementioned synergistic effect is difficult to rationalize since a large number of interactions may take place among the various stabilizers and between the stabilizers and hydrous copper oxide. It is also difficult to explain the sudden decrease in peroxide stability when copper concentrations above 50 ppm were used (Fig. 57). The exhaustion of the chelation capacity of the Na₅DTPA could be an explanation but, as mentioned earlier, the concentration of the latter used is not sufficient to chelate more than 17 ppm of copper under optimum chelation conditions.

The use of Na₅DTPA in brightening either in a pulp pretreatment or in combination with magnesium and sodium silicate in the brightening formulation seems to be imperative for the prevention of peroxide decomposition if significant amounts of copper are present in the brightening system.

3.2.3. Manganese

The effect of manganese on peroxide decomposition in the absence and presence of stabilizers and combinations of stabilizers is illustrated in Figure 58. As in the case of

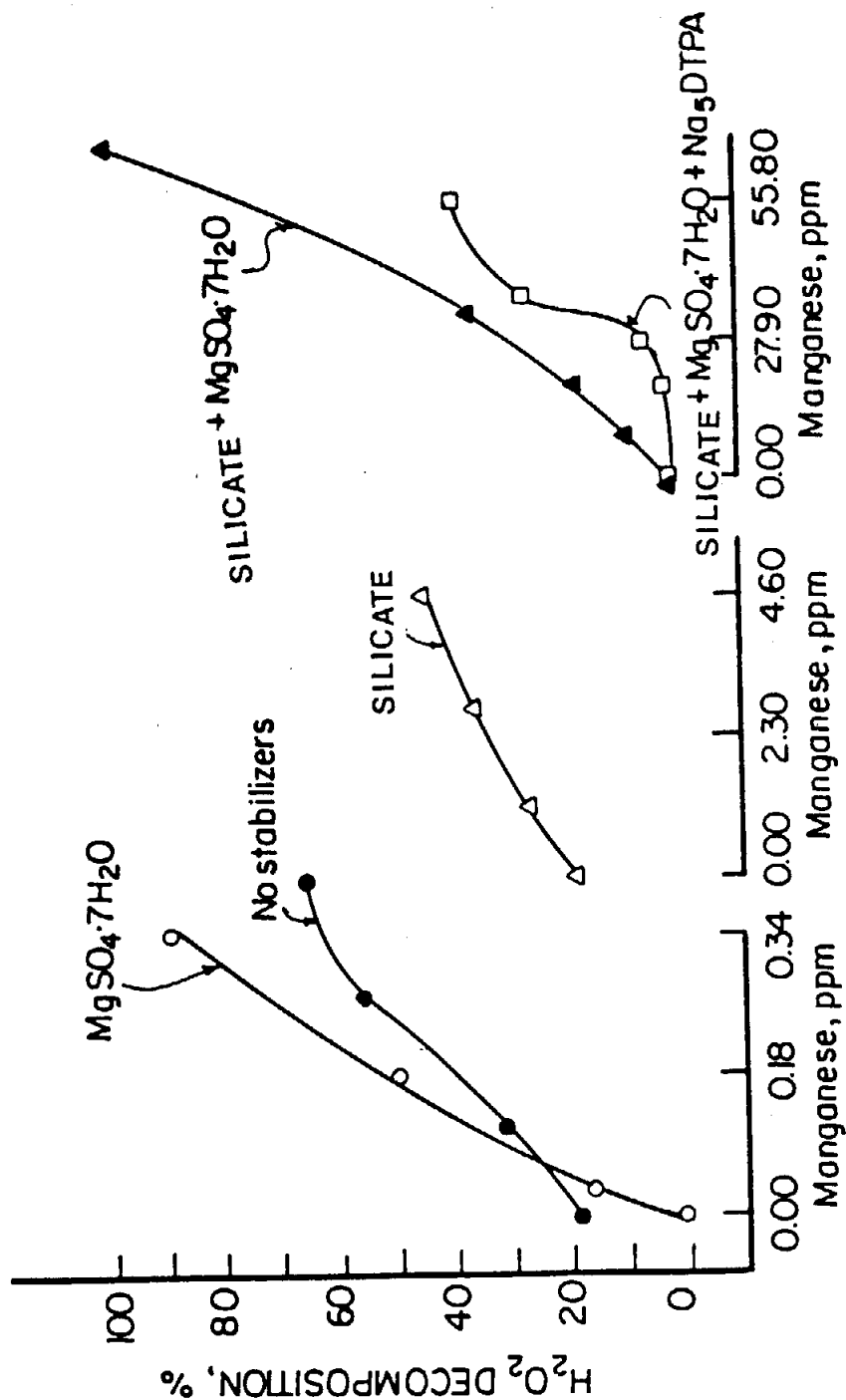


Figure 58. Effect of manganese on the decomposition of 0.098 M H_2O_2 in the presence of various stabilizers and combinations of stabilizers. ($\text{SiO}_2 = 0.08$ M, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 0.17$ g/L, $\text{Na}_5\text{DTPA} = 0.34$ g/L, initial pH 10.8, 50°C , 120 min).

copper, the stability of alkaline peroxide solutions decreases sharply with the addition of small amounts of manganese to unstabilized solutions. Peroxide stability further decreases when magnesium is added to the solutions containing manganese. The adverse effect on peroxide stability caused by the interaction between manganese and magnesium has been reported²⁶ but no explanation for this behavior has as yet been offered. The addition of sodium silicate to solutions containing magnesium results in some peroxide stabilization which decreases almost linearly with increasing concentration of manganese. Thus, a combination of magnesium and silicate acts synergistically in stabilizing hydrogen peroxide solutions containing manganese but stability decreases sharply with increasing manganese concentration.

The addition of Na₅DTPA in combination with magnesium and silicate to alkaline peroxide solutions containing manganese results in improved stability. Similar to the case of copper, Na₅DTPA seems to interact synergistically with magnesium and silicate to inactivate manganese. Under optimum conditions the concentration of Na₅DTPA used (0.34 g/L) is sufficient to chelate only 15 ppm of manganese. However, no significant peroxide decomposition is observed in the presence of up to 28 ppm of manganese. It is interesting to note that at manganese concentrations above this value peroxide stability decreases rather sharply. This phenomenon has not yet been rationalized.

The combination of Na₅DTPA, magnesium sulfate and, sodium silicate is definitely the most effective stabilizing system for

alkaline peroxide solutions containing copper and manganese. However, under actual brightening conditions in the presence of several transition metals, it is difficult to predict stability behavior since Na_5DTPA can adversely affect peroxide stability through complexing with iron. Furthermore, the effect of interactions between the transition metals is another complicating factor that may influence the choice of a suitable stabilizing system for a particular situation. The effect of a combination of Na_5DTPA , magnesium, and silicate on peroxide stability in the presence of combinations of transition metals is not known.

Although the addition of Na_5DTPA to alkaline peroxide solutions stabilized with magnesium and silicate improves peroxide stability significantly in the presence of copper and manganese, it seems more appropriate to use this chelating agent in a pretreatment of the pulp so that the chelated iron does not interact with peroxide and thereby reduce its stability.

3.3. Effect of Other Peroxide Stabilizers

Among the mechanisms that explain the action of various peroxide decomposition inhibitors in a bleaching solution, the following may be cited: (1) the inhibitor forms a stable complex with peroxide and so counteracts the effects of transition metal catalysts which form unstable peroxides¹⁸, and (2) the inhibitor may form stable complexes with catalytically-active materials such as transition metal cations and thereby prevent the latter

from combining with peroxide to form unstable compounds or from forming catalytic hydroxides¹⁸. Magnesium and calcium are examples of the first category of inhibitors and compounds such as dimethylglyoxime, ethylenediamine, Na_4EDTA , Na_5DTPA , sodium citrate, sodium tartrate, sodium pyrophosphate, and sodium silicate can be cited as belonging to the second category of inhibitors¹⁸.

In this section the stability of alkaline hydrogen peroxide was investigated in the presence of sodium citrate, sodium tartrate, and sodium pyrophosphate and the results compared with those obtained in the presence of sodium silicate, magnesium sulfate, and Na_5DTPA (section 4.2). Although sodium borate has not been evaluated as an inhibitor for peroxide decomposition, it was examined in this study since it has been claimed to have a positive effect in the peroxide brightening of mechanical pulps²²⁷.

The results in Table 27 show the effect of the various inhibitors on peroxide decomposition, including the effect of combinations of citrate and tartrate with silicate. The results shown were obtained using optimized concentrations of the compounds (Tables C-3 and C-4 - Appendix C). Among the new additives studied, only citrate and tartrate result in a significant reduction of peroxide decomposition. The results are almost comparable to those obtained using magnesium or Na_5DTPA .

TABLE 27. Decomposition of 0.098 M H_2O_2 in the Presence of Various Inhibitors. (initial² pH 10.8, 50° C, 120 min).

Inhibitor, g/L	H_2O_2 Decomposition, %
None	20.6
Silicate, 16.7	18.5
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.167	1.5
Na_5DTPA , 0.034	0.0
$\text{Na}_4\text{P}_2\text{O}_7$, 1.67	13.0
$\text{NaKC}_4\text{H}_4\text{O}_6$, 45.5	2.9
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 45.5	3.0
$\text{NaKC}_4\text{H}_4\text{O}_6$, 45.5 + Silicate, 16.7	2.9
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 45.5 + Silicate, 16.7	2.8
$\text{Na}_2\text{B}_4\text{O}_7$, 0.167	30.1

In order to verify the effectiveness of these new additives under brightening conditions where larger amounts of transition metals prevail, the stabilization capacity of citrate was investigated in alkaline peroxide solutions containing iron, copper, and manganese. Tartrate was not tested because it was assumed to have essentially the same characteristics as citrate. The results in Table 28 show that the addition of citrate to peroxide solutions containing iron and copper has no influence on peroxide stability but in the presence of added manganese it increases peroxide stability. Since "aged" transition metal solutions were used, copper and iron were present as insoluble hydrous oxides and therefore were not chelated by the citric acid. Manganese, on the other hand, was present in the form of

free ions and hence was chelated by the citric acid with the result that the formation of insoluble manganese dioxide, a potent peroxide catalyst, was reduced. It is important to note that sodium silicate deactivates manganese much more efficiently than sodium citrate.

TABLE 28. Comparison of the Effects of Sodium Citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) and of Sodium Silicate on the Decomposition of $0.0987\text{ M H}_2\text{O}_2$ in the Presence of Iron, Copper, and Manganese. ²(initial pH 10.8, $\text{SiO}_2 = 0.08\text{ M}$, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 = 45.5\text{ g/L}$).

System	H ₂ O ₂ Decomposition, %		
	Iron ¹	Copper ²	Manganese ³
H ₂ O ₂	31.8	1.5	83.6
H ₂ O ₂ /Silicate	11.8	25.8	18.3
H ₂ O ₂ / $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	36.3	1.6	62.5

¹ Fe = 20 ppm, 50° C, 120 min; ² Cu = 0.1 ppm, RT, 30 min; ³ Mn = 5 ppm, 50° C, 30 min.

4. SUMMARY AND CONCLUSIONS

The mechanism of alkaline hydrogen peroxide stabilization by magnesium was evaluated. The individual and combined roles of Na_5DTPA , magnesium sulfate, and sodium silicate as stabilizers for alkaline hydrogen peroxide in the absence and presence of varying amounts of iron, copper, and manganese under conventional hydrogen peroxide brightening conditions were also examined.

Finally, the effect of peroxide decomposition inhibitors such as sodium pyrophosphate, sodium citrate, and sodium tartrate on peroxide stability was assessed. The principal findings of this work were:

1. Magnesium stabilizes alkaline hydrogen peroxide solutions by scavenging superoxide anion radicals thus interrupting free radical chain decomposition reactions.
2. Magnesium completely prevents peroxide decomposition in the near absence of transition metals but is an ineffective stabilizer in the presence of iron and copper and, becomes a catalyst in the presence of manganese.
3. The combination of magnesium and sodium silicate is very effective in reducing the catalytic activity of iron and manganese but less effective in the case of copper.
4. The addition of Na_5DTPA to an alkaline hydrogen peroxide solution stabilized with a combination of magnesium and sodium silicate further improves peroxide stability in the presence of large amounts of copper and manganese but has a detrimental effect in the presence of iron.
5. Sodium citrate prevents peroxide decomposition almost completely in the near absence of transition metals but is of little effect in the presence of manganese and is completely ineffective in the presence of iron and copper.

FACTORS AFFECTING HYDROGEN PEROXIDE STABILITY IN THE BRIGHTENING
OF MECHANICAL AND CHEMIMECHANICAL PULPS

CHAPTER V - EFFECT OF TRANSITION METALS IN NORWAY SPRUCE TMP ON
HYDROGEN PEROXIDE STABILITY

1. INTRODUCTION

In the peroxide brightening of mechanical pulps, part of the peroxide is consumed in oxidation reactions, part is decomposed into water and oxygen and, finally, a portion of it remains unchanged in the spent liquor. The exact amount of peroxide decomposed under brightening conditions is difficult to determine because the high consistencies used do not allow for accurate determination of the amount of oxygen released which is the conventional way to assess decomposition. However, measurements carried out at low (e.g. 4%) consistencies indicate that as much as one-third of the peroxide's brightening capacity may be lost through decomposition during brightening^{13,119}.

The cause of peroxide decomposition during brightening is well-known. It involves substances present in the pulpwood, brightening chemicals, process equipment and mill water which catalytically initiate the decomposition reaction^{87,175}. The enzyme catalase, a common by-product of bacteria in pulps, has been shown to produce this effect^{176,125}. However, trace amounts of transition metals such as iron, copper and manganese found in the brightening system reportedly have the most serious detrimental effect on peroxide stability⁸⁶.

The principal source of transition metals in the brightening system is the pulpwood⁸⁷. Transition metals in pulpwood originate principally in the growing tree where some of them play a vital physiological role^{177,178}, in saws, in mud adhering to the logs,

and in grinding linings and refiners¹⁷⁹. Finger bars, broken off and ground with the wood, often represent a serious source of iron contamination in the case of stone groundwood (SGW)¹⁸⁰. Refiner plates, on the other hand, are an important source of iron in thermomechanical pulping¹⁸¹.

The effectiveness of transition metals as peroxide catalysts depends on their type, concentration, physical condition and chemical composition. Dick and Andrews⁸⁶ claim that among iron, copper and manganese, the latter has the most deleterious effect on peroxide stability. The authors contend that manganese, which usually comes entirely from the wood, is loosely complexed with wood components. Iron and copper, on the other hand, are viewed as being more firmly held by the pulp. Although present in the original wood, these two metals are also adsorbed during grinding or refining from process equipment and from mill water⁸⁶.

Fragmentary evidence suggests that the metals present in mechanical pulps are relatively inactive catalysts for peroxide decomposition whereas those present in process waters are more likely to have an accelerating effect on peroxide decomposition during brightening⁸⁶. This finding does not agree with the fact that a chelation or acid-washing pretreatment of a pulp prior to brightening results in a substantial improvement in its brightening response^{100,187,191}.

It is possible that the metals which are not removed from the pulp by chelation or acid-washing treatments do not catalyze peroxide decomposition whereas those eliminated are harmful to

peroxide stability. In an attempt to confirm this hypothesis, the stability of hydrogen peroxide was determined in the presence of α -cellulose containing transition metals not removed by an acid wash. The origin of transition metals such as iron, copper, and manganese present in TMP and their distribution among the pulp constituents were also examined.

2. MATERIALS AND METHODS

2.1. TMP Preparation

Norway spruce chips were converted to TMP in a two-stage process using a KRK refiner. The first stage consisted of a 3-min steaming of the chips followed by pressurized refining at 135° C. The discharge consistency was 20%. The second-stage refining was conducted at atmospheric pressure and at room temperature. The discharge consistency was 17% . The brightness of the pulp was 58.2% Elrepho.

2.2. Holocellulose and α -Cellulose Preparation

The holocellulose was prepared by treatment of the TMP with peracetic acid for 2h at 70° C according to the method described by Leopold²²⁸. Following this step, the holocellulose at 2% consistency was reduced twice with 3% sodium borohydride (based on o.d. weight of the holocellulose) for 12 h at room temperature (initial pH 9.5). The holocellulose was not washed between the two reducing treatments. The reduced holocellulose (2%

consistency) was then treated with 0.1 M HCl for 3 h at room temperature and then thoroughly washed with doubly-distilled water. The acid-insoluble lignin content of the exhaustively-reduced holocellulose was determined according to Tappi standard T222 os-74.

The α -cellulose was prepared from the reduced holocellulose as described in Tappi Standard T203 os-74. This material was treated with 0.1 M HCl for 3 h at room temperature and 2% consistency, filtered and washed thoroughly with doubly-distilled water.

2.3. Determination of Transition Metal Contents of TMP, Holocellulose, and α -Cellulose

Two-gram samples of TMP, holocellulose, and α -cellulose were wet-ashed with a mixture of 30 mL of HNO_3 and 5 mL of HClO_4 according to CPPA Technical Section Method G-30 P. Subsequently, the ashed samples were diluted to 100 mL in a volumetric flask and then analyzed for iron, copper, and manganese by conventional flame atomic absorption spectrometry. A Perkin-Elmer model 403 spectrometer was used for these measurements.

2.4. Adsorption of Transition Metals on α -Cellulose

Samples (20 g) of α -cellulose were slurried in water at 2% consistency and the equivalent of 150 ppm of iron, copper, or manganese based on the o.d. weight of the α -cellulose was added to the slurry and mixed thoroughly. The transition metal solutions added to the α -cellulose were prepared by dissolving

the sulfate salts of the metals in HCl 0.1 M. After the addition of transition metals to the slurry, the pH was adjusted to 6.5 with ultrapure NaOH and the mixture was boiled and stirred for 3 h in a 2-L flask fitted with a condenser. The slurry was subsequently treated with 0.1 M HCl for 3 h at room temperature, filtered and thoroughly washed with doubly-distilled water.

In the case of copper a second procedure¹⁹⁷ was used which consisted of the reaction of 10 g of α -cellulose with 3 g of $\text{Cu}(\text{OH})_2$ in 200 mL of an 18% NaOH solution. After 4 h the slurry was washed, treated with 0.1 M HCl at 2% consistency for 3 h at room temperature, filtered and thoroughly washed with doubly-distilled water.

2.5. Hydrogen Peroxide Decomposition Tests

Six-gram samples of holocellulose or α -cellulose at 12% consistency were reacted with 0.040 M hydrogen peroxide (initial pH 10.8, 50° C, 2 h). At the end of the reaction peroxide residuals were determined by the iodometric procedure described by Kraft²⁰⁵ and the peroxide decomposition values were calculated.

2.6. Desorption of Transition Metals from TMP

The following three procedures were used to desorb transition metals from the TMP: (1) treatment of the TMP with 0.5% Na_5DTPA (based on o.d. weight of pulp) at 2% consistency, pH 4.5, and room temperature for 30 min, (2) treatment of the TMP

with 0.1 M HCl at 2% consistency and room temperature for 3 h, and (3) treatment of the TMP with 0.1 M HCl at 2% consistency and room temperature for 3 h followed by a Na₅DTPA treatment (1% based on o.d. weight of pulp) at 2% consistency, pH 4.5, and 90° C for 72 h. After all three treatments, the TMP was filtered and washed thoroughly with doubly-distilled water.

3. RESULTS AND DISCUSSION

3.1. Origin of the Transition Metals Present in TMP and their Distribution among the Pulp Constituents

The results compiled in Table 29 show that contamination of the TMP by iron and copper occurred principally during the refining process. This is inferred because the concentrations of iron and copper in the TMP are substantially larger than in the wood from which it was produced. The iron sorbed onto the pulp during refining probably results from attrition of the refiner plates. In the case of copper, the source of contamination is very likely the process water. Manganese, on the other hand, originates basically in the wood and its concentration is actually reduced during the refining process.

It is interesting to note that treatment of the TMP with 0.1 M HCl for 3 h removed less than 25% of the 78 ppm of iron originally present in the pulp. This result indicates that a large fraction of the iron sorbed during the refining process is attached strongly to the TMP since the original wood contained

only 9.5 ppm of strongly attached iron. The iron originally present in the wood is considered strongly attached because it is not removed to any extent by a strong chelation treatment (Table 29). The fact that iron become strongly attached to the TMP during the refining process may be attributed to the conversion of the colloidal amorphous iron (III) oxide from the refiner plates to crystalline iron (III) oxide. This conversion is favored by the high temperatures existing in the refining zone. Crystalline iron (III) oxide, goethite, reportedly is capable of becoming strongly attached to mechanical pulps whereas colloidal amorphous iron (III) oxide is not¹⁸¹.

TABLE 29. Transition Metal Content of Norway Spruce Wood, TMP, and TMP Treated with 0.1 M HCl and/or Na₅DTPA.

Material	Transition Metal Content, ppm		
	Iron	Copper	Manganese
Wood meal	9.5	4.5	114.9
Wood chips	10.6	4.8	116.2
Wood meal Treated with Na ₅ DTPA ²	9.7	4.1	<1.0
TMP	78.0	19.5	97.0
TMP Treated With 0.1 M HCl ³	60.8	3.8	<1.0
TMP Treated With Na ₅ DTPA ⁴	59.8	4.0	<1.0
TMP Treated With 0.1 M HCl and Na ₅ DTPA ⁵	23.5	2.3	<1.0

¹ Based on o.d. wood

² 2% Na₅DTPA on o.d. wood, 2% consistency, 72 h, RT, pH 4.5.

³ 0.1 M HCl, 2% consistency, 3 h, RT.

⁴ 0.5% Na₅DTPA on o.d. pulp, 2% consistency, 30 min, RT, pH 4.5.

⁵ 0.1 M HCl, 2% consistency, 3 h, RT; 1.0% Na₅DTPA on o.d. pulp, 2% consistency, 72 h, 90° C, pH 4.5.

The acid treatment removed approximately 80% of the copper originally present in the TMP. The small fraction of strongly-attached copper remaining in the pulp after acid treatment probably originates from the wood since the copper content of woodmeal after a strong chelation treatment with Na_5DTPA (Table 29) is similar to that of the acid-treated TMP. These results indicate that the copper originally present in the wood is strongly attached to its lignin and carbohydrate components.

In agreement with the results of other workers^{181,187,191} manganese was completely removed from the wood and TMP by the acid treatment. Manganese is apparently loosely complexed with the wood components⁸⁶ and thus is easily removed from the wood or pulp by acid washing or chelation. It is important to point out that nearly all of the manganese was removed from the TMP regardless of the desorption treatment used (Table 29).

The expression "strongly-attached iron and copper" used throughout this text refers to the iron and copper which are not removed from TMP or α -cellulose by treatment with 0.1 M HCl for 3 h at room temperature. As can be observed in Table 29, the 3-h acidic treatment had approximately the same effect as the conventional 30-min chelation treatment with Na_5DTPA normally used in the industry.

In an attempt to remove the strongly-attached iron and copper from the TMP, a more severe treatment of the pulp was performed which consisted of acid washing for 3 h followed by

chelation with Na_5DTPA for 72 h. The data in Table 29 show that the iron and copper contents of the TMP are reduced significantly (~50%) but total elimination of the metals is not achieved. Therefore, it should be expected that considerable amounts of iron and copper will accompany the TMP to the peroxide brightening tower even after a strong acid and/or chelation pretreatment.

The component of the TMP which contains the major part of the strongly-attached iron is the cellulose because of the predominance of this component in the TMP. The removal of lignin from the TMP results in a decrease of ~18% in the concentration of the strongly-attached iron. This was inferred because the amount of iron in the holocellulose is approximately ~18% lower than that of the TMP treated with 0.1 M HCl (Table 30). Similar results are observed for copper.

The results for α -cellulose indicate that removal of hemicelluloses from the holocellulose results in a significant decrease in the concentrations of strongly-attached iron and copper (Table 30). The fact that the hemicelluloses contain copper and iron is in agreement with theories which postulate that transition metals can be chelated by the carboxyl and carbonyl functionalities present in these wood constituents^{189,190,192}.

TABLE 30. Transition Metal Contents of Norway Spruce TMP, Holocellulose, and α -Cellulose.

Material	Transition Metal Content, ppm ¹		
	Iron	Copper	Manganese
TMP	82.3	20.6	102.3
TMP Treated With 0.1 M HCl ²	63.7	4.3	<1.0
TMP Holocellulose ³	49.4	3.1	<1.0
TMP α -Cellulose ³	36.8	1.4	<1.0

¹ Based on o.d. TMP

² 3 h, RT.

³ Treated with 0.1 M HCl for 3 h at RT.

Although a large fraction of the iron strongly attached to the TMP is bound to the carbohydrate component of the fibers, it is not clear whether this association is a chemical or a physical phenomenon. It has been suggested¹⁹² that iron is bound to cellulose either through hydrogen bridges between the hydroxyl groups of cellulose and the hydroxyl groups of iron (III) hydroxide or possibly through the adsorption of positively-charged iron (III) hydroxide micelles by negatively-charged cellulose micelles. In contrast, it is also possible that the strong attachment of the crystalline iron (III) iron occurs via an adsorption process which does not involve chemical bonding between iron and cellulose chains (e.g. adhesion).

The results discussed in this section clearly demonstrate that, for all practical purposes, it is impossible to eliminate all of the iron and copper present in TMP. The question that remains is whether these strongly-attached metals have any

impact on hydrogen peroxide stability during pulp brightening. In the next section this issue is discussed in detail.

3.2. Effect of the Transition Metals Strongly Attached to TMP on Hydrogen Peroxide Decomposition

This set of experiments was designed to determine if the transition metals which are not removed from the TMP by a 0.1 M HCl treatment (3 h, RT) have any impact on hydrogen peroxide stability. To achieve this goal it was necessary to prepare a pulp substrate which had some characteristics of the original TMP but which did not consume hydrogen peroxide. The first and more obvious approach was to remove the lignin from the TMP via preparation of holocellulose. The results in Table 31 show that peroxide decomposition in the presence of holocellulose made from the TMP is approximately 10% higher than in its absence. This result indicates that either the holocellulose consumes peroxide or that the metals strongly bound to it initiate peroxide decomposition. In order to verify whether the additional consumption of peroxide in the presence of the holocellulose was caused by reaction of peroxide with organic substrates in the holocellulose or by decomposition reactions, α -cellulose was prepared from the holocellulose and reacted with peroxide under the same conditions. The results (Table 31) show that peroxide decomposition in the presence and absence of α -cellulose is similar. This is an indication that peroxide consumption in the presence of holocellulose is due to reactions with organic substrates other than α -cellulose since the major fraction of

the strongly-attached metals which could cause peroxide decomposition was still present in the α -cellulose. It should be pointed out that the holocellulose contained 1.8% of Klason lignin which was probably removed by the strong alkali treatment used in the preparation of the α -cellulose. This lignin residue present in the holocellulose may have accounted for at least a part of the 10% of peroxide consumed.

The fact that the α -cellulose does not contribute to peroxide decomposition indicates that the metals strongly attached to it are not active peroxide catalysts. It should be noted that the α -cellulose reacted with peroxide contained 36.8 ppm of iron and 1.4 ppm of copper. These amounts represent a very large fraction of the original iron and copper strongly attached to the TMP (Table 30). Therefore, it is reasonable to conclude that the strongly-attached iron and copper present in the TMP are not effective peroxide catalysts.

TABLE 31. Consumption/Decomposition of 0.040 M H_2O_2 in Reaction with Norway Spruce TMP, Holocellulose,² and α -Cellulose made from TMP. (initial pH 10.8, 50° C, 120 min, 12% consistency).

System	H_2O_2 Consumption/ Decomposition, %
H_2O_2	29.8
H_2O_2 + TMP ¹	100.0
H_2O_2 + Holocellulose ¹	40.1
H_2O_2 + α -Cellulose ¹	28.8

¹ TMP, holocellulose, and α -cellulose were treated with 0.1 M HCl for 3 h at RT prior to reaction with peroxide.

To further confirm the finding that the metals strongly attached to TMP are not effective peroxide catalysts, attempts were made to add iron and copper irreversibly to TMP α -cellulose. No attempts were made to add manganese because this metal is not firmly attached to the original TMP fibers. Iron was easily deposited on the α -cellulose by boiling the latter in an iron (III) chloride solution at pH 6.5. Copper, on the other hand, did not adhere strongly to the α -cellulose using this procedure. Strong attachment of copper to the α -cellulose was achieved by treating the latter with copper hydroxide under strongly alkaline conditions. The results in Table 32 show that an approximately 2.5-fold increase in the iron concentration of the α -cellulose does not result in any significant increase in peroxide decomposition. The same trend was observed in the case of the copper where an eight-fold increase in its concentration did not change peroxide decomposition. It is important to point out that the artificially-introduced iron and copper that were strongly attached to the α -cellulose may not bear any structural similarity with the metals originally present in the TMP. This is especially true in the case of the copper which required rather strong alkaline conditions in order to bind to the α -cellulose.

TABLE 32. Effect of the Concentration of Strongly-Attached Iron and Copper in α -Cellulose on the Decomposition of 0.040 M H_2O_2 . (initial pH 10.8, 12% consistency, 50° C, 120 min)².

α -Cellulose	Metal Conc. in α -Cellulose, ppm ¹			H_2O_2 Decomposition, %
	Iron	Copper	Manganese	
Untreated ²	47.9	2.1	<1.0	28.8
Fe Treated ³	108.3	2.1	<1.0	29.9
Cu Treated ³	47.9	2.0	<1.0	30.5
Cu Treated ⁴	47.9	16.3	<1.0	31.3

¹ Based on o.d. α -cellulose.

² Washed with 0.1 M HCl for 3 h at RT.

³ Treated with 150 ppm of $FeSO_4$ or $CuSO_4$ for 3 h, pH 6.5, 100° C; washed with 0.1 M HCl for 3 h⁴ at RT.

⁴ Treated with $Cu(OH)_2$ + 18% NaOH for 4 h at RT; washed with 0.1 M HCl for 3 h at RT.

As a final comment in this section it must be emphasized that, although metals strongly attached to the pulp are not catalysts, the effect of transition metals in TMP on peroxide stability during brightening cannot be neglected. The metals that are removed from the TMP by acid or chelation treatments certainly play an important role on peroxide decomposition. This fact is clearly observed in the commercial brightening of mechanical pulps where an acid or chelation pretreatment of the pulp prior to the peroxide stage to remove transition metals is almost imperative for successful brightening. Among the metals removed in the pretreatment stage, manganese probably is the most deleterious to peroxide stability not only because of its effectiveness as a peroxide catalyst but also since it is usually present in high concentrations.

4. SUMMARY AND CONCLUSIONS

The effect on hydrogen peroxide decomposition of transition metals strongly attached to TMP was assessed. The origin of transition metals such as iron, copper, and manganese present in TMP and their distribution among the pulp components was also determined. Finally, the effect of acid washing and/or Na_5DTPA chelation on the removal of transition metals from TMP was evaluated. The principal findings of this work are:

1. The iron and copper strongly attached to TMP are not catalysts for hydrogen peroxide decomposition.
2. All the iron and copper originally present in the wood is strongly attached to its lignin and carbohydrate components.
3. Approximately 75% of the iron present in TMP is strongly attached to the fibers whereas a smaller fraction of the copper (~20%) and none of the manganese is similarly bound.
4. Most of the iron (~90%) and copper (~80%) present in TMP is picked up during the refining process. Manganese, on the other hand, originates totally from the wood.
5. Complete removal of iron and copper from TMP is not achieved by chelation and/or acid treatments.

CONCLUDING REMARKS

In this investigation the mechanisms of hydrogen peroxide decomposition and of hydrogen peroxide stabilization by sodium silicate and magnesium sulfate in weakly alkaline solutions were clarified. Additionally, the effect of stabilizers such as sodium silicate, magnesium sulfate, chelating agents (Na_5DTPA), and their combinations on peroxide stability in the presence of transition metals such as iron, copper, and manganese was investigated for the purpose of establishing optimum stabilizing systems for peroxide in the presence of each transition metal. Finally, the origin of the transition metals present in termomechanical pulps (TMP) and the effect of non-chelatable transition metals in TMP on peroxide stability was assessed. The most important findings of this work are: (1) the decomposition of alkaline peroxide during pulp brightening is a transition metal-induced reaction, (2) peroxide decomposition involves hydroxyl and superoxide anion radicals but a free radical chain reaction is not the main decomposition pathway, (3) the catalytic decomposition of peroxide by iron, copper, and manganese in alkaline media is caused by insoluble forms of these metals, (4) sodium silicate does not stabilize peroxide by itself but it inactivates certain transition metals that catalyze peroxide decomposition, (5) sodium silicate stabilizes peroxide under brightening conditions by inactivating iron hydrous oxides and manganese ions, (6) sodium silicate inactivates manganese ions

through the presumed formation of manganese silicate, (7) magnesium completely prevents peroxide decomposition in the near absence of transition metals but is an ineffective stabilizer in the presence of iron and copper and, becomes a catalyst in the presence of manganese, (8) magnesium stabilizes alkaline peroxide solutions by scavenging superoxide anion radicals thus interrupting free radical chain decomposition reactions, (9) the combination of magnesium and silicate is very effective in reducing the catalytic activity of iron and manganese but less effective in the case of copper, (10) the addition of Na_5DTPA to an alkaline peroxide solution stabilized with a combination of silicate and magnesium sulfate further improves peroxide stability in the presence of large amounts of copper and manganese but has a detrimental effect in the presence of iron, (11) all of the iron and copper originally present in the wood is strongly attached to its lignin and carbohydrate components, (12) approximately 75% of the iron present in TMP is strongly attached to the fibers whereas a smaller amount of the copper (~20%) and none of the manganese is similarly bound, (13) complete removal of iron and copper from TMP is not achieved by chelation and/or acid treatments, and (14) the iron and copper strongly attached to TMP are not catalysts for peroxide decomposition.

Throughout this investigation a number of problems were identified as potential topics for future work, the following being of immediate interest: (1) determination of the form in which strongly-attached iron and copper are held by mechanical pulps, (2) clarification of the mechanism by which sodium

silicate deactivates iron during pulp brightening, (3) assessment of the effects of combinations of transition metals such as iron, copper, and manganese on hydrogen peroxide stability, (4) assessment of the effect of combinations of stabilizers such as magnesium, silicate, and chelating agents on hydrogen peroxide stability in the presence of combinations of transition metals, (5) determination of the role played by transition metal oxides/hydroxides particle size on peroxide stability, (6) determination of the cause of increased peroxide decomposition resulting from the combined presence of silicate and copper in alkaline peroxide solutions, and (7) determination of the cause of increased peroxide decomposition with increasing pH in the range 9.8-11.8 in the presence of transition metals.

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APPENDIX A

TABLE A-1. The Amounts of p-Nitrosodimethylaniline (PNDA) Decolorized by Hydrogen Peroxide Decomposition in Various Systems. ($\text{H}_2\text{O}_2 = 0.04 \text{ M}$, $\text{PNDA} = 2.5 \cdot 10^{-4} \text{ M}$, $\text{SiO}_2 = 0.04 \text{ M}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 0.069\text{g/L}$, $\text{Na}_5\text{DTPA} = 0.014 \text{ g/L}$, $\text{Fe} = 7.7 \text{ ppm}$, $\text{Mn} = 0.12 \text{ ppm}$, $\text{Cu} = 0.03 \text{ ppm}$, initial $\text{pH} = 10.8$, 50° C , 120 min).

System	PNDA Decolorized, $\text{M} \cdot 10^5$
H_2O_2	1.70
$\text{H}_2\text{O}_2 - \text{Fe}$	0.97
$\text{H}_2\text{O}_2 - \text{Cu}$	2.95
$\text{H}_2\text{O}_2 - \text{Mn}$	1.02
$\text{H}_2\text{O}_2 - \text{Na}_5\text{DTPA}$	0.11
$\text{H}_2\text{O}_2 - \text{Mg}$	0.41
$\text{H}_2\text{O}_2 - \text{Silicate}$	1.18
$\text{H}_2\text{O}_2 - \text{Silicate} - \text{Mg}$	0.36

TABLE A-2. Solubility Product Constants (K_{sp}) of Iron (III), Copper (II), and Manganese (II) Hydroxides at 25° C^{225} .

Transition Metal Hydroxide	K_{sp}
$\text{Fe}(\text{OH})_3$	$2.67 \cdot 10^{-39}$
$\text{Cu}(\text{OH})_2$	$6.07 \cdot 10^{-20}$
$\text{Mn}(\text{OH})_2$	$2.04 \cdot 10^{-13}$

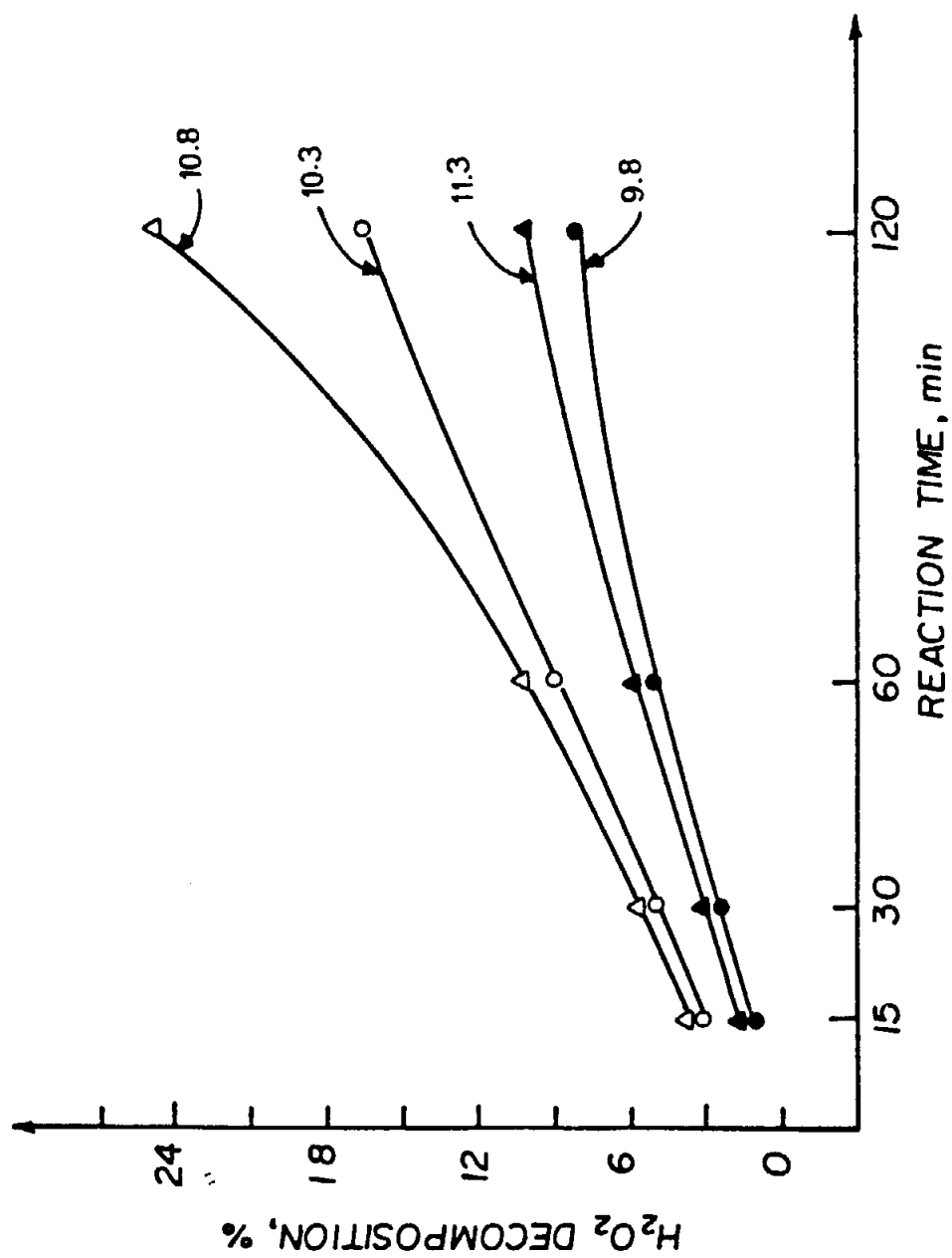


Figure A-1. Rate of decomposition of 0.098 M H_2O_2 under pH-controlled conditions at 50° C.

APPENDIX B

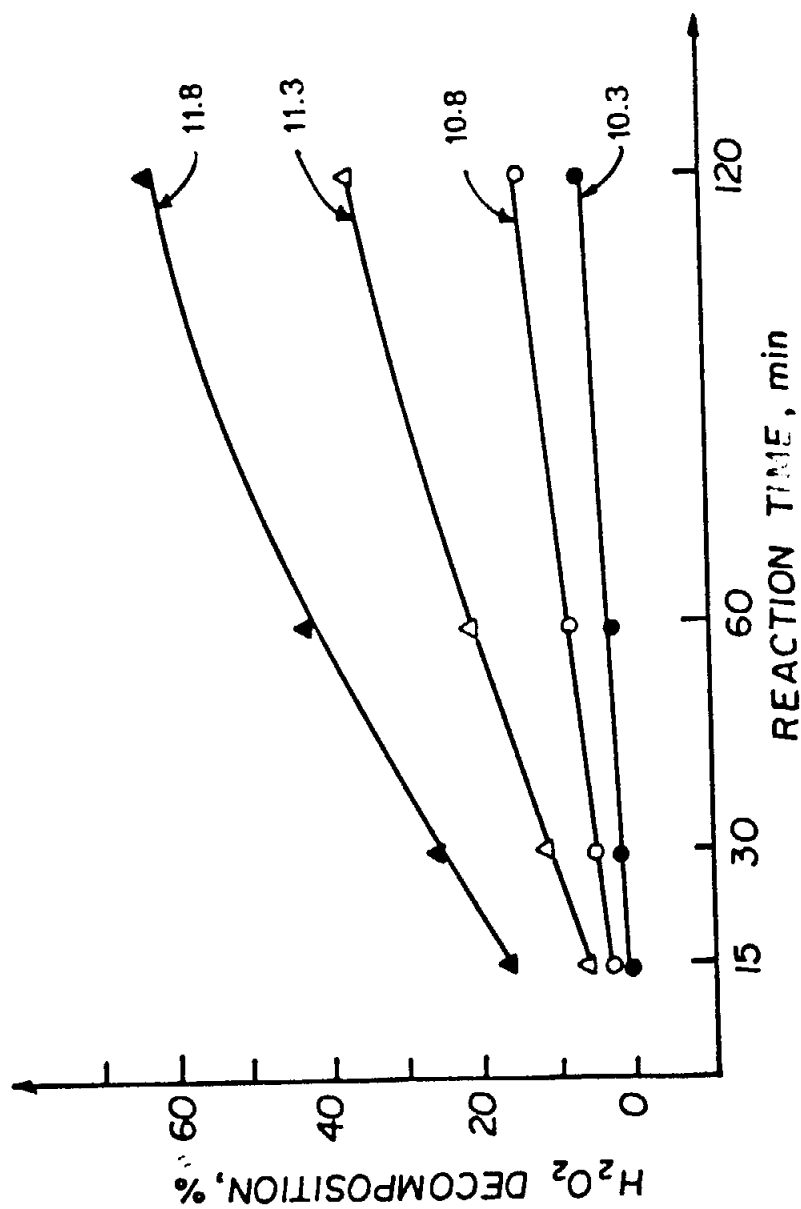


Figure B-1. Rates of decomposition of 0.098 M H_2O_2 in the presence of sodium silicate under pH-controlled conditions. ($SiO_2 = 0.08$ M, 50° C, 120 min).

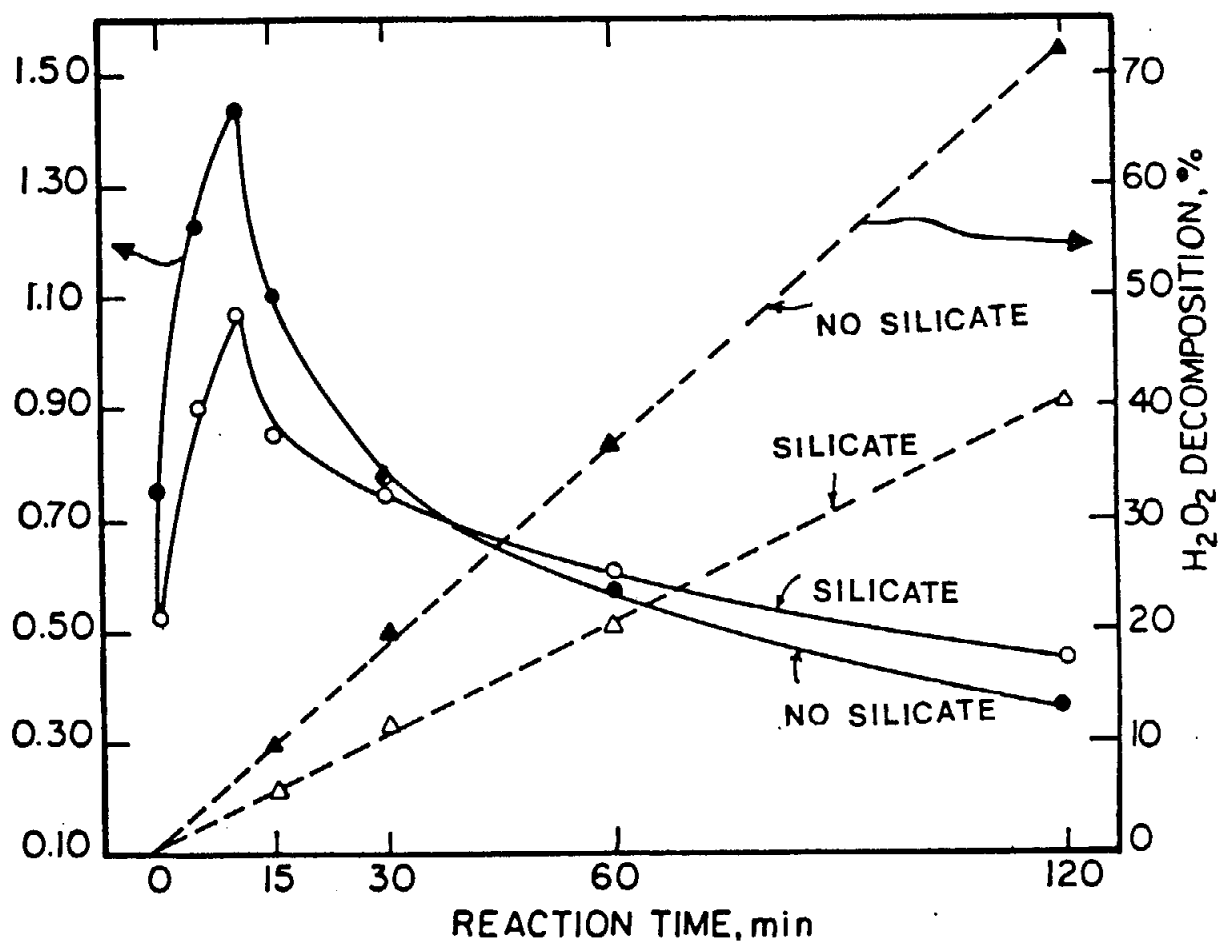


Figure B-2. Rates of superoxide anion radical generation in the decomposition of 0.49 M H_2O_2 in the presence and absence of sodium silicate. ($\text{SiO}_2 = 0.4$ M, initial pH 10.8, 50°C).

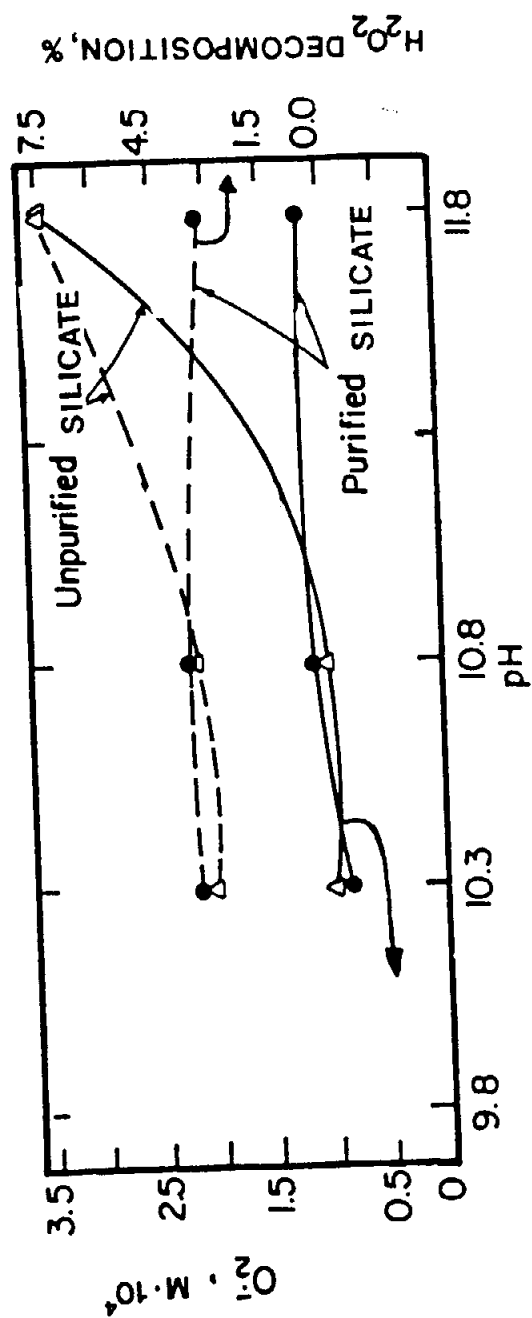


Figure B-3. Effect of pH on superoxide anion radical generation in the decomposition of 0.49 M H_2O_2 in the presence of purified and unpurified sodium silicate. ($\text{SiO}_2 = 0.4 \text{ M}$, 50°C , 10 min).

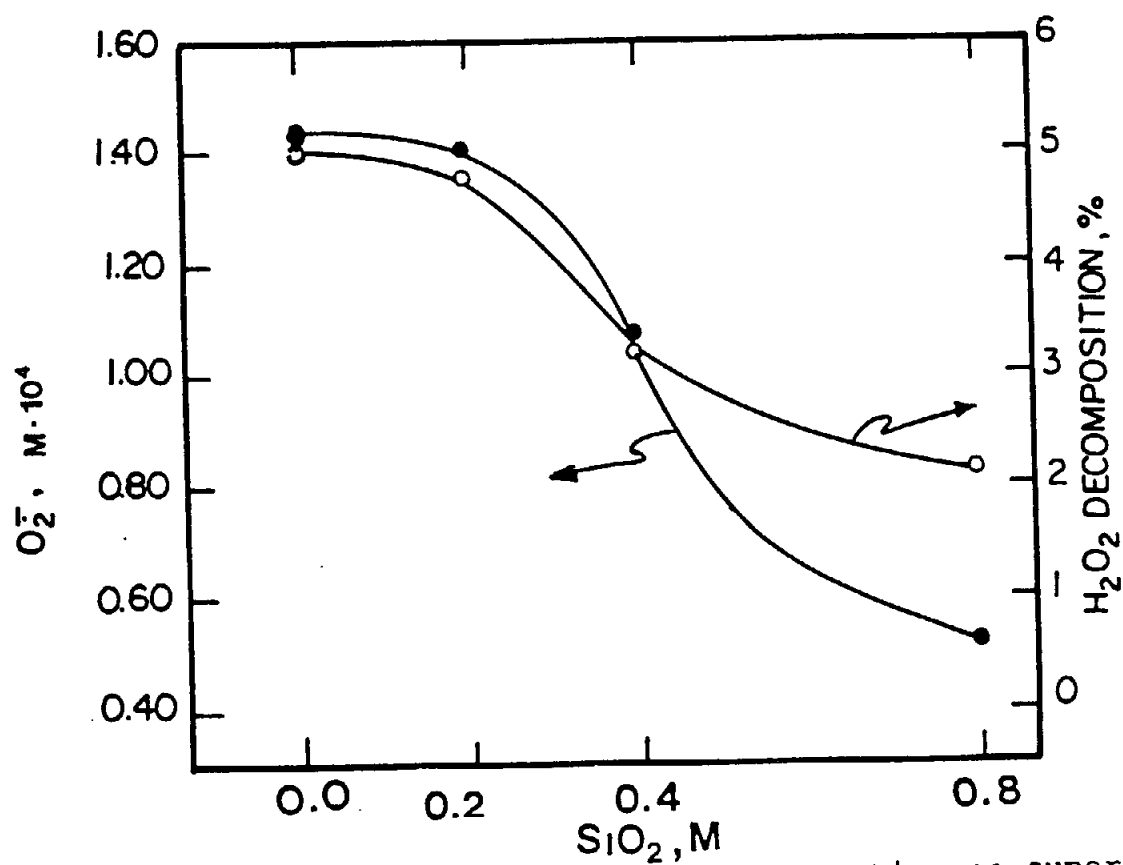


Figure B-4. Effect of sodium silicate concentration on superoxide anion radical generation in the decomposition of 0.49 M H_2O_2 . (initial pH 10.8, 50° C, 120 min).

APPENDIX C

TABLE C-1. Individual and Combined Effects of Transition Metals (Fe, Cu and Mn) on the Decomposition of 0.098 M H_2O_2 in the Presence of Magnesium. ($MgSO_4 \cdot 7H_2O = 0.17g/L$, Initial pH 10.8, 50° C, 120 min).

Metal Combination	Hydrogen Peroxide Decomposition, %					Combined Effect
	Individual Effect					
	No Added Metals	Fe ¹	Cu ¹	Mn ¹	Total	
Fe + Cu + Mn	1.5	20.0	31.0	15.0	67.5	100.0
Fe + Cu	1.5	20.0	31.0	-	52.5	100.0
Fe + Mn	1.5	20.0	-	15.0	36.5	28.0
Cu + Mn	1.5	-	31.0	15.0	47.5	70.0

¹ Fe = 12.6 ppm, Cu = 5.4 ppm, Mn = 0.10 ppm

TABLE C-2. Individual and Combined Effects of Transition Metals (Fe, Cu and Mn) on the Decomposition of 0.098 M H_2O_2 in the Presence of Magnesium and Sodium Silicate. ($MgSO_4 \cdot 7H_2O = 0.17 g/L$, $SiO_2 = 0.08 M$, Initial pH 10.8, 50° C, 120 min).

Metal Combination	Hydrogen Peroxide Decomposition, %					Combined Effect
	Individual Effect, %					
	No Added Metals	Fe ¹	Cu ¹	Mn ¹	Total	
Fe + Cu + Mn	1.0	4.0	19.0	19.0	43.0	95.0
Fe + Cu	1.0	4.0	19.0	-	24.0	28.0
Fe + Mn	1.0	4.0	-	19.0	24.0	79.0
Cu + Mn	1.0	-	19.0	19.0	39.0	50.0

¹ Fe = 18.8 ppm, Cu = 2.0 ppm, Mn = 18.5 ppm

TABLE C-3. Effect of Sodium Citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) and Sodium Potassium Tartrate ($\text{NaKC}_4\text{H}_4\text{O}_6$) Concentrations on the Decomposition of $0.098 \text{ M H}_2\text{O}_2$ in the Presence and Absence of Sodium Silicate. ($\text{SiO}_2 = 0.08 \text{ M}$, 50° C , 120 min).

Concentration, g/L	H_2O_2 Decomposition, %			
	Without Silicate		With Silicate	
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	$\text{NaKC}_4\text{H}_4\text{O}_6$	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	$\text{NaKC}_4\text{H}_4\text{O}_6$
0.00	20.6	20.6	18.5	18.5
1.42	17.9	18.4	16.7	16.9
2.84	16.8	17.9	13.6	12.6
5.68	13.3	12.2	10.2	9.8
11.37	6.1	6.1	8.7	8.4
22.74	4.8	4.8	6.3	6.1
45.47	2.9	3.0	2.9	2.8
90.90	0.9	1.1	0.5	0.8

TABLE C-4. Effect of Sodium Pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) and Borax ($\text{Na}_2\text{B}_4\text{O}_7$) concentration on the Decomposition of $0.098 \text{ M H}_2\text{O}_2$. (Initial pH 10.8, 50° C , 120 min).

Concentration, g/L	H_2O_2 Decomposition, %	
	$\text{Na}_4\text{P}_2\text{O}_7$	$\text{Na}_2\text{B}_4\text{O}_7$
0.167	19.3	30.1
1.670	13.0	31.2
3.340	14.8	36.2
5.010	18.5	40.7
10.020	31.0	44.0
15.030	-	45.7

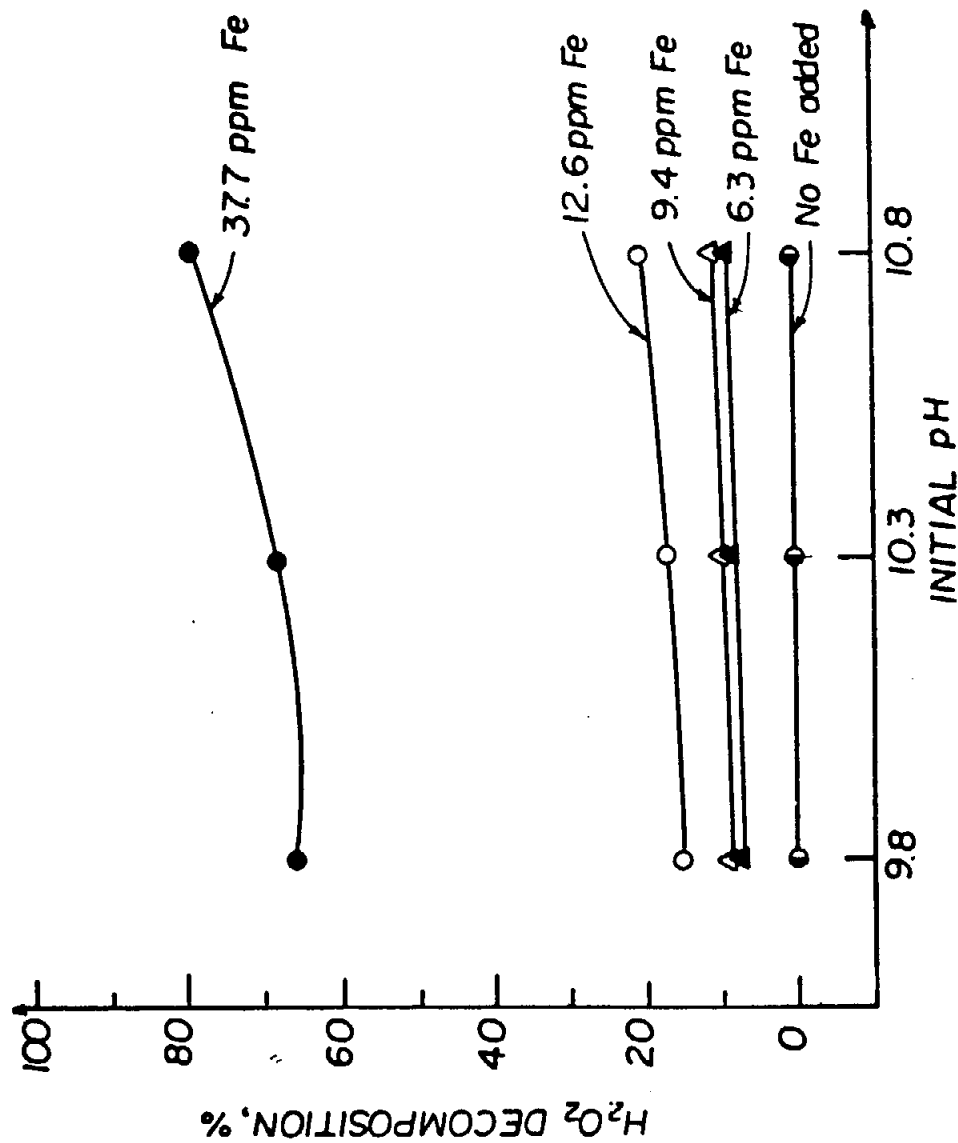


Figure C-1. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of magnesium and varying amounts of iron. ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 0.17 \text{ g/L}$, 50°C , 120 min).

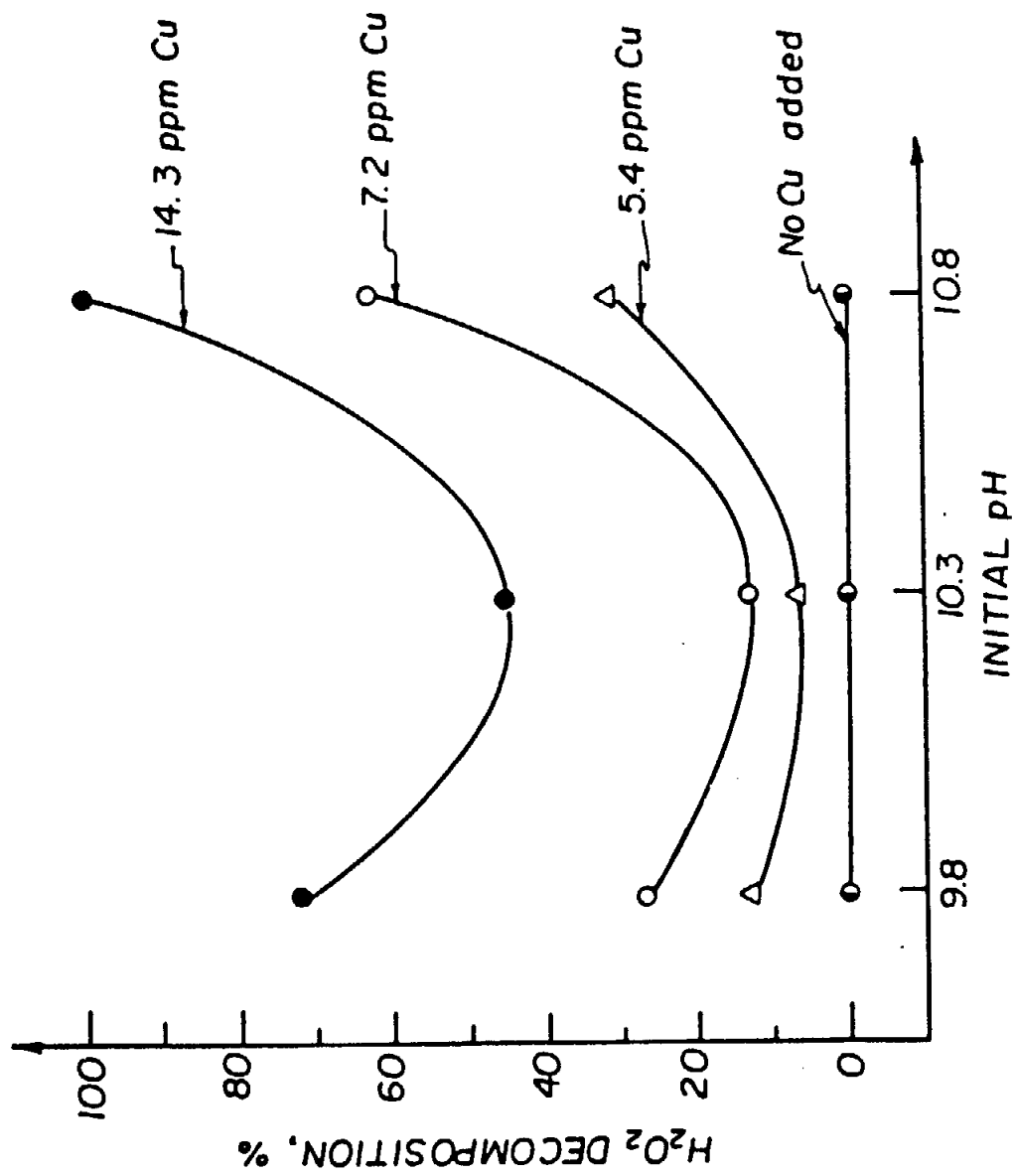


Figure C-2. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of magnesium and varying amounts of copper. ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 0.17 \text{ g/L}$, 50°C , 120 min).

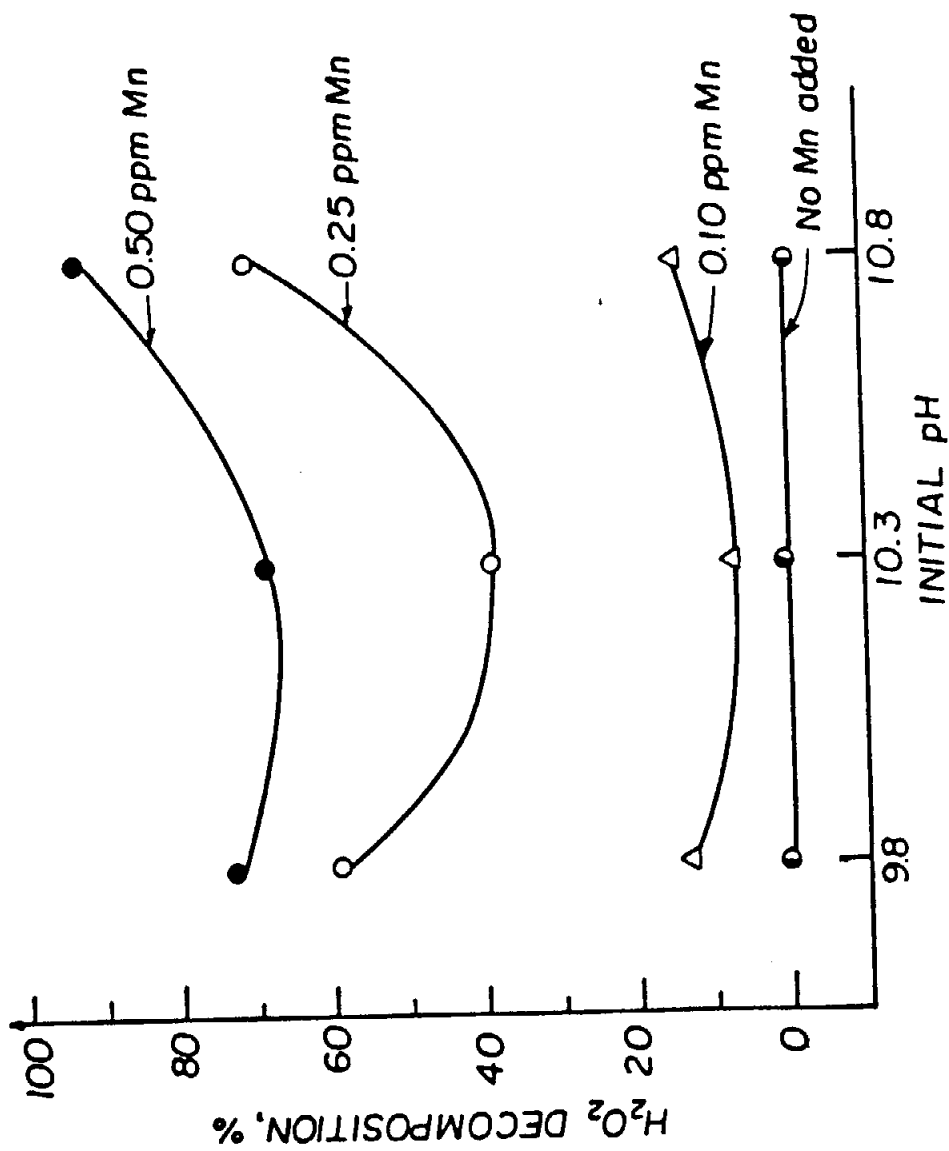


Figure C-3. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of magnesium and varying amounts of manganese. ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 0.17 \text{ g/L}$, 50°C , 120 min).

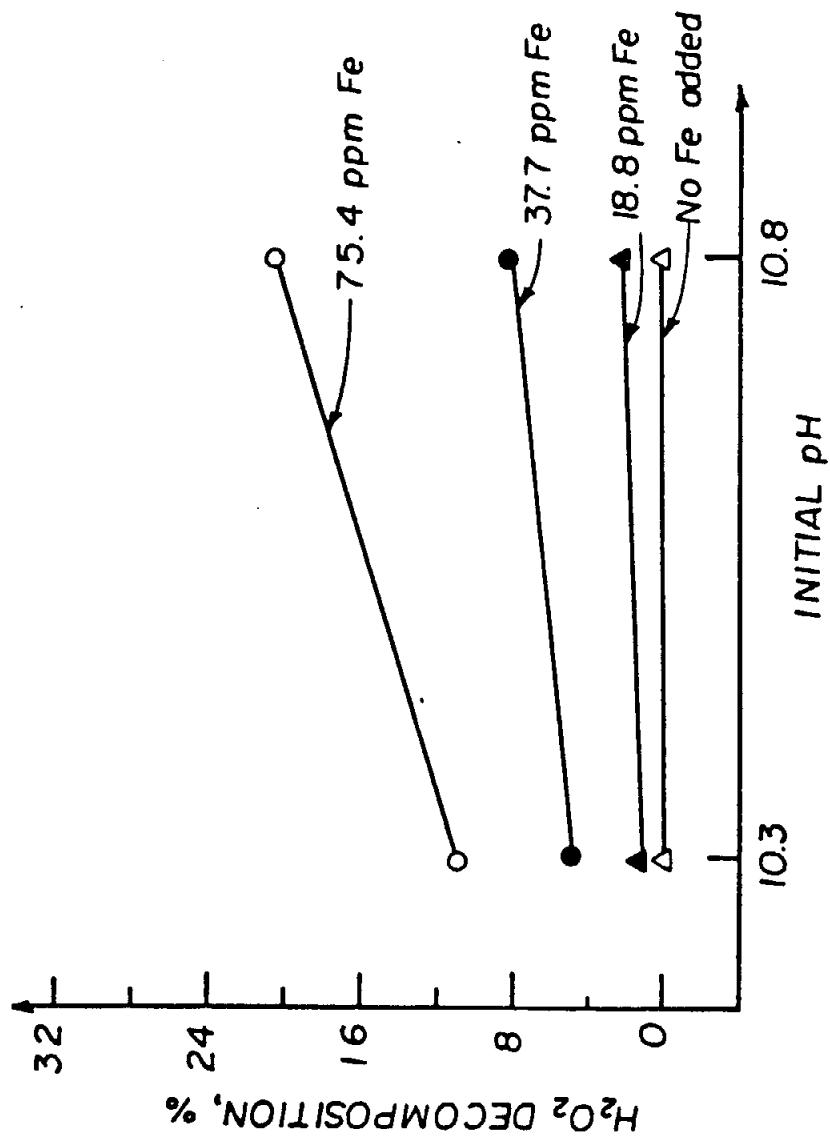


Figure C-4. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of magnesium, sodium silicate, and varying amounts of iron. ($MgSO_4 \cdot 7H_2O = 0.17$ g/L, $SiO_2 = 0.08$ M, $50^\circ C$, 120 min).

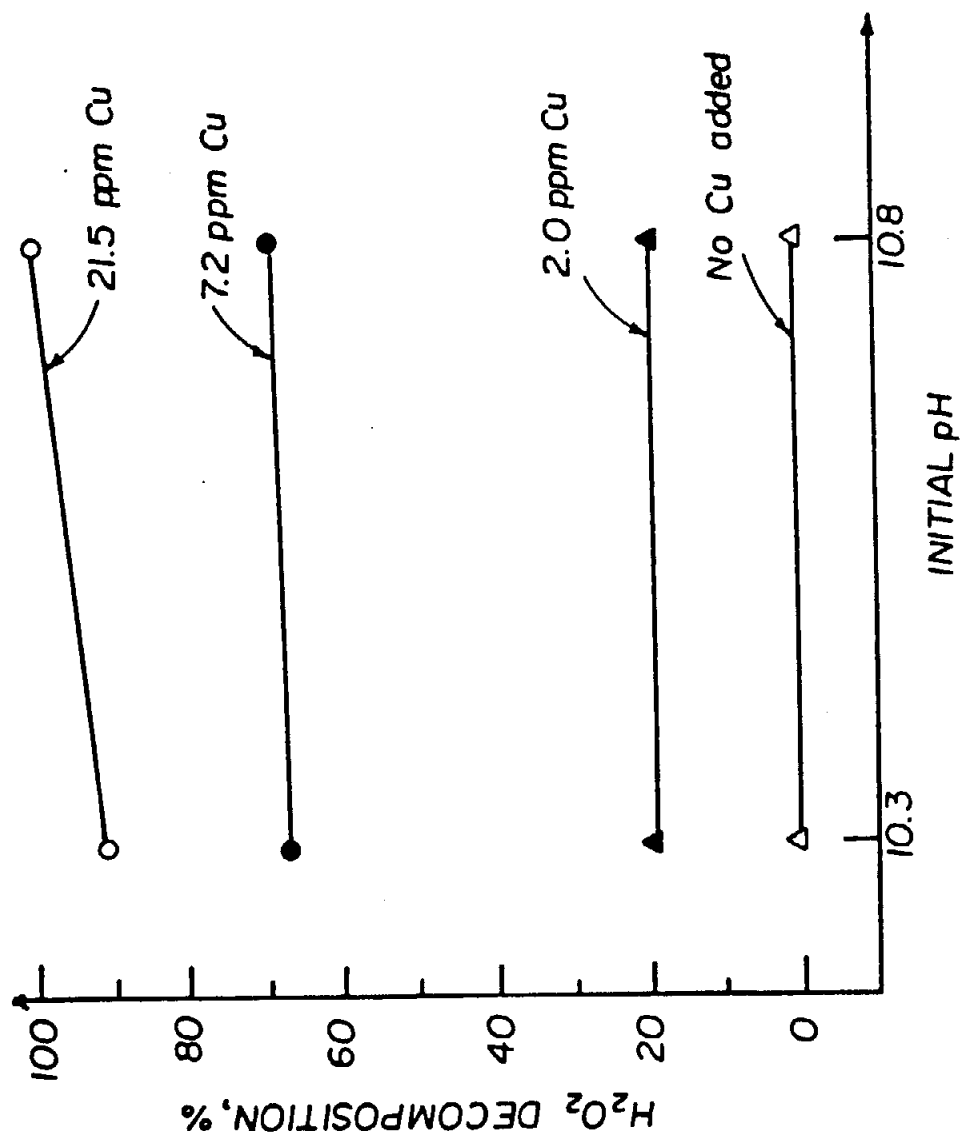


Figure C-5. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of magnesium, sodium silicate, and varying amounts of copper. ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 0.17 \text{ g/L}$, $\text{SiO}_2 = 0.08 \text{ M}$, 50°C , 120 min).

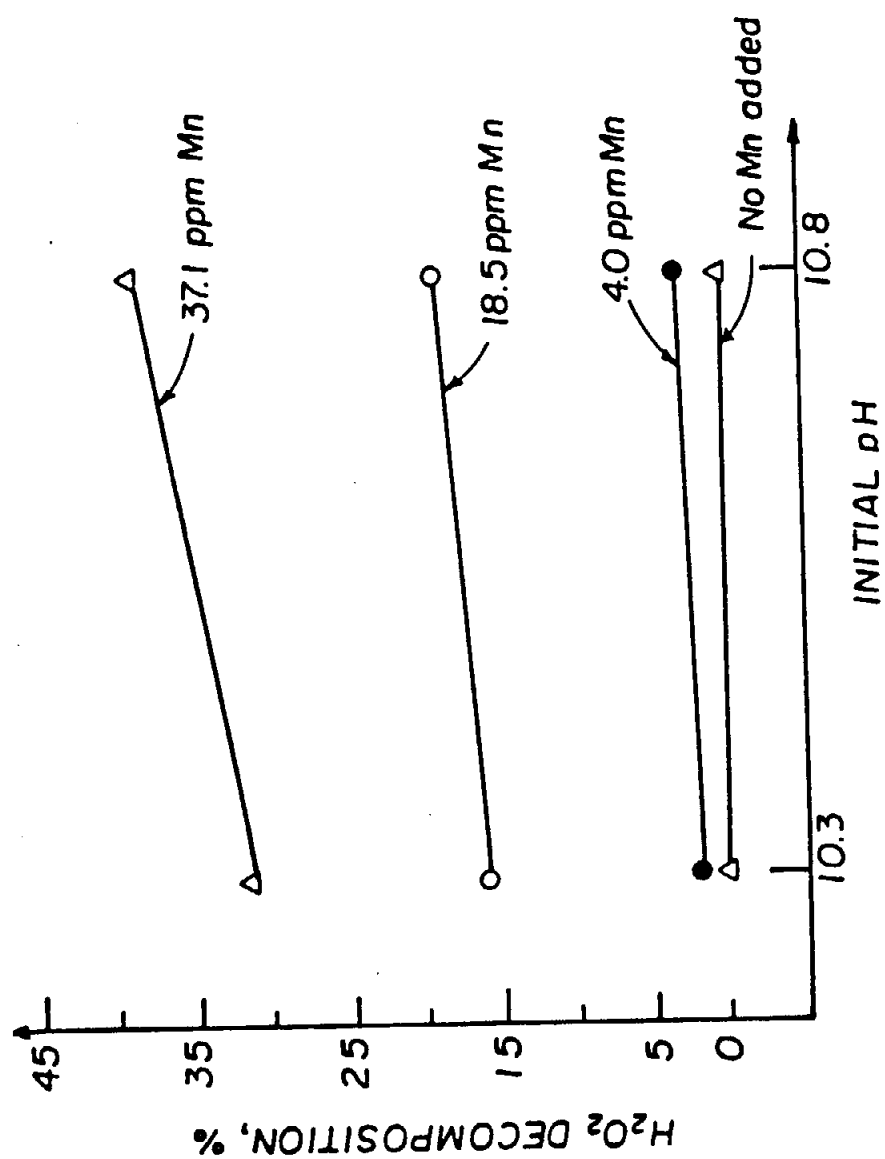


Figure C-6. Effect of pH on the decomposition of 0.098 M H_2O_2 in the presence of magnesium, sodium silicate, and varying amounts of manganese. ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 0.17 \text{ g/L}$, $\text{SiO}_2 = 0.08 \text{ M}$, 50°C , 120 min).

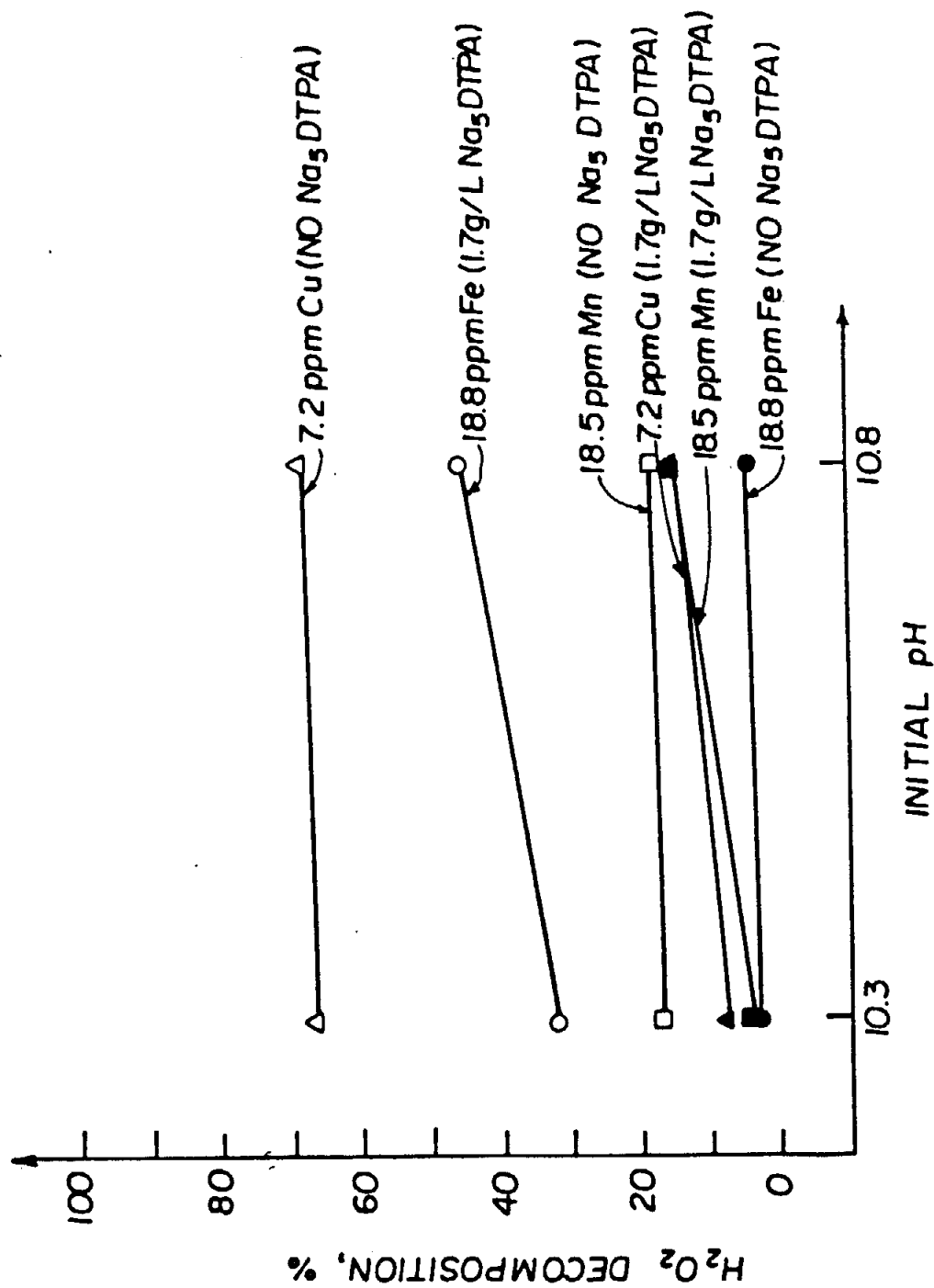


Figure C-7. Effect of pH on the decomposition of 0.098 M H_2O_2 solution stabilized with Na_5DTPA , magnesium, and sodium silicate in the presence of iron, copper, and manganese. ($MgSO_4 \cdot 7H_2O = 0.17$ g/L, $SiO_2 = 0.08$ M, $50^\circ C$, 120 min).

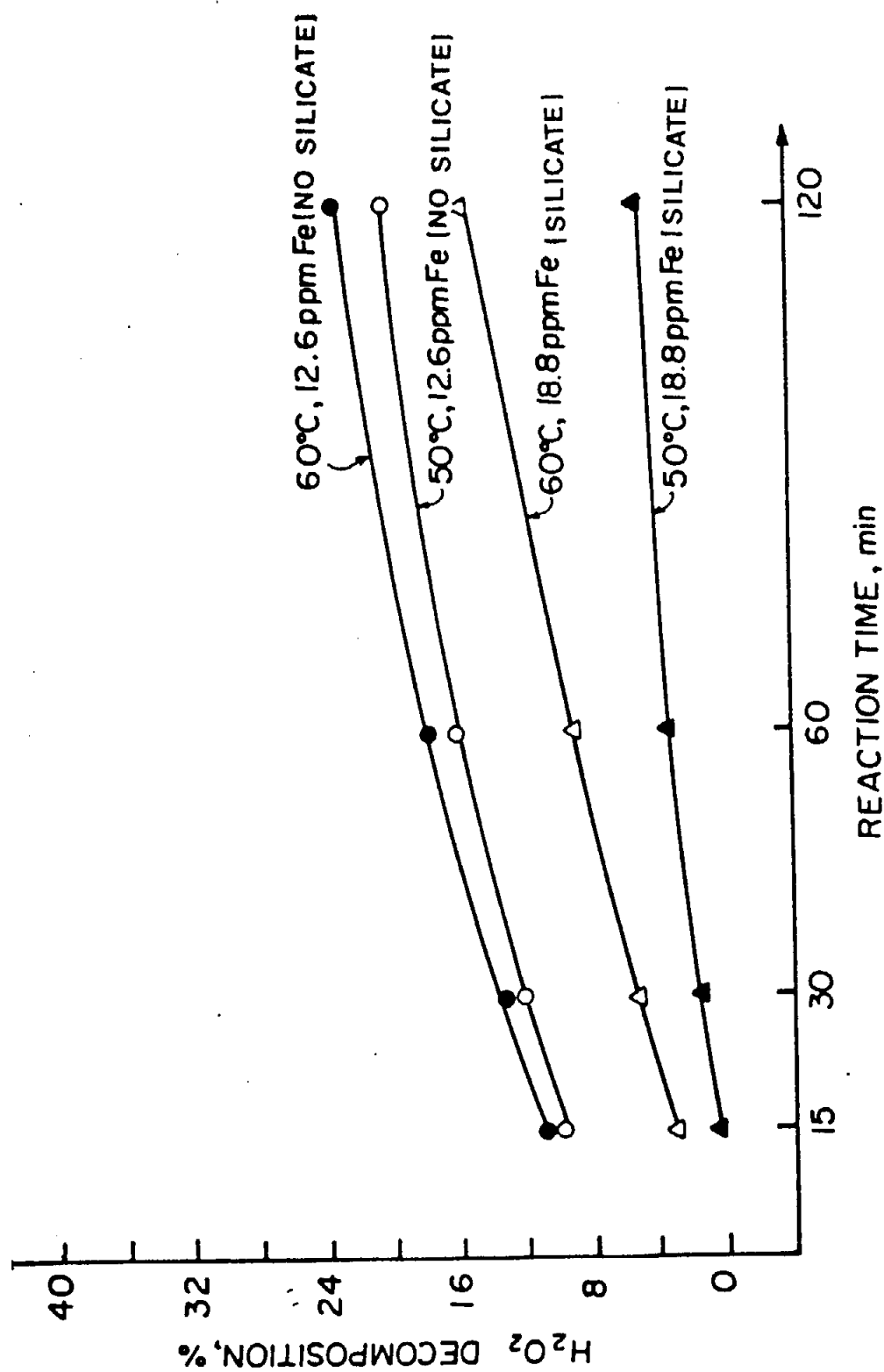


Figure C-8. Effect of temperature on the extent of decomposition of 0.098 M H₂O₂ in solutions containing magnesium and iron, in the presence and absence of sodium silicate. (SiO₂ = 0.08 M, MgSO₄·7H₂O = 0.17 g/L, initial pH 10.8).

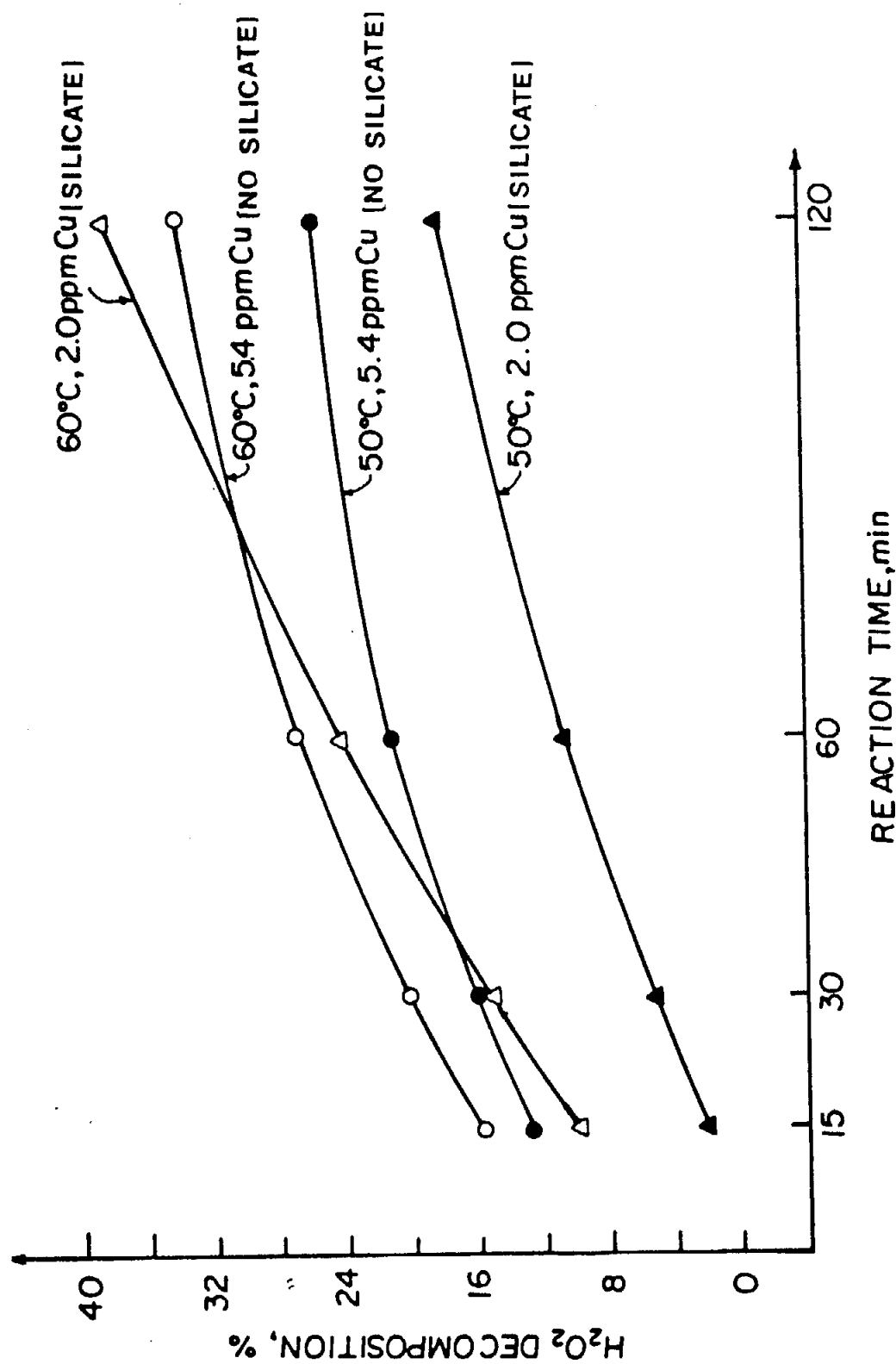


Figure C-9. Effect of temperature on the extent of decomposition of 0.098 M H₂O₂ in solutions containing magnesium and copper, in the presence and absence of sodium silicate. (SiO₂ = 0.08 M, MgSO₄·7H₂O = 0.17 g/L, initial pH 10.8).

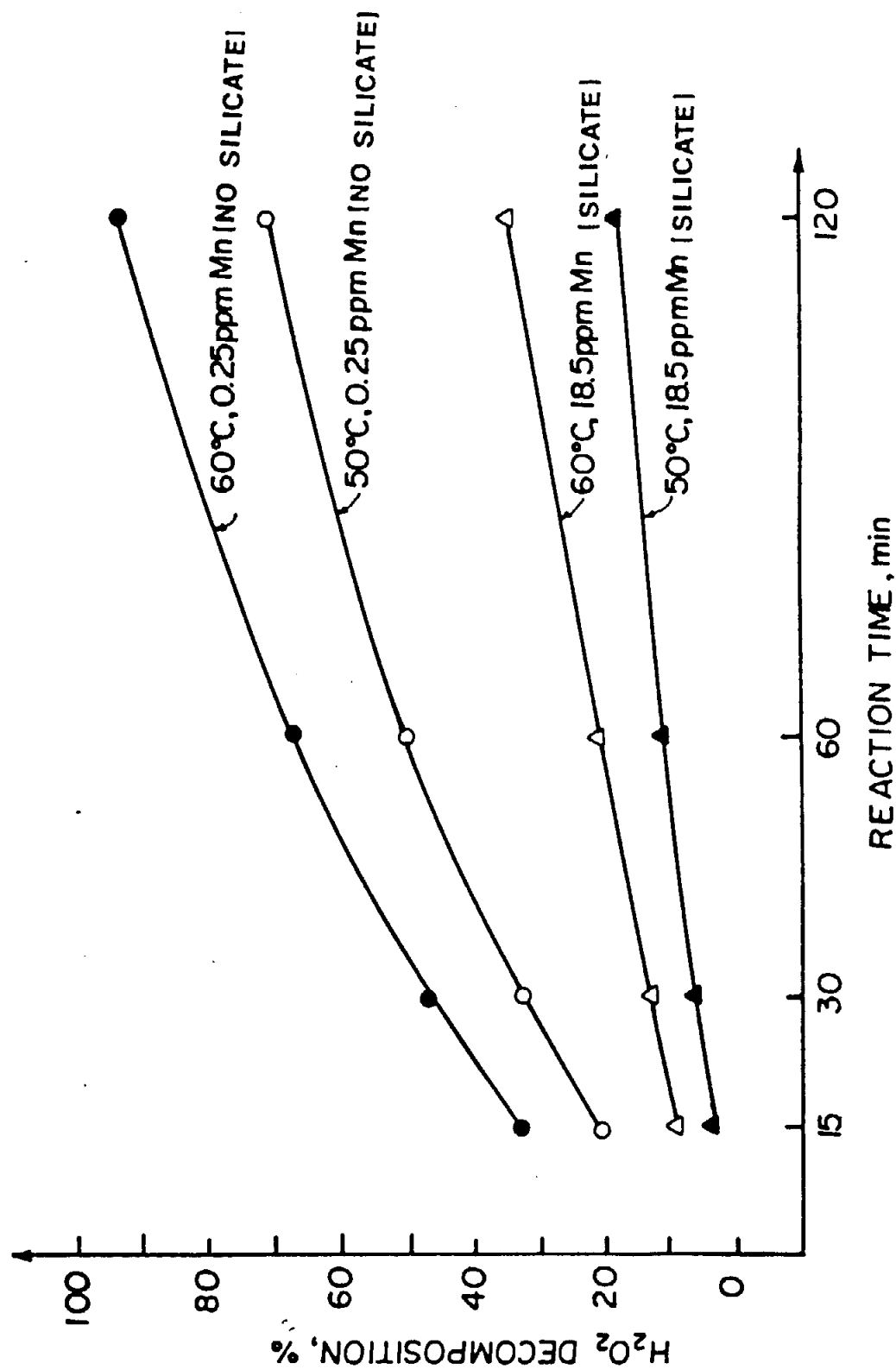


Figure C-10. Effect of temperature on the extent of decomposition of 0.098 M H_2O_2 in solutions containing magnesium and manganese, in the presence and absence of sodium silicate. ($SiO_2 = 0.08$ M, $MgSO_4 \cdot 7H_2O = 0.17$ g/L, initial pH 10.8).

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