# Peroxide bleaching using zeolites Part I: peroxide decomposition

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Addition of certain levels of zeolite and sodium citrate to hydrogen peroxide solutions containing manganese decreased the rate of peroxide decomposition. There were differences in the ability of commercially available zeolites to reduce decomposition of peroxide. Addition of small amounts of sodium citrate to a particular zeolite system improved its ability to chelate metal ions. Sodium citrate appears to act as a transfer agent, facilitating the migration of metal ions to the zeolite. However addition of excess zeolite and citrate increase manganese induced peroxide decomposition.

If the manganese-oxygen complex that decomposes peroxide under alkaline conditions was allowed to form prior to the addition of either the zeolite or citrate then the two chelating agents were unable to interact with the complex and prevent decomposition.

## Keywords

alternative chelating agents, manganese, peroxide bleaching, peroxide decomposition, sodium citrate, zeolites

IN RECENT YEARS the effects of chlorinated organics from bleach plant effluent on the environment have caused some concern. Consequently there has been great interest in adopting more environmentally friendly bleaching chemicals such as oxygen, ozone and hydrogen peroxide (1).

Hydrogen peroxide in particular has been used by manufacturers of high yield mechanical pulps as the preferred bleaching chemical. For example, Australian Newsprint Mills Ltd operate a hydrogen peroxide refiner process bleaching radiata

pine TMP at its Albury mill and peroxide tower bleaching at the Boyer mill processing eucalypt cold caustic soda pulp.

Hydrogen peroxide bleaching requires alkaline conditions to form the active bleaching species $OOH^-$. However, under these conditions hydrogen peroxide is very susceptible to transition metal ion catalysed decomposition (2,3). The metals manganese, iron and copper promote the greatest rate of peroxide decomposition (2,4,5).

Consequently, most peroxide bleaching sequences involve either a chelation stage and/or addition of stabilization chemicals to prevent or inhibit the effects of this metal catalysed decomposition. In particular, diethylenetriamine pentaacetic acid (DTPA) (chelation) and sodium silicate (stabilization) are used to limit the effects of metal induced decomposition (6). These two chemicals have their own drawbacks. Sodium silicate is known to precipitate leading to clogging of wires and felts downstream of the bleach plant. There are environmental concerns about DTPA, a known carcinogen, and handling needs to be controlled. The other concern is its ability to form strong metal complexes. The high stability constants of these complexes can be a liability in the environment, where for example, DTPA can mobilize heavy metals in silt and soil back into the food chain (7,8). Consequently, there has been some investigation into use of alternative chemicals for chelation of transition metal ions from pulp. Zeolites (9,10) are one such example.

Zeolites are aluminosilicates that have porous cage structures. They have a high internal surface area available for adsorption due to the channels and pores that uniformly penetrate the entire volume of the solid. There are many types of naturally occurring and synthetic zeolites, varying in aluminate to silicate ratio, water content, pore size and ion exchange capacity. They are used in a diverse range of applications such as molecular seives,

catalysis, and ion exchange. Zeolites are also being used as water softeners in detergents to replace phosphates which can cause eutrophication in waterways.

Investigations into the effect of addition of zeolites and citrate on peroxide decomposition, on peroxide bleached radiata pine thermomechanical pulp and on eucalypt cold soda pulp have been conducted. The results from the decomposition study are presented in this paper.

## EXPERIMENTAL

### Materials

All chemicals were analytical grade quality except for laboratory grade potassium iodide (deionized), a commercial sample of sodium diethylenetriaminepentaacetic acid ($Na_5$-DTPA) and Milli Q water.

Three sodium zeolites were obtained from various commercial suppliers: zeolite-A from Albemarle Corporation (USA), zeolite-X from PQ Zeolites (Netherlands) and zeolite-Y from Linde Division of Union Carbide (USA).

### Peroxide decomposition

Prior to any experimental work, all vessels were washed with a 10% $m/m$ sulfuric acid/Milli Q water solution, followed by two rinses with Milli Q water. The purpose of this procedure was to remove residual metal ions on the surface of experimental vessels which might induce peroxide decomposition.

### Method

In a polyethylene vessel, 475 g of Milli Q water and 45 ppm manganese as solid manganese sulfate were mixed. This mixture was placed in a water bath at either 20 or 70°C over a magnetic stirrer. The appropriate chelating agent was then added, followed by 0.01% sodium hydroxide (or 0.001% in some cases) and 25 mL of stock (30% $m/v$) hydrogen peroxide. Using the time of addition of hydrogen peroxide as time zero, 5 mL of solution were removed to determine the residual

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peroxide every five minutes for an hour. A blank with only Milli Q water and hydrogen peroxide was used to determine the residual peroxide at time zero. The pH of the solution was measured for all samples.

## Residual peroxide determination

Five mL samples were pipetted into a 250 mL conical flask containing 10 mL of 10% $m/m$ sulfuric acid, 1 drop of 10% $m/m$ ammonium molybdate and 50 mL of distilled water. Potassium iodide (2 g) was then added, swirled and titrated against standardized 0.1 M sodium thiosulfate (11). The residual peroxide was then calculated by standard methods from these reactions:

$$H_2O_2 + 2H^+ + 2I^- \leftrightarrow I_2 + 2H_2O$$

$$2S_2O_3^{2-} + I_2 \leftrightarrow S_4O_6^{2-} + 2I^-$$
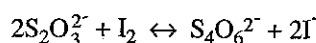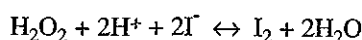
## RESULTS AND DISCUSSION

### Effect of manganese and pH

It is well known that metal ions such as Fe, Cu and Mn decompose peroxide. Figure 1 shows the effect of manganese induced decomposition at pH 11 and 4, at 70 and 20°C. The manganese concentration of the solutions was 45 mg/L. Clearly manganese is able to decompose peroxide completely at high pH, while at low pH no effect is observed. Under alkaline conditions, manganese is oxidized from $Mn^{2+}$ to various states such as $Mn^{3+}$, $Mn^{4+}$, and $Mn^{7+}$ (12,13,14). The catalytic species that decompose peroxide may be manganese dioxide ($MnO_2$) or a more complex ion with Mn-O-Mn linkages (15). Once the active decomposition species is formed, decomposition of all peroxide occurs within the five minutes at both 20 and 70°C. Because manganese

produces such rapid decomposition of peroxide under alkaline conditions, it is an ideal system to investigate the effect of additives in preventing decomposition of peroxide.

### Effect of zeolite

Figures 2 and 3 show the effect of three different commercially available zeolites (Z-A, Z-Y, Z-X) on peroxide decomposition at 20 and 70°C. The zeolites were added prior to the addition of alkali and peroxide to a solution of 45 mg/L of manganese.

At 20° C, experiments were performed at two levels of alkali addition, 0.01% and 0.001% (Fig. 2). At 0.001% alkali, all three zeolite types reduce peroxide decomposition. At the higher alkali charge, performance of the three commercial zeolites differed greatly; zeolite-A inhibiting decomposition, zeolite-X reducing the decomposition rate and zeolite-Y having very little effect on decomposition.

Results at the lower alkali charge are close to the pH at which oxidation of manganese occurs. Addition of zeolite may buffer the solution and so prevent the manganese decomposition species from forming. At the higher alkali charge, there is sufficient alkali to oxidize the manganese and so induce decomposition. These results suggest that zeolite-A and zeolite-X to a lesser extent are able to interact with manganese prior to its oxidation and to inhibit peroxide decomposition. Lack of inhibition by zeolite-Y tends to indicate that it does not interact as readily with manganese prior to its oxidation.

The difference in performance of the three zeolites appears to correlate to the Si:Al ratios of the three zeolites (Table 1).

It is believed that the lower Si:Al allows for more rapid and complete ion exchange (16). The lower Si:Al ratio for zeolite-A allows more manganese to be trapped inside the pore structure than the other two zeolites even though the pore size is smaller.

## Table 1: Properties of commercially available zeolites

|  | Si:Al ratio | Pore size (nm) |
|---|---|---|
| Zeolite-A | 1.0 | 0.4 |
| Zeolite-X | 1.25 | 0.8 |
| Zeolite-Y | 2.5 | 0.8 |

At 70°C, zeolite-A still inhibited decomposition more than the other zeolite types. Its ability to prevent the decomposition is reduced at 70°C when compared to the results at 20°C (Fig. 2). Performance of zeolite-X is also somewhat reduced at 70°C when compared to the results at 20°C, while zeolite-Y slowed down the decomposition rate better at 70°C than at 20°C. The improved cation exchange for zeolite-Y may be due to the increased temperature and energy allowing the manganese ion to overcome some of the structural energy barriers in zeolite-Y (16).

Generally it has been found that zeolites such as zeolite-A increase their binding capacity with increase in temperature (17). The decrease observed in Figure 3 for zeolite-A and zeolite-X may be a result of an increase in the rate of formation of the active manganese decomposition species with temperature. At the higher temperature, manganese may be oxidized at a faster rate than $Mn^{2+}$ binds to the zeolite.
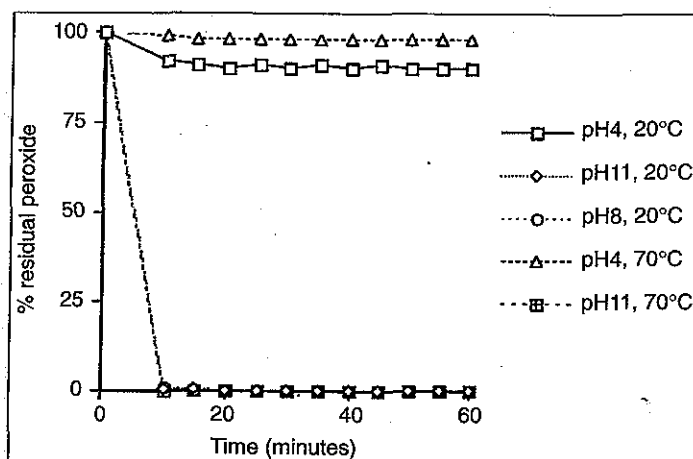


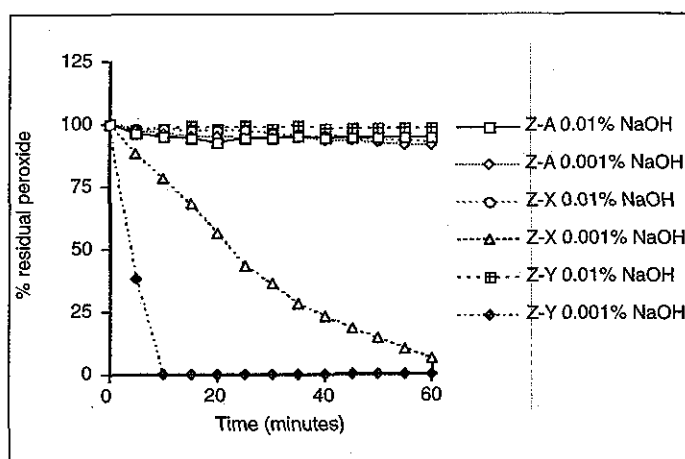Fig. 1    Peroxide decomposition with manganese at various pHs and at 20 and 70°C.



Fig. 2    Peroxide decomposition with 1% zeolite at 20°C and two alkali levels.

## Effect of order of alkali addition

The ability of zeolite to prevent decomposition when alkali is already present is shown in Figure 4, where a comparison is made in manganese solutions between zeolite addition prior to the alkali and peroxide and zeolite addition after the alkali. These results show that zeolite is unable to prevent peroxide decomposition if the solutions are alkaline prior to zeolite addition. This suggests that zeolite is unable to deactivate the active manganese decomposition species once it is formed and is only able to prevent the decomposition if manganese is in its $Mn^{2+}$ state. It is possible that the zeolite does not interact as effectively with the larger uncharged manganese dioxide or manganese-oxygen species as with the manganese cation.

## Effect of zeolite-A addition

For manganese induced decomposition, the effect of varying the amount of zeolite-A added is shown in Figure 5, where at 20 and 70°C the residual peroxide in solution after 30 minutes is plotted as a function of the amount of zeolite-A added at 0.01% NaOH.

The highest residual peroxide was obtained with 1% addition of zeolite-A. Higher additions resulted in the residual peroxide decreasing. At higher temperatures, the effect is more pronounced due to the increased rate of peroxide decomposition.

Two possible explanations for the increase in peroxide decomposition with addition of zeolite are:
- Increasing the amount of zeolite produces more surface sites for the manganese to exchange on. As these surface sites are more readily available than the internal pores, manganese on surface sites may be oxidized when alkali is added and so induce peroxide decomposition, while manganese trapped in the pores is not oxidized.
- Zeolite may cause decomposition of the peroxide.

A series of experiments were conducted to see if zeolite decomposes the peroxide in the absence of manganese. At 20°C, no effect was observed, while at

70°C, increasing the amount of zeolite-A decomposed the peroxide (Fig. 6). At the higher temperature, the kinetics for the decomposition reaction between zeolite-A and the peroxide appears to be much faster than at the lower temperature. Some authors note that the performance of laundry detergents using inorganic/organic peroxides has been reduced when triphosphate chelating agents were replaced with zeolites (18). Schepers and Verburg (19) observed gas release which they concluded was oxygen, one of the primary peroxide decomposition products.

The decomposition observed in Figure 6 at 20°C is likely to be due to the increased availability of surface sites and oxidation of the manganese located at these sites. The decomposition with increasing zeolite-A addition observed at 70°C is more likely to be due to a combined effect of zeolite decomposing the peroxide and increased surface sites.

## Effect of sodium citrate

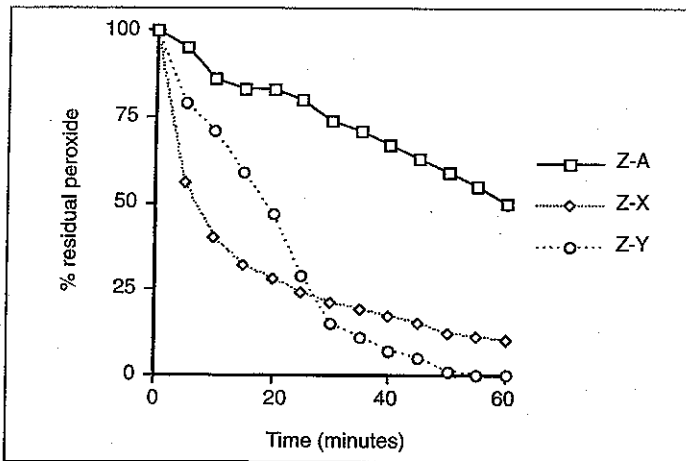The effect of sodium citrate addition on manganese induced peroxide



**Fig. 3    Peroxide decomposition with 1% zeolite using three different zeolites, at 70°C and 0.01% NaOH.**
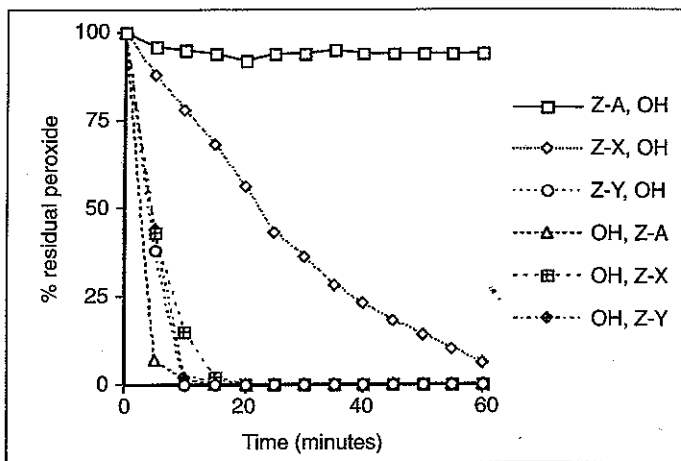


**Fig. 4    Effect of order of addition of zeolite and alkali.**
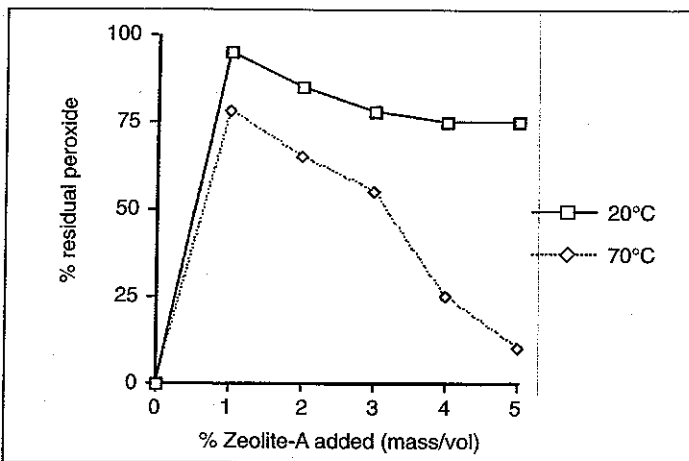


**Fig. 5    Effect of zeolite-A addition on manganese induced peroxide decomposition at 20°C and 70°C.**
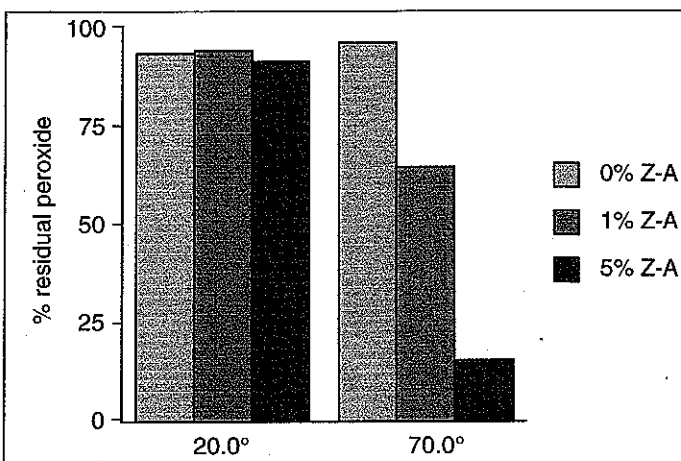


**Fig. 6    Effect of zeolite-A addition on peroxide decomposition in the absence of manganese.**

decomposition at 20 and 70°C is shown in Figure 7, where the residual peroxide measurements are plotted after 30 minutes. At 20°C, addition of 0.5% sodium citrate greatly reduced peroxide decomposition. There were no further gains in reducing decomposition by additional citrate up to 3% citrate. At 70°C, a reduction in peroxide decomposition occurred with addition of 0.5% citrate. However when 1% citrate was added the residual peroxide decreased. Further additions of citrate increased the residual peroxide concentration indicating reduced peroxide decomposition. The local minimum in Figure 7 at 1% citrate coincided with the formation of a hard to remove black film. This film is likely to be a surface active manganese decomposition species possibly formed by an interaction with the citrate and then oxidizing after the addition of the alkali. Higher additions of citrate above 1% may bypass the formation of this species.

As with zeolite, it appears that sodium citrate does not prevent manganese induced peroxide decomposition if the alkali is added prior to the citrate (Fig. 8). This indicates that sodium citrate is also unable to interact with the manganese decomposition species once it is formed or, if it does, it does not prevent it from decomposing the peroxide. Sodium DTPA, on the other hand, reduces decomposition even when the alkaline manganese species is formed, (Fig. 8). This may be due to the stronger complexing action of DTPA (20).

## Effect of zeolite and citrate
The combined effect of zeolite-A and sodium citrate on peroxide decomposition is illustrated in Figure 9. Residual peroxide concentrations after 30 minutes are plotted for solutions containing 45 mg/L of manganese and 5% zeolite-A as a function of percent sodium citrate added. These results show that increasing

the sodium citrate concentration has very little effect at 20°C but is detrimental to peroxide stability at 70°C. A small amount of citrate (0.2%) will dramatically improve the effect of 5% zeolite. Higher additions of citrate to 5% zeolite-A, in fact, increase the decomposition of peroxide. A possible explanation of this phenomenon could be that the citrate acts as a charge transfer agent helping to move the manganese cation into the zeolite structure. As the citrate charge is increased, more manganese-citrate complex is bonded to the surface of the zeolite forming a catalytic species rather than allowing the metal ions to migrate into the porous zeolite structure. At the low citrate charge, the manganese-citrate species formed may be small enough to migrate into the pores of the zeolite cage.

## CONCLUSIONS
The chelating agents, zeolite and sodium citrate, reduce manganese induced decomposition of peroxide solutions under alkaline conditions at certain addition levels. Of the three commercially available zeolites tested, zeolite-A with its lower Si:Al ratio and hence greater cation exchange capacity prevented decomposition of peroxide, provided the active manganese decomposition species had not formed prior to the addition of the zeolite. Increasing the amount of zeolite added increased the rate of peroxide decomposition in solution due to more surface active sites on the zeolite at which the manganese cation might exchange. At higher temperatures, the decomposition rate was further increased by the action of zeolite itself decomposing the peroxide.
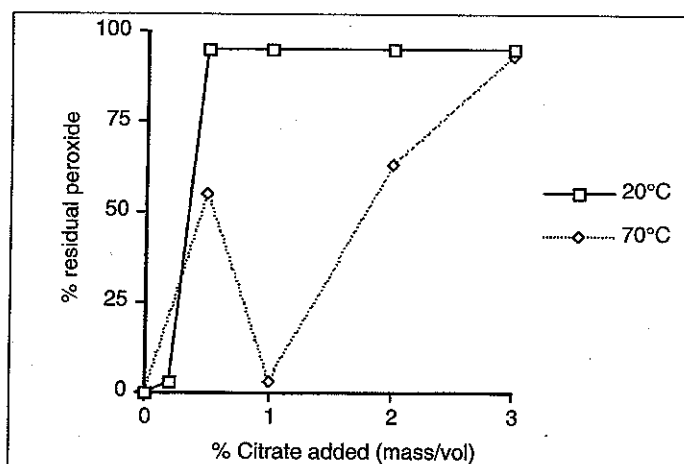


Fig. 7    Effect of sodium citrate on manganese included peroxide decomposition at 20 and 70°C and 0.01% NaOH.
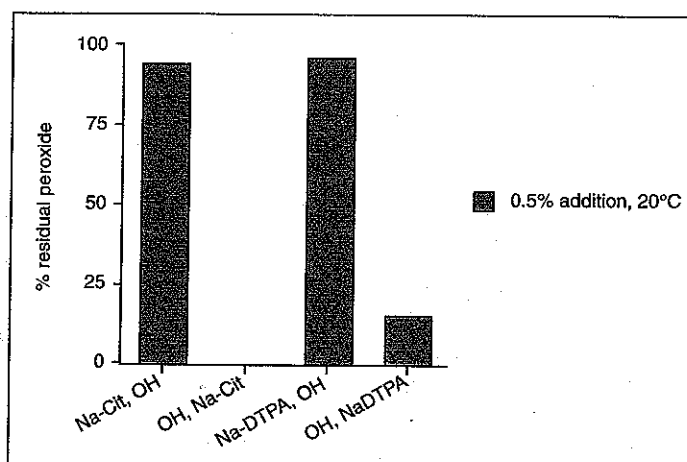


Fig. 8    Effect of order of alkali addition on manganese induced peroxide decomposition using sodium citrate and sodium DTPA at 20°C.
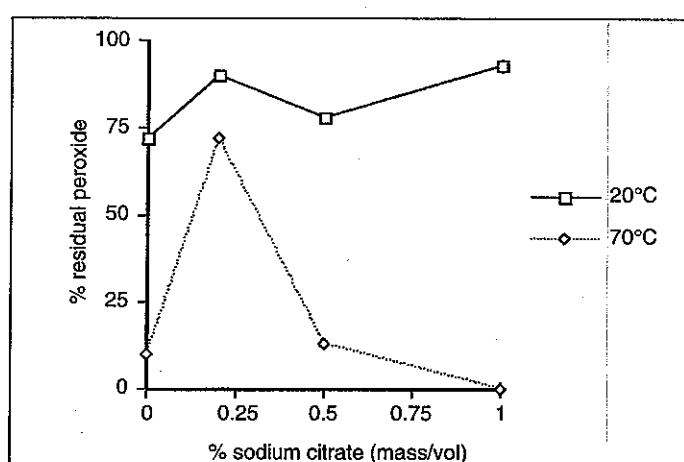


Fig. 9    Effect of manganese induced peroxide decomposition of sodium citrate addition to 5% zeolite-A at 20 and 70°C (0.01% NaOH).

Small amounts of sodium citrate alone and also with 5% zeolite-A decreased manganese induced peroxide decomposition but only if the active manganese decomposition species had not formed.

Sodium citrate is believed to act as a charge transfer agent to improve the ability of zeolite to complex manganese cations and to prevent them from forming an oxidized manganese complex that decomposes peroxide.

The complexing ability of sodium citrate and the zeolites evaluated is lower than that of DTPA. DTPA prevents decomposition regardless of the manganese species present. If zeolites and sodium citrate are to be used in industrial applications then they will need to be added prior to the addition of alkali and peroxide to chelate the metal ions, particularly manganese.

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