Silicate-Free Peroxide Bleaching of Mechanical Pulps: Efficiency of Polymeric Stabilizers

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ABSTRACT

Sodium silicate (waterglass) is commonly used to stabilize hydrogen peroxide in bleaching mechanical pulps to high brightness. Though efficient stabilizer, silicate causes problems in papermaking by contributing to silicate deposit formation, decreased retention and sheet strength and as well as increased anionicity leading to higher consumption of wet-end chemicals. In this study the efficiency of peroxide stabilizers consisting of various polymeric compounds with different molecular weights were compared to conventional silicate. Unbleached mechanical pulp samples were taken from pulp mills and used in laboratory bleaching experiments. In addition, different complexing and stabilizing agents were screened in an alkaline peroxide solution (without pulp) containing transition metals. Several polymeric compositions were found to match the efficiency of waterglass. It was found that results obtained in the alkaline peroxide solution test did not always reflect what is observed in real pulp bleaching environment, indicating that the behaviour of transition metals in free solution is somewhat different to a pulp suspension where the activity of metals depends on location, activity state, counter ions etc. The results of our project and the chemistry of different polymeric stabilizers are discussed in this paper.

INTRODUCTION

High brightness mechanical pulps are today bleached with hydrogen peroxide. The main reactive compound is hydroperoxide anion, a strong nucleophile formed when alkali is added into the bleaching process. There are numerous other peroxy species formed in situ in the process during the course of transition metal induced radical decomposition of peroxide. Since most of the peroxide is consumed in transition metal induced decomposition [1], the control of radical decomposition of peroxide is of crucial importance due to the fact that manganese, iron and copper always come in to the process with the wood raw material, with the process waters or as impurities with bleaching chemicals [2]. The control of radical decomposition is complex and not solely dependent on the concentration of metals. Also the type of metals and their complexes formed, their activity state, interactions and the local environment (wood type, process temperature and set-up, water loops, stabilizers etc.) will affect the chemistry involved in peroxide decomposition. Hence, the lowest possible metal concentration does not necessarily result in the best bleaching result. For example, in chemical pulping some peroxide degradation is proposed to actually promote delignification [3]. The optimal behaviour of a stabilizer in bleaching is a combination of complexing and deactivating detrimental metal ions, deactivating catalytically active surfaces i.e. metal hydroxides, allowing radical reactions to occur in a controlled manner etc.

Sodium silicate as stabilizer

Sodium silicate (waterglass) is a commodity product used to enhance peroxide bleaching of mechanical pulps, since it is relatively cost-effective, rather easy to apply and universally available. Several theories on the role of silicate in peroxide bleaching have been suggested [2,4,5]. However, the exact stabilization mechanisms are still partially unknown. Silicate can act as peroxide stabilizer, a metal ion sequestrant, a buffering agent and as a metal surface passivator. With regard to peroxide stabilization, surface passivation and metal ion sequestration are the most important functions. Experiences show, that even when bleaching pulp in the absence of soluble transition metals, the use of silicate gives higher brightness and residual peroxide. Although silicate is beneficial in peroxide bleaching, it may generate serious detrimental effects in the pulp and paper making processes. As papermaking operations more frequently take place in closed-loops and with as low water usage as possible, silicate builds up in the process. Silicate may cause deposits on the paper machine [6] and it also introduces anionicity into paper making system, leading to higher wet-end chemicals consumption. Typically,

bleaching plant may not have any problems with silicate as far as the operating pH is alkaline, but paper machines operating at lower pH will encounter problems related to silicate chemistry. The solubility of silica has its minimum at pH around 7-8 with concentration around 100-150 ppm at pH below 8. Solubility increases with alkalinity as well as higher temperature [7]. Paper machines running at neutral or acidic pH thus operate at unstable process conditions regarding silicate scaling. The solubility is also strongly affected by salt concentration and amount of dissolved organic compounds. Cationic polymers or aluminium salts can remove colloidal silica, but have no effect on dissolved silica [8]. Typical SiO_2 content in white water is around 200 ppm of which 50 ppm is soluble and the rest is colloidal. There is also interaction between polymeric SiO_2 and wood extractives - colloidal silica seems to be agglomerated with pitch particles [8]. Other negative effects of silica found in the literature are for example: lower performance of retention aids, lower drainage and impaired sizing,. Hence, there is a strong demand for silicate-free peroxide stabilizers in order to get rid of the aforementioned problems. On the other hand, it is also possible to modify silicates so that less scaling and higher brighness is obtained by altering the molar distribution of silica species [9].

Silicate replacement

Conventional aminocarboxylates such as DTPA or EDTA are sometimes referred to as stabilizers, due to their ability to complex transition metals. However, their contribution to improve bleaching is usually limited when going to high brightness applications because their complexing power is suppressed at high pH of alkaline peroxide bleaching. In fact, it was recently reported that DTPA-Mn complex is actually prone to decompose peroxide at alkaline conditions [10]. Instead, complexing agents are preferably used in a pre-treatment (at their optimal complexing pH) to complex as much of the metals and wash them out prior to peroxide bleaching, whereas silicate is normally used to stabilize alkaline peroxide environment.

Magnesium sulphate ($MgSO_4$, or Epsom salt) is likewise referred to as a stabilizer. It is given that magnesium salts generally have a positive effect on peroxide bleaching, but their effect is also limited to function as a "support chemical". The stabilization mechanisms of magnesium salts are as much under debate as the mechanisms of silicate. More detailed discussion on the effect of magnesium on stabilization of peroxide bleaching is given in a recent review by Wuorimaa et al. [11].

Zeolites (crystalline aluminosilicates) with ion exchange capacity towards transition metals, have been reported as stabilizers [12,13], but their effect is usually comparable to that of aminocarboxylates.

The use of organic polymers as stabilizers in peroxide bleaching have been studied since 1950's. Polyvinylpyrrolidone [14], maleic acid-styrene or propene [15], copolymers of butadiene-maleic acid [16], and grafted polymers [17] are examples of reported polymeric stabilizers in the literature. Sodium poly-α-hydroxyacrylate (PHAS, figure 1) in peroxide bleaching has been reported to be an effective stabilizer in peroxide bleaching [15,18,19]. Biodegradable, PHAS is also environmentally benign, as the polymer is extensively degraded by a co-metabolism type of mechanism [20]. The stabilizing effect of PHAS may be partly due to the ability of the α-hydroxyl groups to form metal complexes with transition metals. The α-hydroxyl structure is capable of forming energetically favoured five members ring structures with transition metals and thus efficiently complexing them. On the contrary, β-hydroxy acrylate, which is capable of forming six members ring structures, does not have stabilizing ability. In addition, the α-hydroxyl groups are capable of forming stable radicals and therefore PHAS may be able to act as a radical scavenger [11]. It is difficult though to estimate stabilizing ability of polymers, since the process environment is complex. The ability of polymers to bind metal ions is not a well known area. Molecular modelling has been utilized by Pesonen et al. [21] in order to predict the complexing ability and the coordination of polymers with metal ions, which can help in developing suitable polymeric and monomeric structures of the stabilizers and reduce laboratory routines.

Monomeric chelating agents and aminophosphonic acids are frequently suggested in literature to have synergy with polymers. The use of phosphonates as stabilizers are widely reported in the literature, but their efficiency is usually lower than that of silicate. Furthermore, some legislations have banned their use for environmental reasons (phosphorous content).
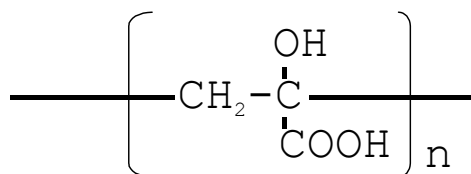

Figure 1. PHAS : poly-α−hydroxy acrylic acid

METHODS AND MATERIALS

Unbleached mechanical pulp samples taken from pulp mills were used as raw material in laboratory scale bleaching experiments. Laboratory-scale bleaching trials at medium consistency (10%) were conducted in plastic bags and in the case of high consistency trials (30%), a Mark Quantum mixer was used as chemical mixer. The properties of the pulps were determined according to SCAN standards. In addition, different complexing and stabilizing agents were screened in an alkaline peroxide solution (ion exchanged water without fibers) in the presence of transition metals (Fe and Mn as sulphates). Stabilization ability was determined by measuring residual peroxide concentration (iodometric titration) left in the solution after certain reaction time in a certain pH, temperature and time. The polymers used in the study were of commercial grades. The average molecular weight of PHAS was approx. 30 000, polyacrylic acid with approx. 10 000 and maleate/acrylate copolymer approx. 50 000 if not otherwise stated. The silicate used had 30,8% SiO_2 content with 2,5:1 ratio of SiO_2:Na_2O.

RESULTS

Stabilization experiments of hydrogen peroxide solutions

In order to easily assess the efficiency of various chemicals on stability of peroxide, a simple experimental system was set up comprising a peroxide solution in ion exchanged water having 2 ppm iron and 2 ppm manganese ions and stabilizators present. The effect of pH and stabilizers on the peroxide stability was then evaluated by measuring residual peroxide left after certain time (figure 2).
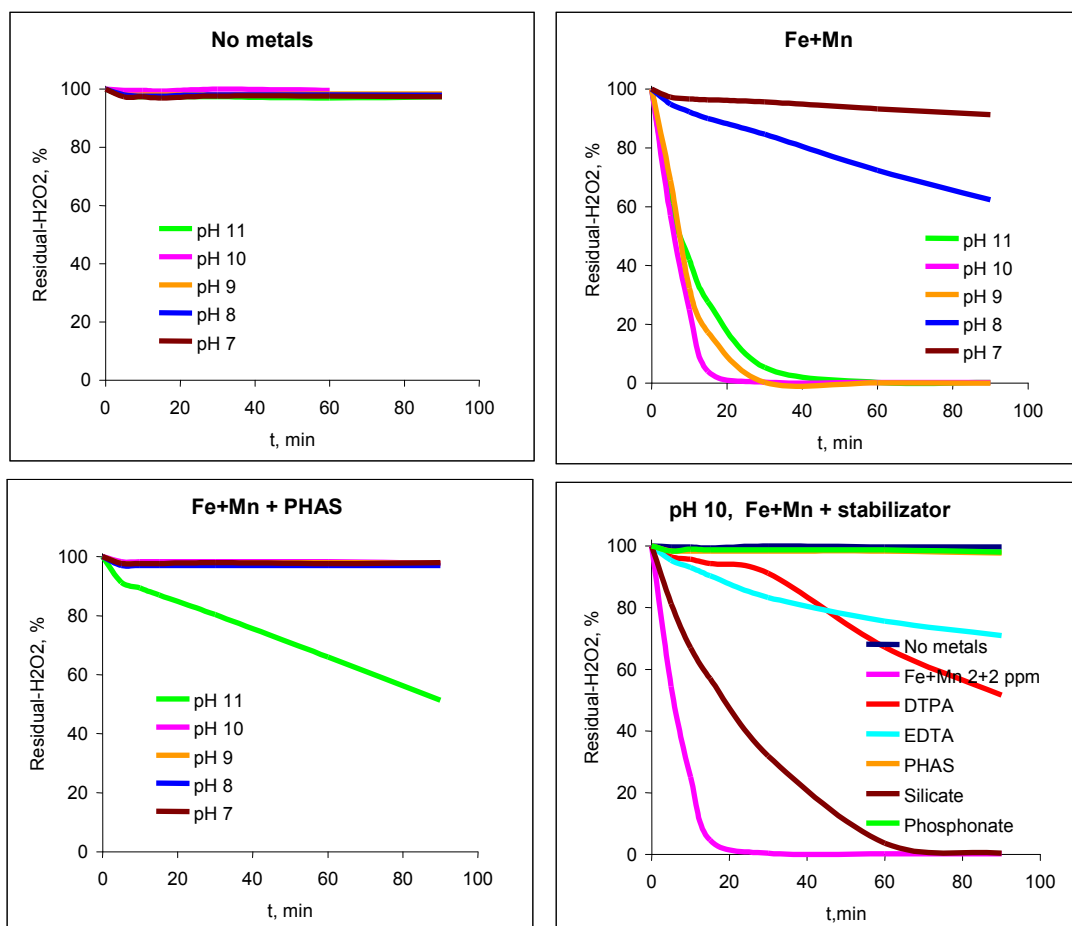

Figure 2. Peroxide stabilization tests. Conditions: $50^{\circ}C$, H_2O_2 3g/l.

In water solution, peroxide is fairly stable even at fairly high pH in the absence of metals, but degraded in alkaline conditions when metals are present (fig. 2). PHAS stabilizes peroxide up to pH around 11. We can also see that in pH 10, stabilization efficiency of conventional aminocarboxylates (DTPA and EDTA) is poor, whereas phosphonate (DTPMPA) shows high stabilization efficiency. On the other hand, the efficiency in this test with silicate was surprisingly low. Nevertheless, one has to keep in mind that in this test there was no fiber present - the stabilization mechanisms are different in pure water solutions compared to pulp suspension. The stabilizing effect of silicate in fiber suspensions is most probably connected with interactions with fibers and colloidal particles. Fibers and lignin may also play a significant role in the coordinating of metal ions. Thus, even though the experimental setup shown here is simple and serves its purpose, proper care must be taken when drawing conclusions based on the results.

Metal management: synergistic effect of iron and manganese on decomposition of peroxide

It is known that with regard to peroxide bleaching efficiency the two most detrimental transition metals are iron and manganese. Therefore it is vital to control these elements since they always come in with wood to the process,. Together Fe and Mn can be more active in decomposing peroxide than either of them alone, which makes the control more difficult. We tried to elucidate this by varying iron:manganese ratio (figure 3), and then by assessing how different complexing agents or stabilizers work in these varying conditions.
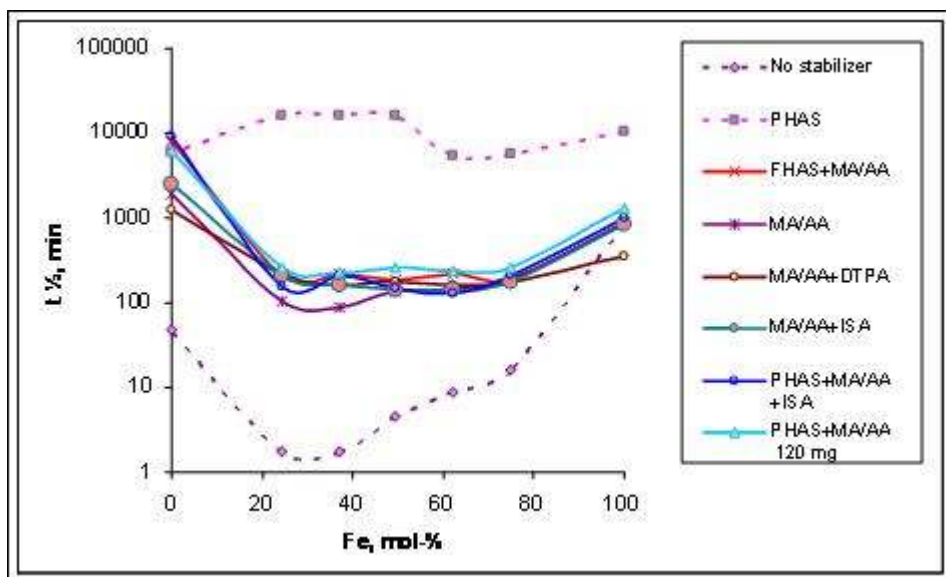

Figure 3: Effect of Mn:Fe molar ratio and PHAS, maleate-acrylate co-polymer (MA/AA) and combinations with chelating agents on peroxide stability. $[Fe^{2+}]+[Mn^{2+}] = 72,2$ μmol/l, T = 50°C, pH 10, H_2O_2 3 g/l. Half-life time is calculated according to 1st order reaction rate. Applied amount of polymer was 80ppm, but in conjunction with monomeric complexing agents, the stabilizer dose was 60 ppm polymer + 20 ppm DTPA or ISA.

The combination of iron and manganese decomposes peroxide faster than either of them alone. The decomposition is fastest when molar ratio Mn:Fe is 2:1 (33,3 mol-% Fe). Usually the amounts of Mn and Fe vary from process to process and we have used 50/50% ratio as a compromise throughout the study. Also the effect of different chelating agents on decomposition of H_2O_2 is shown in figure 3. Iminodisuccinic acid (ISA), a biodegradable chelating agent [22], or DTPA failed to stabilize peroxide alone (as described in figure 2), but when applied together with maleate/acrylate polymer some stabilization effect was obtained. However, the effect was remarkably lower than for pure poly-α-hydroxyacrylate (PHAS).

Magnesium or calcium ions are also known to affect stabilization efficiency. $MgSO_4$ is universally applied as a supplement to improve stabilization of peroxide bleaching. Different dosage levels of $MgSO_4$ and PHAS is illustrated in figure 4. Calcium has been reported to be inert in bleaching as such, but it can affect the system by binding with complexing agents and the same effect is assumed for magnesium. Thus it is of interest to study

the interaction between MgSO$_4$ and PHAS as peroxide stabilizers. It can be seen (figure 4) that the addition of Mg^{2+} decreases the stabilization efficiency. For a small Mg^{2+} dosage (2-5 mg/l) there is a minuscule increment in residual peroxide, but higher dosages impair stabilization effect. This is simply due to formation of Mg-PHAS or Ca-PHAS complexes. In fact, our trials to mix MgSO$_4$ together with PHAS as a premixed liquor resulted in precipitation of the chemicals in the liquor. The natural content of Mg^{2+} in pulp suspension originating from wood may thus be optimal and additional magnesium may instead deactivate organic stabilizers.
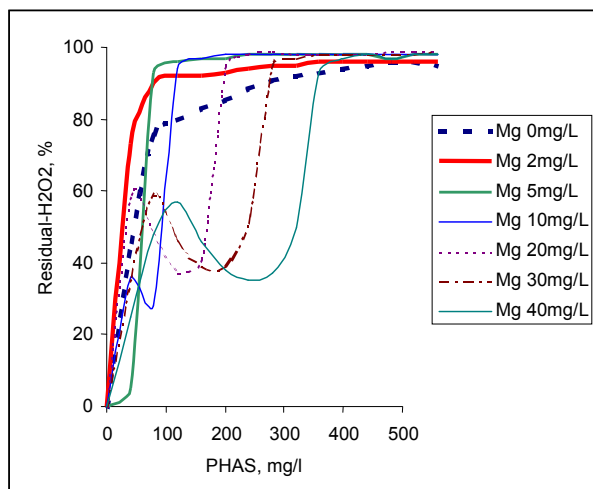
Figure 4. The synergistic effect of Mg^{2+} and PHAS addition on stability of peroxide. Conditions: pH 11, T = 60°C, t = 180 min, Mn 2 mg/l, H$_2$O$_2$ 1 g/l. PHAS calculated as 100% Na-salt.

The effect of polymeric composition

It was found that the effect of magnesium impacts stabilization system (fig. 4). Calcium would be even more relevant as it is abundant in the pulping process and is thus able to consume at least part of the polymers. It would be beneficial to bind calcium with less expensive polymers in order to save the most efficient PHAS polymer for stabilizing Fe and Mn. Thus we applied different formulations of PHAS together with other polymers that have high affinity towards calcium, such as maleate-acrylate copolymers and polyacrylates. Figure 5 illustrates tests, where 2 ppm Fe^{2+}, 2 ppm Mn^{2+} and 10 ppm Ca^{2+} ions were added in solution at pH 10 at 50°C and the residual peroxide left in the liquor was measured with time. The concentration of PHAS in these trials was 40 ppm and the amount of accompanying polymer, PAA (polyacrylate) or MA/AA (maleate-acrylate co-polymer) was 100 ppm. The results show that the higher the molecular weight of the polymers, the better is the stabilization efficiency. This is probably due to passivation of colloidal metal oxides by polymers. It is also evident that the presence of high calcium concentration calls for supporting polymers to complex calcium, since PHAS alone did not give encouraging results. In the absence of calcium though, PHAS did stabilize peroxide. Another study on polyacrylate's complexing ability stated that an increase in MW increases total polyelectrolytic charge and therefore interaction with Ca^{2+}, but at high MW the complex stability becomes less effective due to the high level of dispersion producing more linear polymer shape [23]. The same effect is seen with high ionic strength, which implies why polyacrylates lose efficiency in high pH applications. The use of solely polyacrylic acid or maleate-acrylate does not stabilize peroxide, which is seen in figure 6.
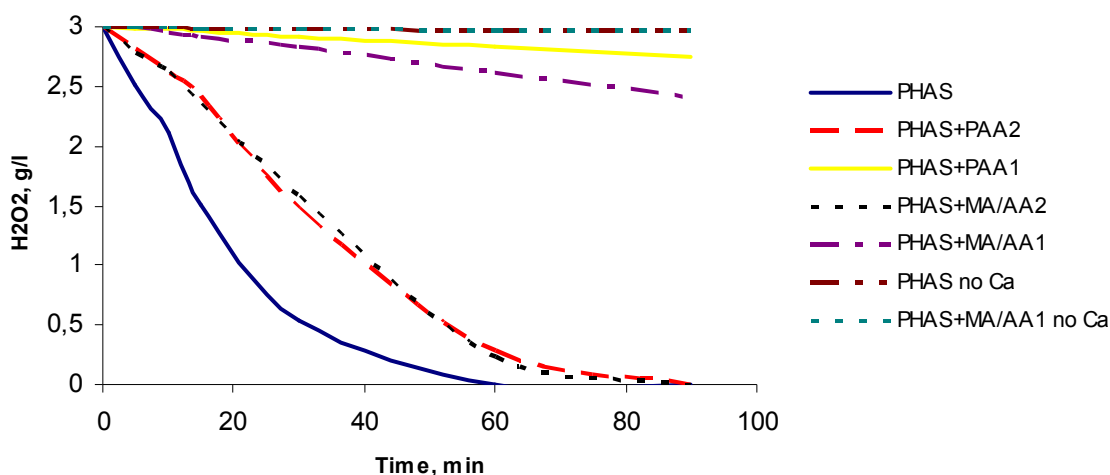
Figure 5. Effect of calcium-binding polymers to the behaviour of PHAS as a stabilizer. PAA2 is sodium salt of polyacrylate with average MW 3000, for PAA1 MW is 200 000. MW for PHAS is 200 000. MA/AA2 is sodium salt of a copolymer with 70:30 (mol:mol) maleic acid and acrylic acid with MW 7000. MA/AA1 is sodium salt of a copolymer with 60:40 (mol:mol) maleic acid and acrylic acid with MW 44 000.

Bleaching trials with different polymeric compositions

In addition to PHAS, other polymeric compounds were tested in bleaching trials with aspen CTMP pulp (figure 6). Some industrial applications have been explained earlier by Jäkärä et al. [24] and the most successful cases have been with chemimechanical pulps [24,25]. There are mills running with polymeric stabilizers and Kemira has patented several polymeric compositions under trademark Fennobrite[TM].
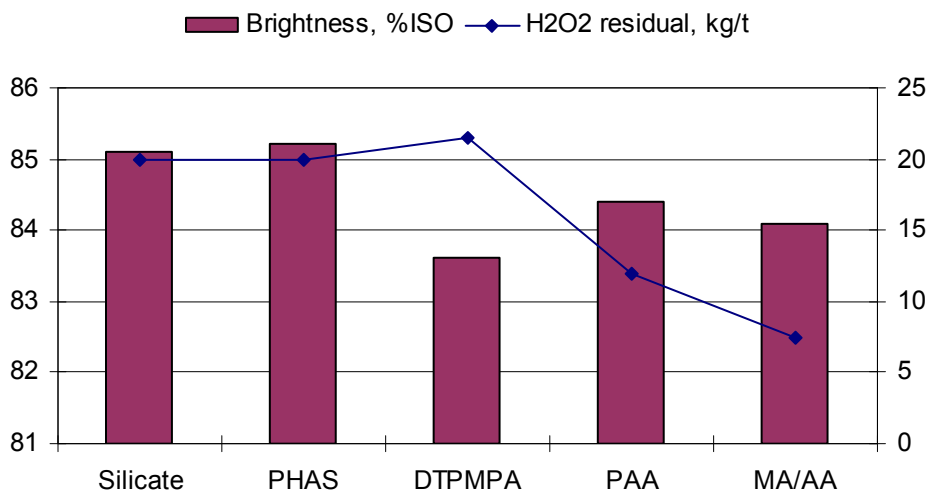

Figure 6. The effect of different stabilizers on brightness and peroxide residual. MA/AA stands for maleate-acrylate copolymer, PAA for polyacrylate and DTPMPA is a phosphonate. The trial set-up was similar in all cases.

Figure 6 shows that silicate and PHAS have the highest peroxide stabilizing efficiency in terms of brightness and residual peroxide. Phosphonate gives high residual peroxide, but brightness development is poorer. MA/AA and polyacrylate failed to show proper stabilization effect. It was though depicted in the stabilization tests in figure 5, that PHAS can be mixed with other polymers to provide a composition which is less expensive in Ca^{2+} rich applications but with remaining selectivity towards Mn and Fe ions. What makes the stabilizer choice and

development difficult is the varying amounts of metals in different pulps. Moreover, we have in practice found that pulps treated in different way (PGW, TMP or CTMP) show different stabilization ability. Silicate, which is conventionally used as stabilizer, is easy to use as brightness normally increase the more it is applied. Our experiences show that polymeric agents need to be tailor-made according to each specific process. We have even found that too high charge of polymers may decrease brightness – there must be some fundamental difference in the mechanisms related to polymeric stabilization vs. silicate. To find a suitable polymeric composition is not a straightforward task as discussed in this paper. In our development of suitable stabilizers, a molecular modelling method has also been utilized to estimate different complexing agents' stability and the conformation of different complexes . This will reduce the enormous amount of stabilization tests and bleaching trials needed for optimizing polymeric compositions.

CONCLUSIONS

The concentration of transition metals dramatically affect the stability of alkaline hydrogen peroxide. It was found that iron and manganese have a synergistic effect in catalyzing the decomposition of peroxide. The Mn/Fe ratio 2/1 (mol/mol) seems to be the most active cedomposition catalyst. Poly-a-hydroxyl acrylic acid is an effective stabilizer due to its metal binding ability and possibly due to its radical scavenging ability. Earth alkali metals Ca amd Mg affect the performance of the polymeric stabilizers by complex formation with the polymers. In many cases it is advantageous to apply PHAS together with a calcium binding polymer. The molecular weight of the polymers have a remarkable influence on the stabilizing power. This is supposed to be due to deactivation of solid and colloidal particles in the bleaching liquor. The bleaching results depend highly on the metal concentrations and on the process conditions, i.e. raw material, water circulation, processes etc. Therefore, an optimal bleaching result is usually obtained after tailoring the right stabilizer formulation for each process.

REFERENCES

1. Xu, E. C., Journal of Pulp and Paper Science, vol. 28, no. 11, 2002.

2. Colodette, J.L., Rothenberg, S. and Dence, C.W, Journal of Pulp Paper Science, vol. 15, no.1, 1989.

3. Backman, L., Gellerstedt, G., ISWPC, 1993.

4. Fairbank M. G., Colodette, J.L. Ali, T., McLellan, F. and Whiting, P., Journal of Pulp and Paper Science, vol. 15, no. 4, 1989.

5. Burton, J. T., Journal of Pulp and Paper Science, vol. 12, no. 4,1986.

6. Ali, T., Evans T.D., Fairbank M.G., 74th Annual meeting Tech. Sect. CPPA, 1989

7. Iler, R. The chemistry of silica, John Wiley & sons, 1979.

8. Huuha T., Msc thesis, Univ. of Oulu, 2003.

9. Larnicol. P., Cabanne L., Cudelou J., Guillaume J-P., IMPC, 2001.

10. Parén, A., Aksela, R., Jäkärä, J., Renvall, I., 6th EWLP, 2000.

11. Wuorimaa, A., Jokela, R., Aksela, R., Nordic Pulp and Paper Research Journal, no. 3, 2006.

12. von Raven, A., Koch, H.-G., Mayer, H., Wochenblatt fur papierfabrikation, vol. 20, 1991.

13. Leduc, C., Rouaix, S., Turcotte, F., Daneault, C., Pulp and Paper Canada, no. 4, 2005.

14. Freytag, H., DE patent. 968992, 1958.

15. Bergmann, G., DE patent. 1804504, 1970

16. Tahara, H., Itoh, H., Kofuji, K., Takagi, M., US patent 5523380, 1996.

17. Nunn, M. B., Ramesh, M., Wetegrove, M. L., EP patent 0831169, 1998.

18. Nishino, F., Kayama, R., Kusano, S., EP patent 0814193, 1997.

19. Parén, A., Jäkärä, J., Renvall, I., Ahlgren, J., Laitinen, R., Nikkarinen, J., Viitanen, T., WO patent 2004063461, 2004.

20. Mulders, J., Gilain, J., Water Research, vol. 11., 1977.

21. Pesonen, H., Sillanpää, A., Aksela R., Laasonen, K., Polymer, 46, 2005.

22. Hyvönen,H., Orama, M., Saarinen, H., Aksela, R., Green Chemistry, no. 5, 2003.

23. De Stefano, C., Gianguzza, A., Piazzese D., Sammartano, S., Talanta, vol. 61, 2003.

24. Jäkärä, J., Parén, A., Pitkänen, M., Nickull, O., Hämäläinen, H., IMPC, 2005.

25. Hämäläinen H., Xu, E., IMPC, 2007.

SILICATE-FREE PEROXIDE BLEACHING OF MECHANICAL PULPS: EFFICIENCY OF POLYMERIC STABILIZERS

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PEROXIDE BLEACHING BASICS

- Standard for high brightness
- Variables involved
  - Wood
  - Metal management
    - metal distribution in wood
    - metal type and form
    - chelation
    - passivation

    FOCUS HERE!
  - Bleaching conditions
  - Process design
- Peroxide stability in pulp suspension the key focus!

SILICATE AS STABILIZER

- "BENEFITS" OF WATERGLASS
  - + Metals (Fe, Mn) binding
  - + Buffer capacity
  - + Corrosion inhibitor
  - + <u>Cheap & universal</u> chemical

- "CONS" OF WATERGLASS
  - – Precipitation of silica ($SiO_2 \cdot nH_2O$)
  - – Anionicity
  - – Increased conductivity
  - – Dissolved silica is difficult to fix and disturbs microparticle silica

SILICATE - ALTERNATIVES?

- Leave out silicate, use more peroxide – not practical

- DTPA – limited power, risk of decomposition

- Zeolites – limited power, efficiency similar to aminocarboxylates

- $MgSO_4$ (Epsom salt) – limited power, function only as "support chemical"

- Phosphonates – high cost / phosphorous is unwanted in certain places

- Polymeric stabilizers – environmentally friendly

SILICATE REPLACEMENT - POLYMERS

- PHAS – poly-α-hydroxyacrylic acid
  - Only α is effective, β is not
  - Reported effective
  - Biodegradable

$$-\left[CH_2-\underset{COOH}{\overset{OH}{\underset{|}{C}}}\right]_n$$
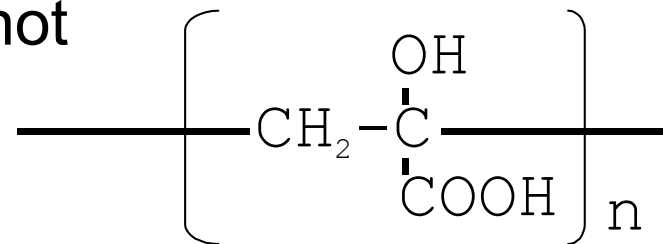
- Polyvinylpyrrolidone, maleic acid-styrene or propene, copolymers of butadiene-maleic acid, and grafted polymers are other patented examples (*Wuorimaa et al. 2006*)

EXAMPLES OF POLYMERIC COMPOUNDS

■ Compounds used in our study

✖ PHAS – poly-α-hydroxyacrylic acid

✖ PAA – polyacrylic acid

✖ MA/AA – maleic acid / acrylic acid copolymer

✖ Comparison to silicate

✖ Comparison to DTPMPA – phosphonic acid

EXPERIMENTAL SET-UP

- Peroxide stability in
  - pure water phase
  - different Mn / Fe ratios
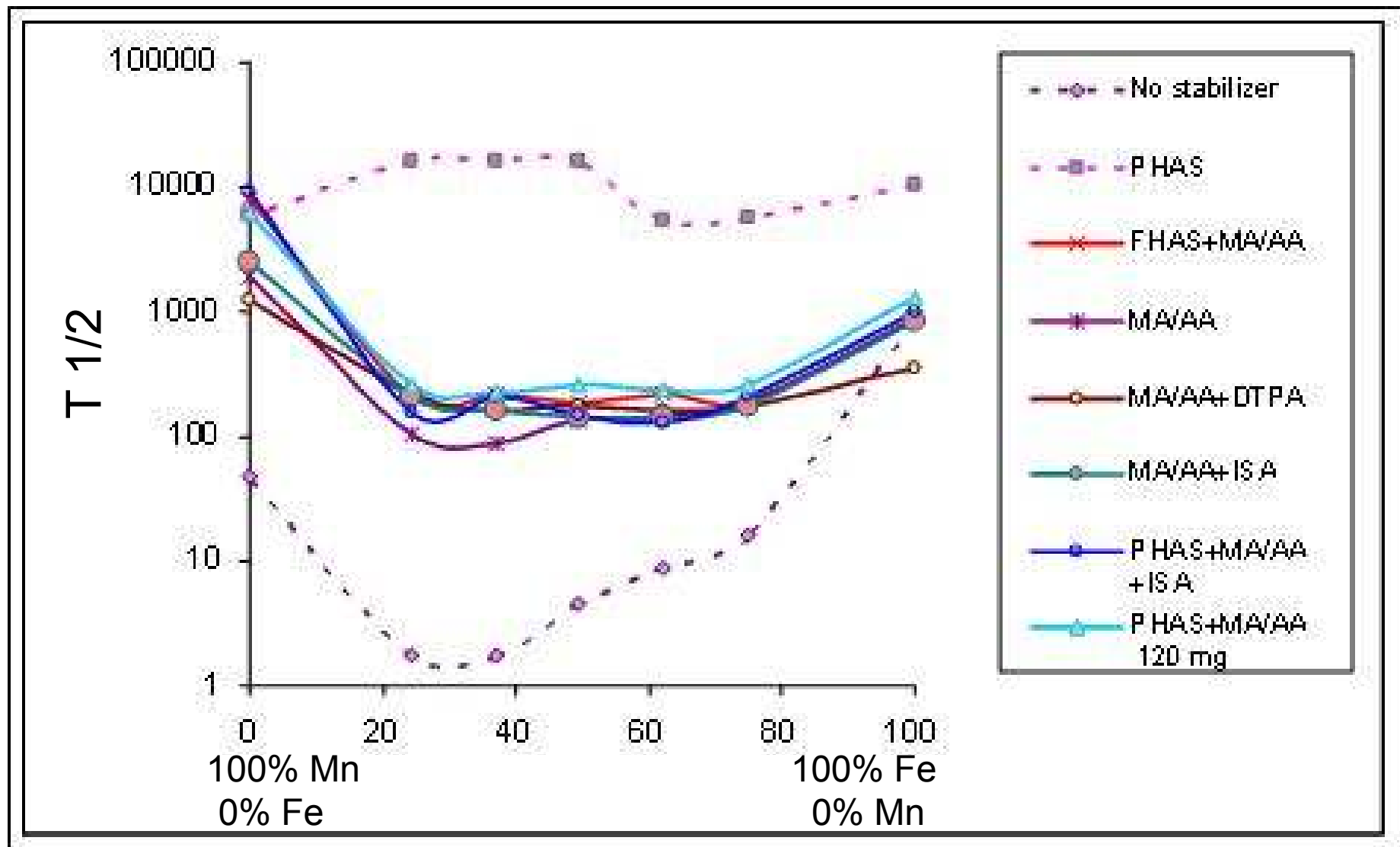 - varying Mg-content
  - varying Ca-content
- Pulp bleaching trials

STABILIZATION OF PEROXIDE SOLUTIONS

Conditions:

- 50°C
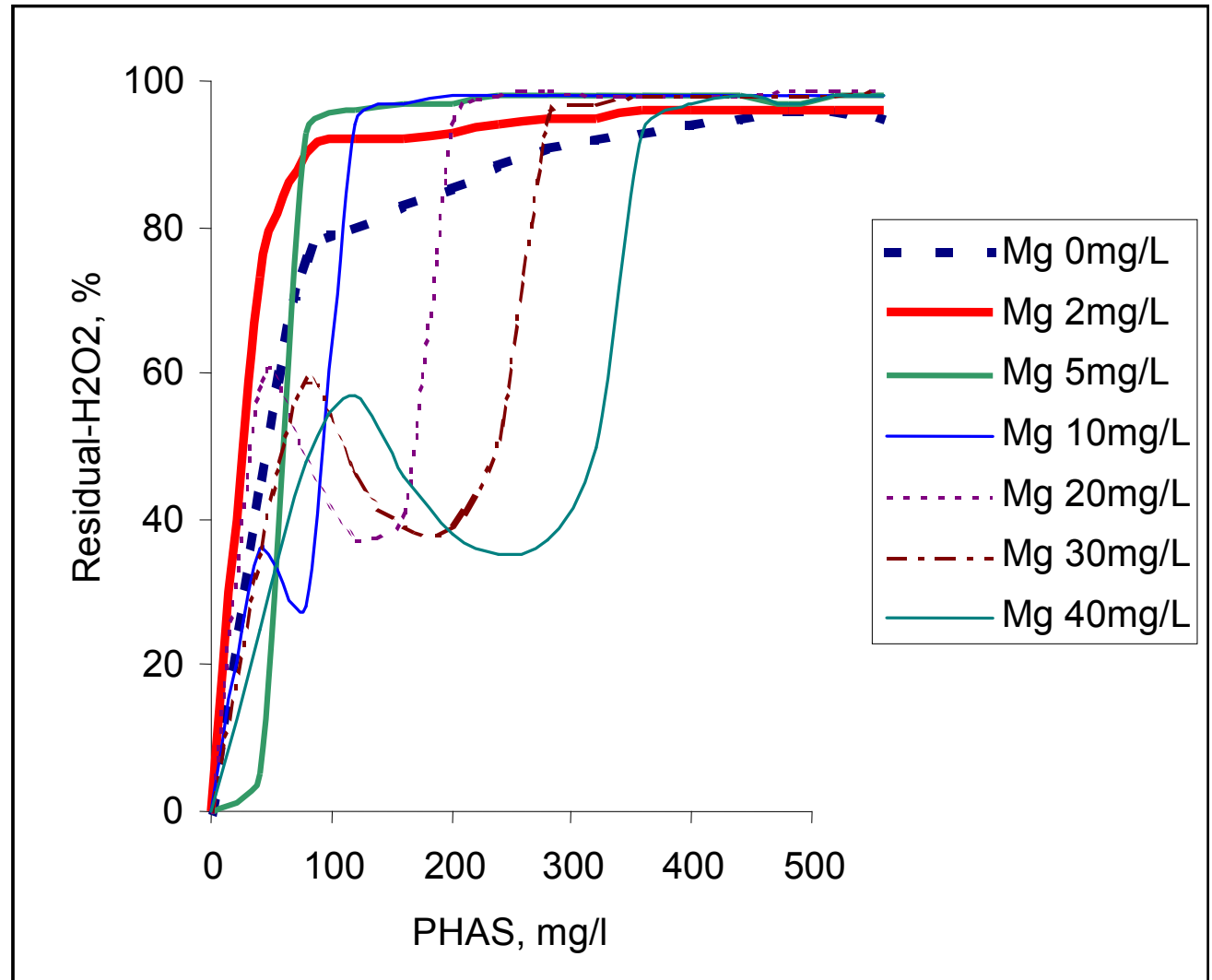- H_2O_2 3g/l
- Fe&Mn 2+2ppm
- Stabilizer 140mg/l
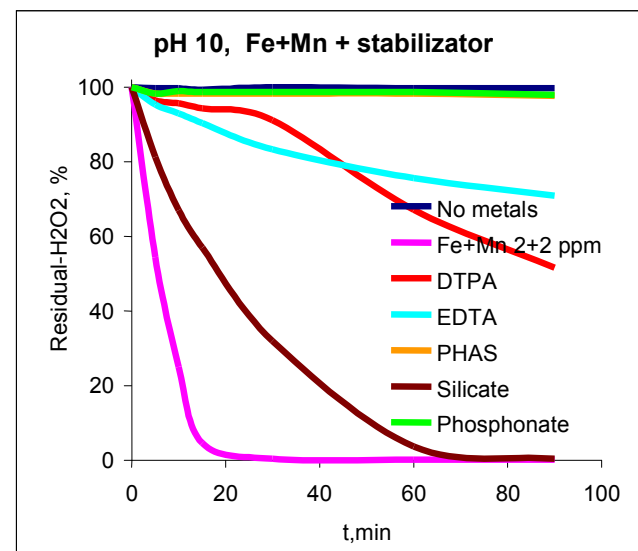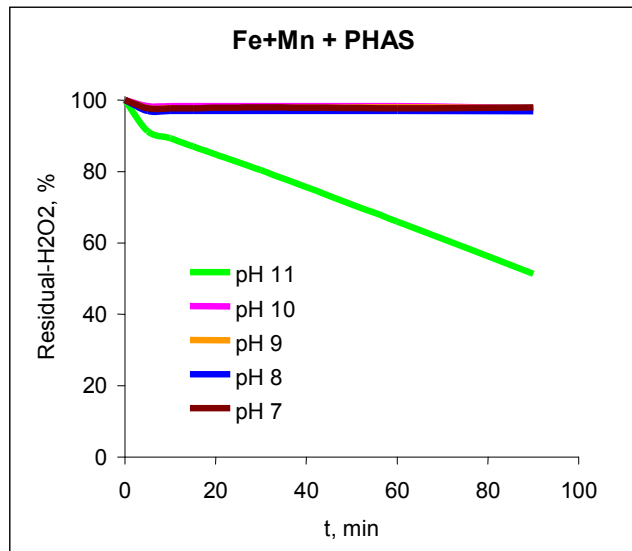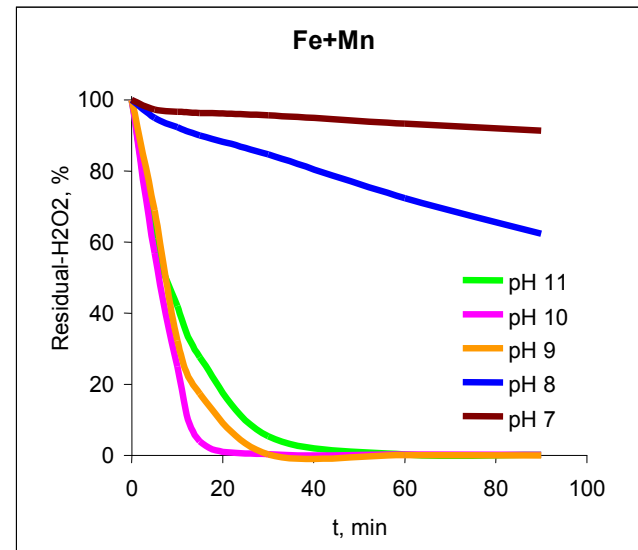
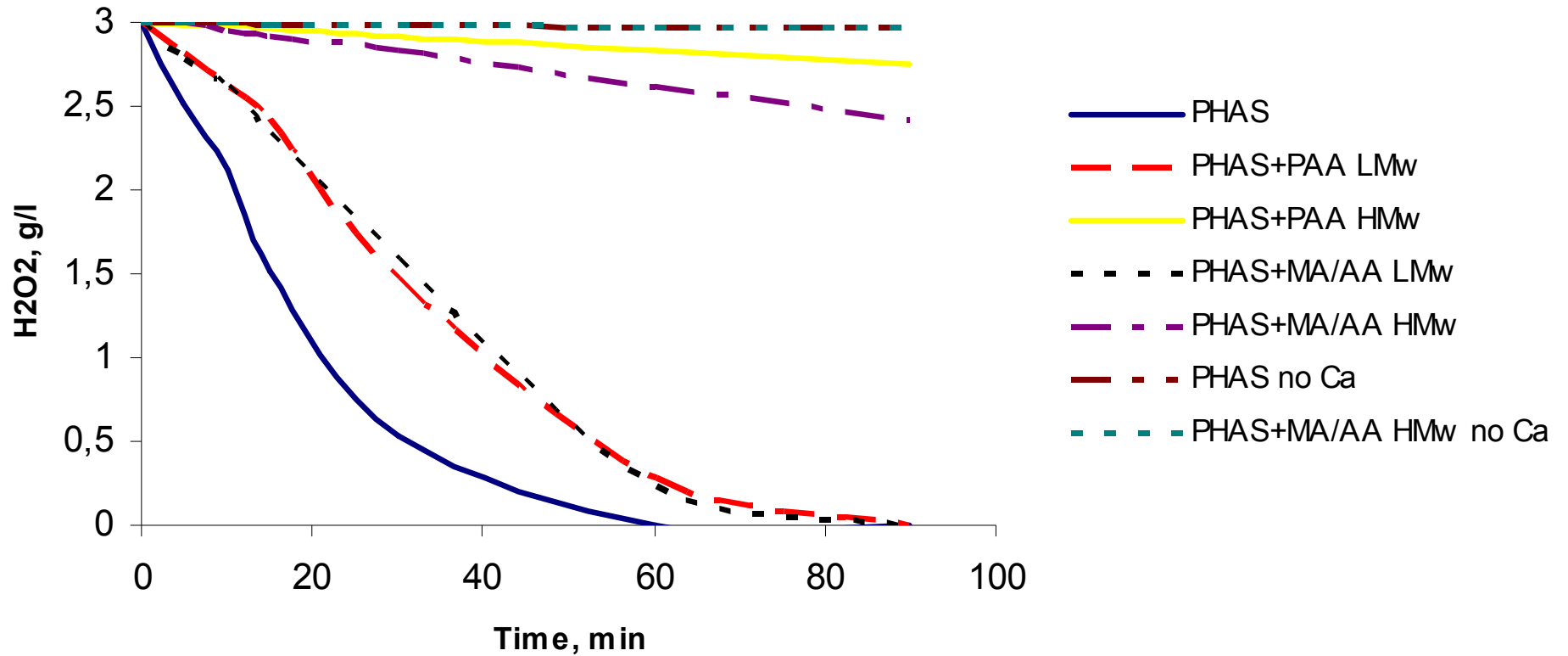# SYNERGY OF Fe & Mn ON DECOMPOSITION OF PEROXIDE

SYNERGISTIC EFFECTS OF Mg AND PHAS

Conditions:

- pH 11
- $T = 60^oC$
- t = 180 min
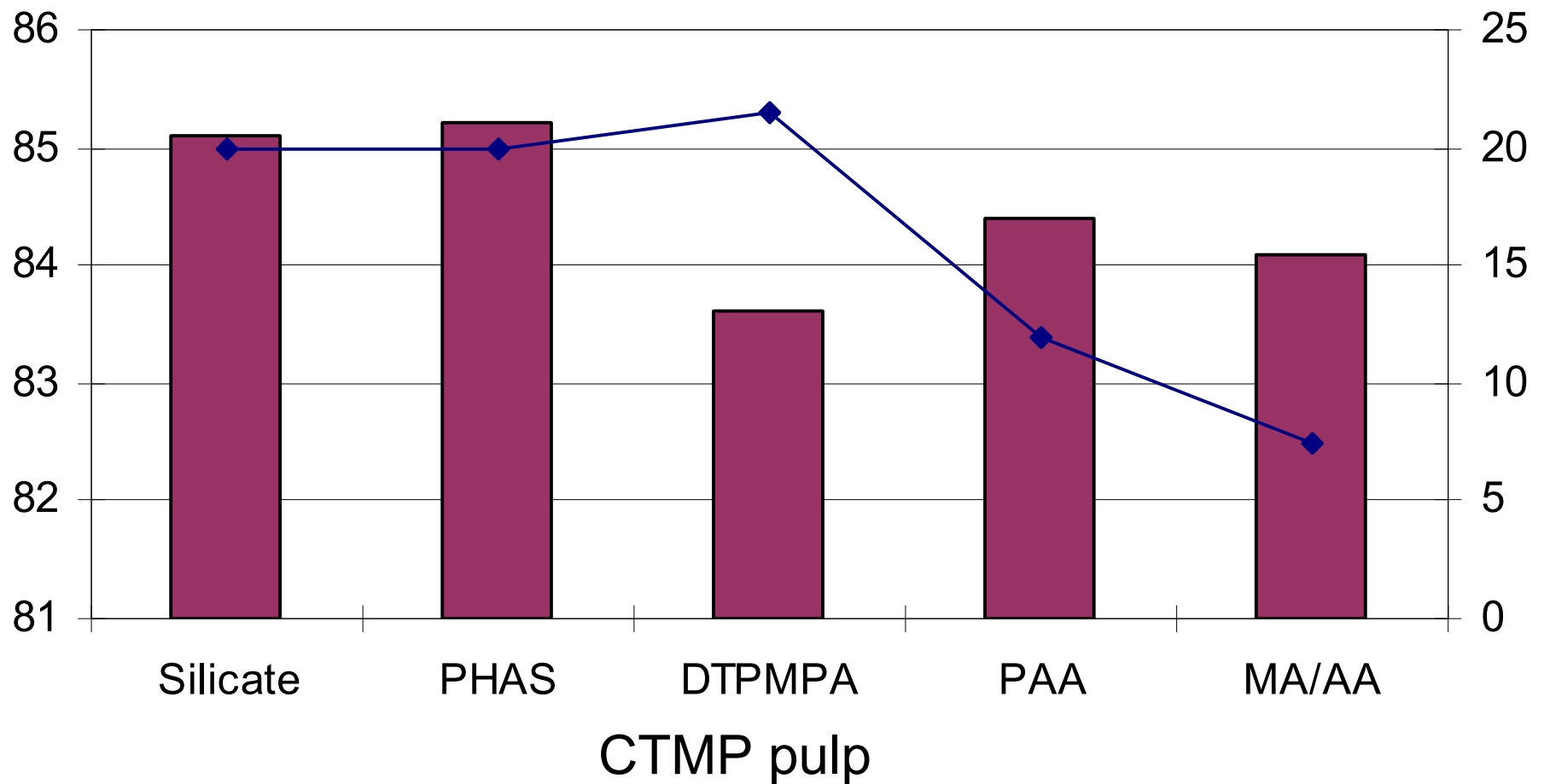- Mn 2 mg/l
- H_2O_2 1 g/l
- PHAS calculated as 100% Na-salt.

EFFECT OF POLYMER COMPOSITION

BLEACHING EFFICIENCY WITH DIFFERENT POLYMER COMPOSITIONS

CONCLUSIONS

- Metals play a vital role in peroxide stabilization. Mn/Fe ratio 2/1 (mol/mol) is the most active decomposition catalyst.

- PHAS is an effective stabilizer to replace silicate.

- Earth alkali metal content in process hinders the efficiency of polymeric stabilizers, which calls for a supporting polymer to bind calcium.

- Higher molecular weight of the polymer is better for stabilization.

- Polymeric stabilizers have to be tailor-made to each specific application, unlike silicate which is universal.

THANK YOU!