A COMPARATIVE RHEOLOGICAL STUDY OF LIME/MOLASSES AND SUCROSE/LIME/WATER MIXTURES IN THE PRESENCE OF ADDITIVES

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ABSTRACT
Molasses containing sucrose, pectins, water and alcohol interacts with lime to form homogeneous blends. Rheological studies indicate that they exhibit viscoelastic behaviours as entangled polymers. Elastic modulus in these blends is much higher than for sucrose/lime/water model system. This difference is attributed to the presence of polysaccharide and ethanol in molasses. To verify this hypothesis, a model system was investigated in the presence of pectin and ethanol. Both additives were found to enhance viscosity and elasticity. In the presence of pectins, the formation of interpenetrated networks takes place, where calcium interacts with sucrose and pectins. Ethanol may have an influence on the complexes' stability.

ZUSAMMENFASSUNG
Sirupmischungen aus Saccharose, Pektin, Wasser und Alkohol interagieren mit Kalk und bilden eine homogene Masse. Rheologische Untersuchungen deuten darauf hin, dass diese Mischungen ein viskoelastisches Verhalten ähnlich wie das vernetzter Polymere zeigen. Der elastische Modul in diesen Mischungen ist viel höher als im reinen Saccharose/Kalkstein/Wasser-Modellsystem. Dieser Unterschied wird auf die in Sirupmischungen vorhandenen Polysaccharide und Ethanol zurückgeführt. Um diese Hypothese zu verifizieren, wurde ein Modellsystem unter Anwesenheit von Pektin und Ethanol untersucht. Es konnte gezeigt werden, dass beide Additive die Viskosität und die Elastizität erhöhen. In Anwesenheit von Pektinen entstehen sich durchdringende Netzwerke, wobei Kalzium mit Saccharose und Pektinen wechselwirkt. Zusätzlich könnte Ethanol einen Einfluss auf die Stabilität dieser Komplexe haben.

RÉSUMÉ
Nous nous sommes intéressés au comportement rhéologique des mélanges mélasse/chaux. La mélasse contient essentiellement du saccharose, des sels, des polymères tels que pectines et des produits de fermentation tels que l'éthanol. Les mélanges mélasse/chaux ont des propriétés viscoélastiques caractérisées par un module G' et une viscosité bien plus élevés que ceux obtenus sur des mélanges modèles de même composition saccharose/chaux/eau. Grâce à l'étude de l'influence de pectines et d'éthanol sur le comportement rhéologique des systèmes modèles, nous pouvons montrer que les propriétés viscoélastiques des mélanges mélasse chaux sont dues non seulement aux interactions entre les ions calcium et le saccharose mais aussi aux effets gélifiants des peptides et à un effet de stabilisation des complexes par l'éthanol.

KEY WORDS: Molasses, sucrose, lime, calcium, rheology, complexation

1 INTRODUCTION

Molasses/lime/water mixtures lead to the formation of dense pastes. They are used as natural cements for industrial applications such metallic dust agglomeration [1, 2]. Rheological and mechanical properties of these pastes have not been studied and because the origin of their viscoelasticity is yet unknown, it is difficult to obtain cements with reproducible properties. Molasses contain many compounds including sucrose and polysaccharides (pectine, xanthan, gum arabic). Interactions between calcium ions and pectins have been extensively studied and the conditions for physical gelation are known. Also, saccharides of low molecular weight can interact with divalent cations to form complexes [3, 4, 5]. This phenomenon is of great importance in biological systems and has been described for several synthetic and natural sugars. As sucrose is the dominant constituent of molasses, it is expected that sucrose/calcium interactions play an important role in the rheological behaviour of molasses/lime mixtures. If structural or thermodynamic investigations have been led about sugar/calcium interactions in dilute solution, rheological properties in concentrated systems are unknown [6, 7, 8, 9]. Besides, there is no reliable information about the interactions of sucrose with calcium ions. We have recently investigated the physico-chemical behaviour and rheological properties of sucrose/lime/water system, which shall be considered as a reference system [10]. These are homogeneous pastes where (in a region of the phase diagram):

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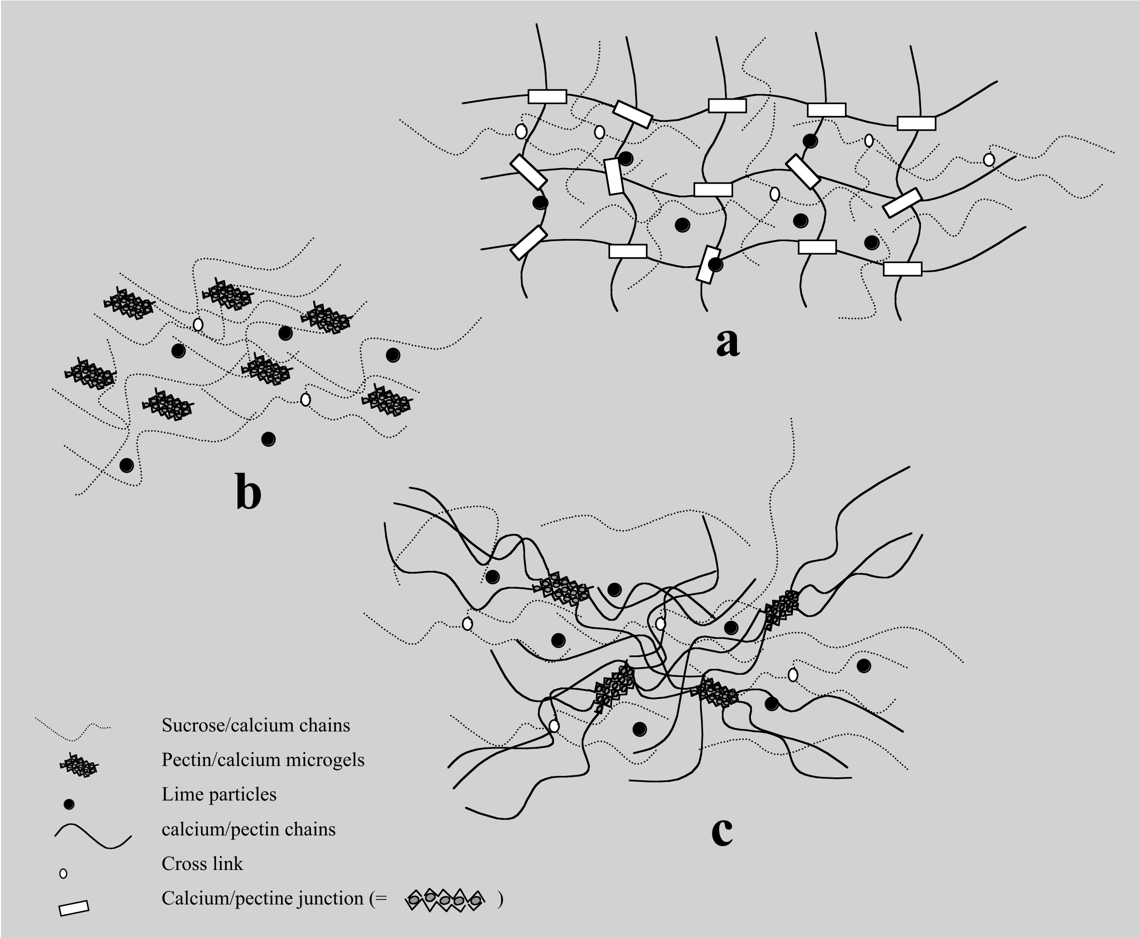

Figure 15: Schematic representation of the hypothetic network formed by the calcium / sucrose / pectin or xanthan interactions.

the previous reactions. At a given concentration of calcium,

$$\frac{[complex\ 2]}{[complex\ 1]} = \frac{K_2[pectin]}{K_1[sucrose]} = \frac{K_2}{K_1 Z} \quad (5)$$

This expression shows that the concentration of complex 2 increases when Z decreases. This effect is more important if $K_2 >> K_1$. Finally, at low pectin concentrations, the number of complexes [pectin]/[calcium] will be relatively low and their formation will induce gelation (Fig. 15a). At higher concentrations, the pectin chains will collapse in dense microgels and the number of sucrose/calcium complexes will decrease. Both effects explain the existence of plateau in the variations of G_N and ω_O against c_p.

4.2 ETHANOL

Fig. 12 shows three regions in the variations of G_N and ω_O versus ethanol content c_{et}:

- for $0 < c_{et} < 2$ %, G_N increases and ω_c decreases strongly
- for $2 < c_{et} < 4$ %, the inverse phenomena is observed, G_N recovers its initial value, but ω_O slightly increases

In the absence of ethanol, these systems behave as viscoelastic materials constituted of polymeric species due to sucrose/calcium complexation and solid lime particles in excess. Literature shows that the interaction of sugars with metal ions is generally much stronger in ethanolic than in aqueous solutions [4, 15]. For example stability constant of the D(-) ribose complex with calcium in a ratio 1/1 is 15 times higher in methanol than in water [16]. We can assume that the addition of ethanol to our system improves the interactions of sucrose with lime , leading to an increase in elastic moduli. This behavior can be explained by the fact that ethanol is involved in the formation of sucrose-calcium complexes which tend to modify its stability constant and its relaxation time.

However, at higher concentrations, a dilution effect takes place and viscosity decreases again. This has been shown in the effect of water concentration on the rheological properties of the reference system (without ethanol), where G_N decreases strongly upon dilution [10]. However, the variation of ω_O versus ethanol concentration is weak. This behavior seems to support the hypothesis according to which there exists an optimal stoichiometry of ethanol in the formation of sucrose-calcium-ethanol complexes and the excess ethanol may act as solvent.

5 CONCLUSION

The rheological properties of industrial cement molasses/lime were compared to those of a model system : sucrose/lime/water. It appeared that both systems behave almost as entangled polymer solutions. The values of exponents of the variations of log *G'* and log *G"* versus log ω indicate that these systems cannot be represented by one relaxation time Maxwell model. As discussed in other works [17], we assume that the high elastic modulus is due to the formation of polymer - like sucrose - calcium complexes. The ω dependencies of *G'* and *G"* can be adjusted by two large distributions of relaxation times which may be related to various type of sucrose-calcium binds and to different complex molecular weight. The molasses/lime systems exhibit much higher elasticity and viscosity than model system. The difference is attributed to the presence in molasses of polysaccharides and ethanol. Such our hypothesis is confirmed by a series of rheological measurements on the model system in the presence of increasing concentrations of pectin and ethanol. The evolution of *G'* and *G"* upon increasing pectin concentration is qualitatively explained by competition between sucrose-calcium and pectin-calcium interactions. Ethanol also, induces an increase of viscosity and elasticity modulus, and this may be explained by high values of complex stability constants in alcoholic media. This work shows that the viscoelastic properties of industrial molasses/lime cement may be improved by addition of several types of compounds able to interact with calcium.

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