

Interactions between Lignosulphonates and Clinker Minerals and the Hydration Products of Clinker Minerals.

Bernt O. Myrvold

Borregaard LignoTech, P.O.Box 162, N-1709
Sarpsborg, Norway

Abstract

The adsorption isotherms of one sodium lignosulphonate onto cement, and clinker minerals have been investigated together with the adsorption isotherms hydrated cement, hydrated clinker minerals and some known reaction products from the cement hydration. By looking at the changes in adsorption isotherms with time it is clearly shown how the lignosulphonate interferes with and slows the hydration of the silicate phases. Ions released from the reactions of cement modify the adsorption behaviour of the lignosulphonate. A strong adsorption to the aluminate phases leaves little lignosulphonate left to interfere with the silicate. An efficient plasticizer should thus have a strong adsorption towards the aluminate phase. A strong adsorption towards the aluminate phases and the reaction products of the aluminate phases also seems to improve the dispersion, and thus the workability.

1 Background

Lignosulphonates are widely used plasticizers, or dispersing agents, in the concrete industry. Steric interactions and electrostatic repulsion have been suggested as the mechanisms responsible for the stabilisation of the suspension and increased flowability. Irrespective of the mechanism the first step will be for the lignosulphonate molecule to adhere to the particle surface. This adhesion can be probed directly with adsorption isotherms.

Lignosulphonates also retard the setting of concrete to a smaller or larger degree. This retarding effect can be beneficial e.g. in oil well cementing, or when concrete has to be transported longer distances in a warm climate, but particularly in colder environments it restrict the use of lignosulphonates as plasticizers, or superplasticizers.

There has only been few studies of this kind [1-7]. Most of these studies use calcium lignosulphonates while the best performing lignosulphonates in concrete are sodium lignosulphonates.

2 Experimental

2.1 Substrates

The cement used was ordinary Portland cement CEM 52,5 N.

The preparation of the hydrated cements and the clinker minerals C_3S/C_2S and C_3A/C_4AF and their hydration products has been described previously [8].

The ettringite was made by direct reaction. 333.3 gr aluminium sulphate octadeca hydrate and 6 gr calcium sulphate dihydrate were dissolved in 1.5

litres of water. 37.1 gr. calcium hydroxide was dissolved in 1.5 litres of water. The two solutions were mixed and stirred thoroughly for 2.5 hours. The solution was filtered through a blue band filter and dried at 60 °C over night.

Gypsum was fresh gypsum from Norgips a/s. Calcium hydroxide was p.a. quality from Merck.

The studies presented here were performed with the same batch of ultrafiltrated sodium softwood lignosulphonate. The analytical data are as follows: $M_w = 47.8$ kDa, $M_n = 5.8$ kDa, $[Ca^{2+}] = 0.01$ %, and reducing sugars 0.4 %.

2.2 Synthetic pore water

Saturated $Ca(OH)_2$ solution was made by shaking CaO with deionized water. To 1.00 litre of saturated $Ca(OH)_2$ solution was added 7.0 g Na_2SO_4 , 6.5 g K_2SO_4 and 6.0 g KOH. The final pH is around 12.76.

2.3 Testing

The procedure for obtaining adsorption isotherms has been described previously [9]. In all the isotherms presented here we use the term “consumed” about the reduction of the lignosulphonate amount in the solution. All isotherms are fitted to a Langmuir isotherm.

$\theta = bc/(1+bc)$, where θ is the fractional surface coverage, c is the concentration in solution, and b gives the strength of the interaction.

The set times were measured by the heat development for mixtures with a constant cement amount. 350 kg/m³ Embra EN 197-1 CEM 52.5 N were used. The w/c ratio varied from 0.376 to 0.550, and the matrix volume varied from 273 to 331 litres/m³.

3 Results and discussion

3.1 On isotherms

There might be several mechanisms operating when the amount of lignosulphonate in the solution is reduced. We might have true adsorption where the lignosulphonate interacts strongly with the surface.

We might also have precipitation where the lignosulphonate interacts with cations in the solvent to form insoluble complexes that precipitates. In this case there are no direct interactions between the substrate and the lignosulphonate, but the substrate might provide the ions that cause precipitation. For these cases there will be no upper bound on the amount of lignosulphonate consumed and the amount consumed will be a linear function of the amount added.

There is also an intermediate situation, the cation assisted adsorption [10]. Here the substrate provides ions that, partially, or fully cancels the charges in the lignosulphonate molecule. These new ion pairs adsorb to the surface. There will be no adsorption in the absence of the ions. This is also different from the precipitation and the lignin will not be consumed without a substrate to adsorb to.

For cement we also have the possibility that the sulphonate groups of the lignosulphonate takes part in reactions (probably replacing sulphate). This will bury the lignosulphonate inside the newly formed reaction products.

In most of the isotherms we plotted the consumed amount in mg lignosulphonate pr. gram of substrate. As the surface areas for the different substrates were unknown we can not compare the plateau values directly for different substrates. In some cases we have also shown the isotherms as fractional coverage which is the consumed amount divided by the consumed amount at the plateau value. This gives a better indication of the strength of the interactions in cases where we compare different surfaces.

3.2 Cement isotherms

Two sets of isotherms are shown in Fig. 1 and 2. In the first (1a) the cement has been hydrated for the given times before the lignosulphonate solution was added. We could not prehydrate cement for more than 8 hours due to the hardening. The lignosulphonate solution and prehydrated cement has been in contact for 25 minutes. We clearly see how the adsorption rises strongly with time, except for the product hydrated for 1 hour, where there is a small decrease. A new and larger surface is formed and thus the plateau value increases, strongly. In Fig. 1b the data is plotted as fractional coverage. The initial slopes are the same in all cases. Thus it seems reasonable to assume that much new surface is created, but the nature of the surface is the same. This will be the C-S-H phase. We find a value of $4.0 \cdot 10^{-2} \text{ ppm}^{-1}$ for the constant b , in all cases.

In Fig. 2 the lignosulphonate solution has been in contact with cement for the time shown. We see a very small increase in the adsorbed amount. The lignosulphonate clearly interferes with the creation of the new C-S-H surface. We also note that there was no problem in obtaining good isotherms for 16 hours contact time, much longer than the time taken for hardening without lignosulphonates present.

The differences between the two isotherms clearly show that the surface area of cement grows in contact with water, but that this growth was stopped very efficiently with lignosulphonates present. The reactions between water and the cement minerals release ions into the solution. These ions might modify the properties of the lignosulphonates. However, for the pre-hydrated cement (Fig. 1) these ions will be washed away when the water is filtered off, and the hydrated cement isolated. There will thus be less ions in this system. The larger adsorption can thus not be due to more precipitation caused by the ions. In the system where the cement is in contact with both the water and the lignosulphonate at the same time, all the ions leached out will be available to interact with the lignosulphonate in solution. Still, this does not give a higher consumption.

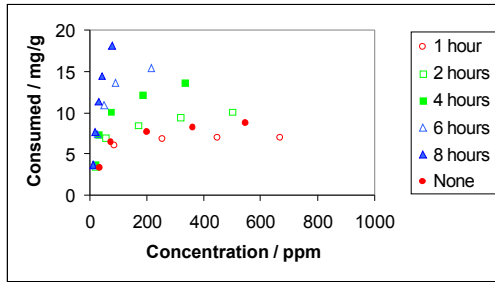


Figure 1a. Adsorption of high molecular weight sodium lignosulphonate to cement that has been pre-hydrated for the times given. There is a large increase in maximum consumption.

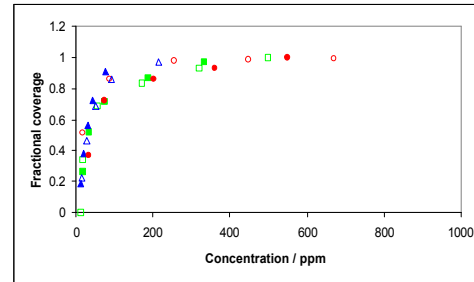


Figure 1b. The adsorption of high molecular weight sodium lignosulphonate to pre-hydrated cement plotted as fractional coverage. The strength of the interaction is the same in all case

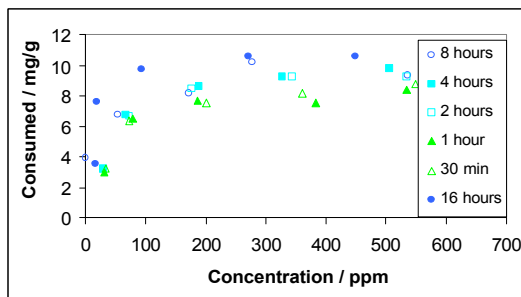


Figure 2. The consumption of high molecular weight sodium lignosulphonate that has been in contact with cement for the times given. There is a very small increase in maximum consumption.

3.3 Gypsum isotherms

As gypsum was mixed with the C_3A/C_4AF phase, the adsorption of lignosulphonate to gypsum was investigated. Fig. 3 shows the results. In pure water there was no adsorption. This is consistent with a zeta-potential of -0.06 for gypsum [11]. In the synthetic pore water there was an adsorption. The hydration of the aluminates phases will release ions into the solution. This will modify the adsorption towards gypsum. However, for the first few seconds, or minutes, there will be no competition from the gypsum, and the lignosulphonate will adsorb to the aluminates phases.

The gypsum will compete fairly effectively for the available lignosulphonate as the constant b for gypsum ($1.5 \cdot 10^{-3} \text{ ppm}^{-1}$) is larger than for C_3A/C_4AF .

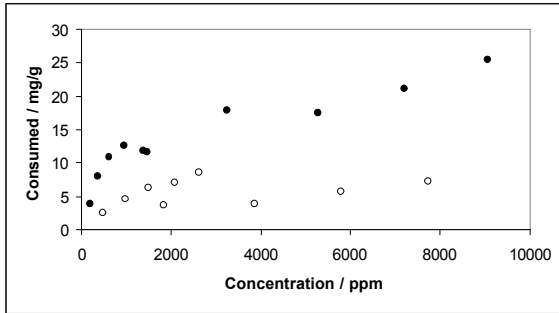


Figure 3. The consumption of high molecular weight sodium lignosulphonate by gypsum. Open symbols in pure water. Filled symbols in synthetic pore water.

The curve in synthetic pore water does not appear to have a good plateau value, and it could be more like a precipitation.

3.4 Tricalcium aluminate/tetracalcium ferroaluminate/gypsum

In figures 4 and 5 isotherms for C_3A/C_4AF is obtained in the same manners as for cement. Here we see hardly any increase in the adsorbed amount with longer hydration times when we use a prehydrated substrate. However, the reactions of the aluminate phases are very fast, so the reaction is probably completed even for the shortest hydration times used. Both the AFt and AFm phases have a positive zeta-potential of +5mV and +0.8 - +1.0 mV, respectively [11]. Other reported a slightly negative zeta-potential for AFm [12], but still an adsorption of sodium lignosulphonate from saturated calcium hydroxide solution.

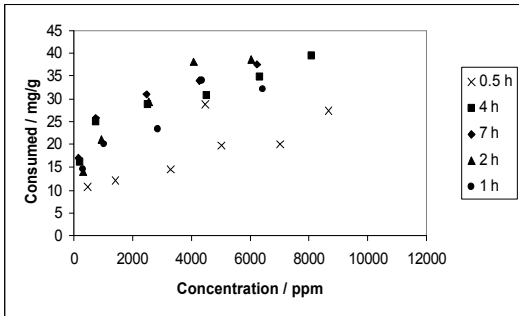


Figure 4. Adsorption of high molecular weight sodium lignosulphonate on aluminate phases in the presence of gypsum. The lignosulphonate solutions have been in contact with the substrate for the times given.

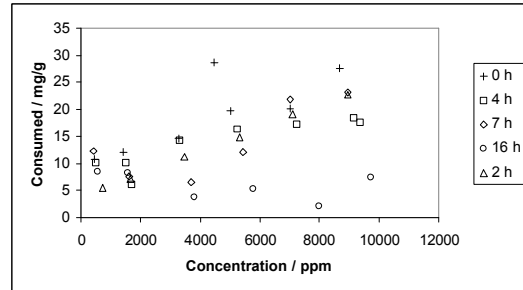


Figure 5. The adsorption of high molecular weight sodium lignosulphonate to aluminate phases that has been hydrated in the presence of gypsum for the times given.

In Fig. 4 we see that the longer the lignosulphonate solution is in contact with the aluminate phases the more lignosulphonate is adsorbed. This behaviour is in contradiction to the behaviour observed for cement itself. Differential thermal analysis has shown that calcium lignosulphonates slow down, but do not completely stop the hydration of C_4AF [13]. We also see that the increases in adsorption are fairly small.

When the aluminate phases are hydrated before the addition of the lignosulphonate (Fig. 5) the situation is reversed. Here the amount adsorbed decreases slightly with longer reaction times. This shows that the reaction products adsorb less lignosulphonates than the starting material. Much of the calcium present stems from the dissolution of the silicate phases. Thus the composition of the water phase will not be quite the same with only the aluminate phases. We thus also obtained a set of isotherms in the simulated pore water. The isotherms are shown in Figure 6. The isotherm rises more rapidly than for the isotherms obtained in water. However, the isotherm is still not as steep as for the cement itself.

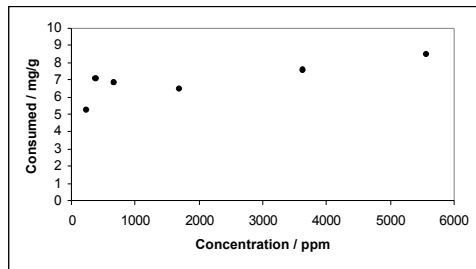


Figure 6. Adsorption of high molecular weight sodium lignosulphonate to the aluminate/gypsum system in simulated pore water.

In pore water the adsorption of lignosulphonates to the aluminate/gypsum phases appears much more like a Langmuir isotherms than it does in pure water. The same was the case for gypsum alone (Fig. 3). The plateau value seen in Fig. 6 is close to that found for 0 hours in Fig. 5. In other words the pore water does not seem to induce any precipitation. The b-value for aluminate phases in pore water is large, $7 \cdot 10^{-3} \text{ ppm}^{-1}$. But it is still less than that found for cement itself.

3.5 Calcium silicate isotherms

Fig. 7 shows the adsorption of lignosulphonates to the C_2S/C_3S phase. For all isotherms the solution and the silicate powder has been shaken for 25 minutes. In pure water there is no adsorption for the sodium lignosulphonate. However, pure water might not be a very realistic model for the adsorption to the silicate parts of the cement grain. In real cement the aluminate phases have already reacted to a large degree, and released ions into the solution. We tested with synthetic pore water. A fairly high plateau value was found. With 10 mM $FeCl_3$ present in the water there was also a high plateau value. With 10 mM Fe^{3+} present we find $b = 7.2 \cdot 10^{-3}$. It is much less in the simulated pore water.

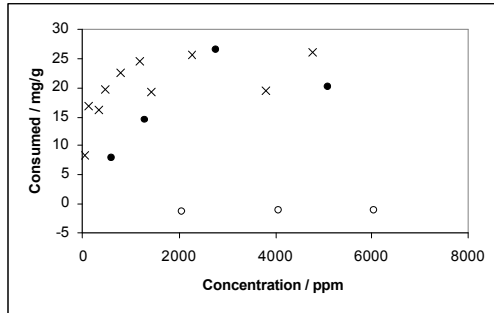


Figure 7. The adsorption of high molecular weight sodium lignosulphonate to the silicate phase. Open circles in pure water. Filled circles in synthetic pore water, crosses in 10 mM FeCl₃.

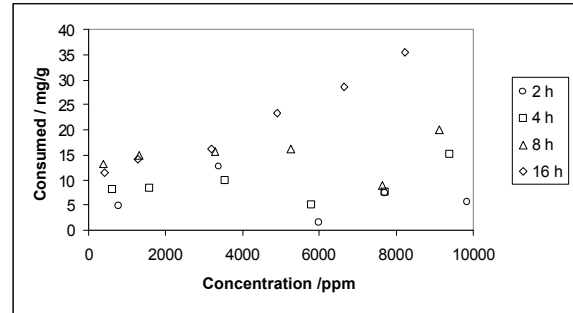


Figure 8. Adsorption of high molecular weight sodium lignosulphonate to prehydrated silicate phases.

We clearly see that sodium lignosulphonates will not adsorb to the negatively charged silicate phases on its own. Cations in the solvent might modify the negative charges in the lignosulphonate macromolecule and render it more surface active towards the silicates. We have previously found that lignosulphonates will adsorb to positively charged substrates, but also to negatively charged substrates if there was ferric ions present [9]. Moon and co-workers found that calcium lignosulphonates retarded the hydration of C₃S, this retardation can be relieved by adding C₃A to the system, while adding C₄AF gives a much stronger retardation [13]. This is consistent with the effect ferric ions has on the adsorption to the silicate phases as shown in Fig. 7. The relief of the retardation by addition of C₃A has been observed by several workers in the field [2,3,14].

Fig. 8 shows the adsorption isotherms when the C₃S/C₂S substrate has been shaken with water for a given time before the lignosulphonate solution was added. The contact time between the lignosulphonate solution and the prehydrated silicates was 25 minutes in each case. Here we see a clear rise in the adsorption. When the hydrated silicate formed the gel phase C-S-H, the surface area increased with time. The lignosulphonate clearly adsorbed or precipitated onto this surface. As the surface area increases so will the plateau value. The surface of the silicate phase might increase by a factor seven when the hydration time increases from 1 to 50 days [1]. These times were much longer than used in our study. The adsorption to hydrated C₃S has been found earlier also [2].

Fig. 9 shows adsorption isotherms when the lignosulphonate solution has been in contact with the C₃S/C₂S substrate for the given time period. Compared to Figure 8 we see a much lower plateau value, thus much less of the new C-S-H surface was formed. The C-S-H is negatively charged at the pH in pore water. However, Ca²⁺ ions extruded from the solid C₃S/C₂S interior through the C-S-H “membrane” might give a positive surface which the lignosulphonate adsorbs on to [15]. The Ca²⁺ ions bound in these way will not be available to form Ca(OH)₂ [15]. The retardation of the Ca(OH)₂ formation

has also been demonstrated by other workers [16], and found to be stronger for pure C_3S than for cement.

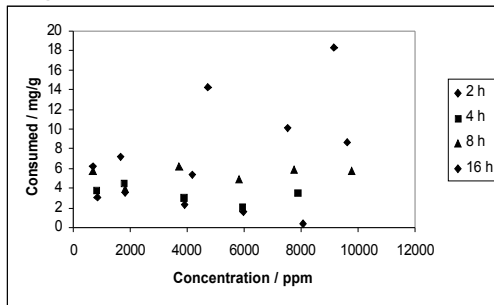


Figure 9. The adsorption of high molecular weight sodium lignosulphonate to silicate phases with different contact times between the substrates and the lignosulphonate solution.

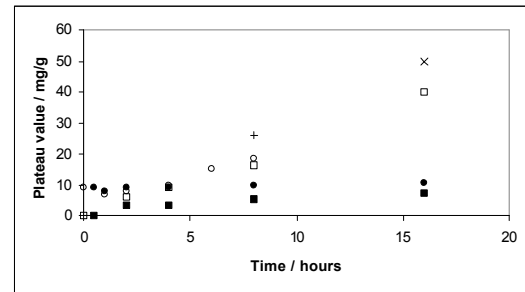


Figure 10. The plateau values for the different isotherms, as a function of time. Circles for cement, squares for C_3S/C_2S . Filled symbols are with lignosulphonate added initially. Open symbols are for lignosulphonates added after the given delay. The cross is for 8 hour prehydration and 16 hours contact with the lignosulphonate solution, while the x is for 16 hour prehydration and 8 hours contact with the lignosulphonate solution

The differences between figure 8 and 9 clearly show how the lignosulphonate was interfering with the normal hydration of the silicate phases. The differences were nearly the same as those seen between the cement isotherms. The much larger adsorption on prehydrated C_2S and C_3S compared to when the lignosulphonate solution was added to the dry substrates has been noticed earlier [17].

In pure water we have no adsorption to the silicate phases, while the presence of ions modifies the lignosulphonate enough to give strong adsorption. The adsorption to the silicate phases strongly retards the hydration of that phase. Differential thermal analysis has shown that calcium lignosulphonates slowed down, but did not completely stop the hydration of C_3S for the first few days, but after a week the development was the same with and without calcium lignosulphonate[13].

In Fig. 10 the plateau values for the adsorption plateaus as a function of the time are compared for cement and the silicate phases. The two systems show nearly identical behaviour. It is clearly the silicate hydration that was slowed down in the cement.

3.6 Ettringite isotherms

In this study we made ettringite directly by reaction of a calcium hydroxide slurry with aluminium sulphate. The adsorption isotherms (Fig. 11) show that the lignosulphonate will adsorb to the reaction product from the aluminate phases. Ettringite has a positive zeta-potential of +5 mV [11].

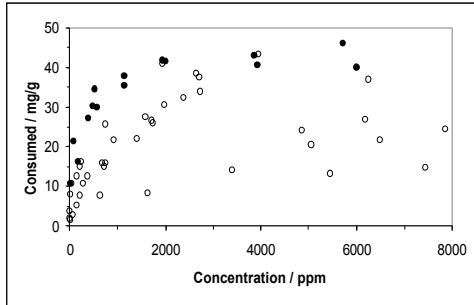


Figure 11. The adsorption of high molecular weight sodium lignosulphonate to the hydration products $\text{Ca}(\text{OH})_2$ (filled) and ettringite (open).

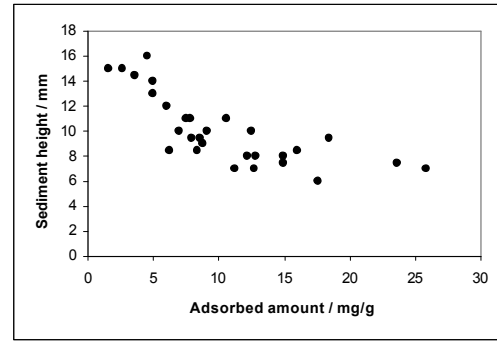


Figure 12. The relationship between adsorbed amount and sediment height for high molecular weight sodium lignosulphonate on ettringite

High concentrations of ettringite gave increased viscosity [18]. Ettringite is formed rapidly during the reactions of aluminate with water and gypsum. Thus a good dispersion of ettringite is essential to keep a good flow of the mortar and concrete.

We noted that there was clear variation in the settling behaviour of these samples (see Fig. 12). More adsorbed lignosulphonate gives a thinner sediment layer, but also a slower sedimentation. A thick sediment shows a flocculated structure with much trapped water. A thin, and dense sediment indicates that the lignosulphonates have broken the floc structure. This very effectively reduces the particle volume fraction, and thus decreases the viscosity of the system. When the flocs are broken the particles are smaller, and we would expect a slower settling as well. The effect is difficult to quantify though, as the flocs also will contain trapped water, thus the density will effectively decrease. The adsorption to the ettringite phase and dispersion of this is probably important for keeping the system dispersed after the aluminate phases starts to react, and will thus be important for workability retention. We notice that above a certain adsorption (probably when all flocs are broken) there is no lowering of the sediment height.

3.7 Calcium hydroxide isotherms

Fig. 11 shows, that the hydration product calcium hydroxide also adsorbed the lignosulphonate. This is in accordance with previous work [2]. The adsorption is strong. With a zeta-potential of +33.5 mV for $\text{Ca}(\text{OH})_2$ in saturated lime [19] solution this is as expected. The higher zeta potential of $\text{Ca}(\text{OH})_2$ compared to ettringite (+33.5 mV vs. +5 mV) is also reflected in a stronger affinity for the lignosulphonate (b $5.27 \cdot 10^{-3} \text{ ppm}^{-1}$ for $\text{Ca}(\text{OH})_2$ vs. $9.75 \cdot 10^{-4} \text{ ppm}^{-1}$ for ettringite).

3.8 Setting times

Fig. 13 shows the retardation for concrete with different dosages of lignosulphonate. The retardation is the increase in setting time compared to a sample without any plasticizer. We here see two clear, straight lines. At low doses there is a small increase in setting time with increasing dosage. Here most of the lignosulphonate adsorbs to the aluminate phases and only a small

non-adsorbing amount is available to interfere with the hydration of the silicate phases. At higher doses there is a much faster increase in retardation with increased dosage. In this regime the aluminates phases are fully covered with lignosulphonates, and all excess lignosulphonate are available to interfere with the hydration of the silicate phases. A similar mechanism has recently been proposed for the polycarboxylate superplasticizers [20].

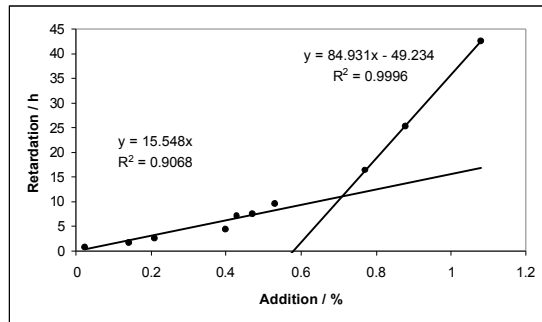


Figure 13. The retardation vs. concentration for high molecular weight sodium lignosulphonate.

The interference of calcium lignosulphonate with the C_3S hydration has been described previously. 0.1% calcium or sodium lignosulphonate lead to a 1.5-2h delay in the C_3S hydration, 0.25% calcium lignosulphonate gave a retardation of ~7 hours [13]. We see that the retardation of cement hydration at high lignosulphonate dosages clearly mirrors that found for the silicate phase at lower dosages.

4 Discussion

When suspended in water the cement minerals will partially dissolve, and the surfaces gain a charge (as measured through their zeta-potential). The charge is different for the different clinker minerals. The C_3A/C_4AF phases are positively charged, while the C_3S/C_2S phases are negatively charged [11, 21]. The overall zeta potential found for cement varies between different studies some find a positive potential other a negative potential, while the absolute value is always small. The variation can be explained by variations in composition of the different cements, specially the surface composition.

Due to the electrostatic interactions different charges at different parts of the surface will attract each other. We will thus build up a large structure, much like the well known house-of-cards structure kaolin makes. This structure will give a high yield value of the system as the structure must be physically broken before the system can flow freely. The workability of concrete, as measured by the slump test, correlates well with the yield point for the concrete.

The lignosulphonates adsorb first to the positively charged areas of the surface. This cancels the positive charges on the C_3A/C_4AF parts of the surface or even reverses them to negative charge. With only negative charge on the surface the extended structure breaks down. The yield point is greatly reduced, and the workability is improved. This explains why the dosage of lignosulphonates (or any other plasticizer) is much smaller than that needed for full surface coverage. Only the positively charged areas need to be

covered. It is agreed in the literature that lignosulphonates interact strongly with the aluminate phases. This is also what we find. This interaction is wanted and contributes to the workability of the concrete mixes. We also find that lignosulphonates adsorb strongly to the hydration products calcium hydroxide and ettringite. For the ettringite we can also clearly see how this breaks the flocs. This will probably contribute to the workability retention.

Not all of the lignosulphonate adsorbs to the C_3A/C_4AF part of the surface. Some remain in solution. The lignosulphonate left in solution will interact with the ions dissolved into the pore water. These ions will partially cancel the negative charges in the lignosulphonate molecule due to ion pairing. The lignosulphonate with cancelled charges can adsorb or precipitate also onto the C_3S/C_2S parts of the cement surface. We see that in pure water there is no adsorption of lignosulphonates to the silicate phases, but as soon as the solvent resembles the normal pore water we get a strong adsorption or precipitation. This will interfere with the normal hydration of the surface and causes the retardation of the setting.

To obtain a good non-retarding plasticizer for concrete we need a lignosulphonate that adsorbs strongly, and nearly completely, to the aluminate phases. There will then be little material left to interfere with the hydration of the silicate phases. A slowing down of the hydration of the silicate phases will give a dramatic increase in the setting time for the concrete. The adsorption to ettringite is not very strong, thus ettringite will be less efficient than the silicate phases in competing for the remaining lignosulphonate. Thus the lignosulphonate that is not already consumed by the aluminate phases will, to a large extent, be adsorbed by the silicate phases.

5 Conclusions

There is strong adsorption to aluminate phases but less to the hydration product ettringite. The adsorption does not seem to have a significant effect on the hydration reaction of the aluminate phases. Lignosulphonates adsorbed to the aluminate phases give increased workability, while excess lignosulphonates adsorbed to the silicate phase, or its hydration products causes retardation. Adsorption to silicate phases more or less completely stops the formation of new surface. There is a strong adsorption to the hydration product calcium hydroxide.

References

- [1] D. R. Rossington and E. J. Runk, Adsorption of Admixtures on Portland cement hydration products, J. Am. Ceramic Soc. 51(1) (1968), 46-50
- [2] V. S. Ramachandran, Interaction of calcium lignosulfonate with tricalcium silicate, hydrated tricalcium silicate, and calcium hydroxide, Cement Concrete Res. 2 (1972) 179-194
- [3] V. S. Ramachandran, Elucidation of the role of calcium lignosulfonate in the hydration of C_3A , 7th International Congress on the Chemistry of Cement, Paris (1980) Septima pg. 535-540

- [4] V. S. Ramachandran, and R. F. Feldman, Effect of calcium lignosulfonate on tricalcium aluminate and its hydration products, *Materiaux et Constructions* 5(26) (1972), 67-76
- [5] S. Monosi, G. Moriconi, M. Pauri and M. Collepari, Effect of retarding admixtures on the Portland cement hydration, , 8th International Congress on the Chemistry of Cement, Rio de Janeiro (1986) pg. 130-135
- [6] B. Blank, D. R. Rossington, and L. A. Weinland, Adsorption of admixtures on Portland cement, *J. Am. Ceramic Soc.* 46(8) (1963) 395-399
- [7] F. M. Ernsberger and W. G France, Some physical and chemical properties of weight-fractioned lignosulfonic acid, including the dissociation of lignosulfonates, *J. Phys. Colloid Chem* 52 (1948) 267-276
- [8] B. O. Myrvold , Adsorption of Lignosulphonates on Cement and the Hydration Products of Cement 8th CANMET/ACI International Conference on Superplasticizers and other Chemical Admixtures in Concrete, Sorrento (2006) SOR-58
- [9] B. O Myrvold, J. Gustafsson and K. Reknes, Adsorption studies on cement and cement model compounds. 11th International Congress on the Chemistry of Cement, Durban (2003) pg. 217-226
- [10] C. Geffroy, J. Persello, A. Foissy, B. Cabane, and F. Tournilhac, The frontier between adsorption and precipitation of polyacrylic acid on calcium carbonate, *Rev. L'Institute Franc. Petrole* 52(2) (1997)183-190.
- [11] J. Planck, personal communication
- [12] F. Massazza, U. Costa and A. Barrila, Adsorption of superplasticizers on calcium aluminate monosulfate hydrate,pg 499-514 in V. M. Malhotra, *Developments in the use of superplasticizers*
- [13] V. Lorprayoon and D. R. Rossington, Early hydration of cement constituents with organic admixtures, *Cement Concrete Res.* 11 (1981) 267-277
- [13] J. Y. Moon, K. S. Han and S. H. Choi, Effect of calcium lignosulfonate on the early hydration process of Portland cement,, *Congresso Internacional de Quimica do Cimento* (8: Rio de Janeiro: 1986). Rio de Janeiro, (1986) 204-210
- [14] V. S. Ramachandran, Differential thermal investigation of the system tricalcium silicate – calcium lignosulfonate – water in the presence of tricalcium aluminate and its hydrates, *Thermal Analysis* 2 (1971) 255-261
- [15] M. Y. A. Mollah, Wenhong Yu, R. Schennach and D. L. Cocke, A Fourier transform infrared spectroscopic investigation of the early hydration of

Portland cement and the influence of sodium lignosulphonate, Cement Concrete Res. 30 (2000) 267-273

[16]. I. Odler and Th. Becker, Effect of some liquefying agents on properties and hydration of Portland cement and tricalcium silicate pastes, Cement Concrete Res. 10 (1980) 321-331

[17] W. C. Hansen, Interactions of organic compounds in Portland cement pastes, J. Materials JMLSA 5(4) (1970) pg 842-855

[18] M. Michaux and E. B. Nelson, Flash-set behaviour of oil well cement slurries containing lignosulphonates. 9th International Congress on the Chemistry of Cement, (1992) pg. 584-590

[19] D. M. Roy and M. Daimon, Effects of admixtures upon electrokinetic phenomena during hydration of C_3S , C_3A and cement, 7th International Congress on the Chemistry of Cement, Paris (1980) Septima pg. 242-246

[20] G. H. Kirby, and J. A. Lewis, Comb polymer architecture effects on the rheological property evolution of concentrated cement suspensions, J. Am. Ceram. Soc. 87(9) (2004) 1643-1652

[21] T. Sebök and O. Stráenel, Relationships between the properties of lignosulphonates and parameters of modified samples with cement binders. Part II. Study of relationships between molar parameters of lignosulphonates and characteristics of the samples tested, Cement Concrete Res. 29 (1999) 591-594