EFFECT OF CALCIUM CHLORIDE AND CITRIC ACID ON THE HYDRATION OF C_3S AND βC_2S PASTES

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1. Introduction

Cement hydration can be influenced by admixtures. According to VAVRIN [1], accelerating agents are either acids, or salts of strong bases, or alkalic salts of weak acids such as Na, K and Ca chlorides, sulphates and nitrates, carbonates, aluminates, K and Na silicates. The most effective accelerator is $CaCl_2$, superimposing its accelerating effect to that of steam curing at 60°C. As early as by the late 1800's it has been stated that from the aspect of high early strength, 1% pure calcium chloride solution was the most efficient [3].

The opinions on the accelerator effect are still not uniform. Catalysation effect of $CaCl_2$ on C_3S and βC_2S hydration without modifying the final product composition has been demonstrated by KURCZYK and SCHWIETE [4] for the case of natural hardening and by BALÁZS and TAMÁS [2,5] for steam curing. Others stated the $CaCl_2$ to be adsorbed on the C_3S surface reducing the alkalinity of the liquid phase, accelerating in turn the C_3S hydrolysis. Also the C/S ratio in the CSH has been stated [1] to change upon accelerator admixture.

Setting retarders include lignin sulphonates, sugar, methyl cellulose, borax, tartaric acid, sodium phosphate, silico-fluorids, gluconic acid, citric acid and certain accelerators in high concentration. The citric acid retarder under Hungarian patent produces the 6-h retardation generally required in concrete technology in a dosage as low as 0.1%. TAMÁS [6] generalized earlier statements on setting control admixtures. Zinc oxide tests by LIEBER [7] showed the early strength to be significantly reduced but the final strength to be increased by about 20%. WALZ and MATHIEU made similar observations [8]. Texture examinations by RICHARTZ [9] showed admixture of 1% zinc oxide to produce 10 to 30 mm silicate hydrate whiskers in the C_3S paste. RICHARTZ and LOCHER [10] came to the final conclusion that setting acceleration brings about shorter, setting retardation longer whiskers, these latter being preferable from the aspect of final strength.

These precedences induced us to test the problem little investigated to our knowledge, how strength of C_3S and βC_2S pastes of different grinding finenesses depends on the $CaCl_2$ and citric acid dosage.

2. Experimental

Clinker minerals C_3S and βC_2S grown by Dr. M. Kovács at the Veszprém University of Chemical Engineering have been ground to different finenesses and made to cubes with 20 mm sides for cube strength tests and to 10 by 10 by 50 mm prisms for prism strength tests with 30% of mixing water, varying $CaCl_2$ and citric acid admixture dosages.

Paste specimens were cast in steel moulds, stripped at 24 h to be stored at 100% r.h. Hydration water content has been determined by derivatography and also paste compactness development with time has been examined.

3. Test results and conclusions

28-day cube strength as a function of $CaCl_2$ dosage and grinding fineness of silicate minerals is seen in Fig. 1. Cube strengths of C_3S pastes were invariably higher than those of βC_2S pastes, but while strength vs. grinding fineness dif-

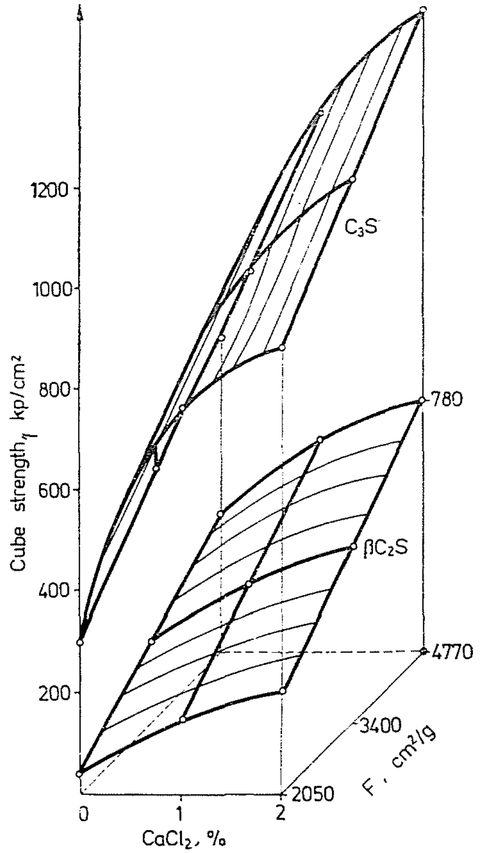

Fig. 1. Effect of $CaCl_2$ on cube strength of C_3S and βC_2S pastes

ferences were nearly constant, for higher $CaCl_2$ dosages, strength of C_3S pastes grew abruptly from 0 to 1%, and moderately from 1 to 2%, while for βC_2S pastes it grew about linearily with $CaCl_2$ dosage.

Comparison of kinetic curves of both silicate minerals shows nearly constant cube strength differences at 28 to 90 days of age, independent of specific surface and $CaCl_2$ dosage, while for chloride-admixed βC_2S pastes, cube strength grew two or even three times faster than for C_3S pastes and increased with $CaCl_2$ content. This phenomenon is attributed to the differences partly between the initial structural compactnesses of both silicate minerals and partly between the hydration product morphologies. Hydration and hardening velocities of βC_2S are known to be much lower than those of C_3S — especially for low grinding finenesses — to achieve the 90-day strength of C_3S only at about 360 days of age. Namely, compact texture of βC_2S prevents hydration from starting earlier than at 28 days. From this time its cube strength grows faster than does that of C_3S (with greater corresponding differences), still

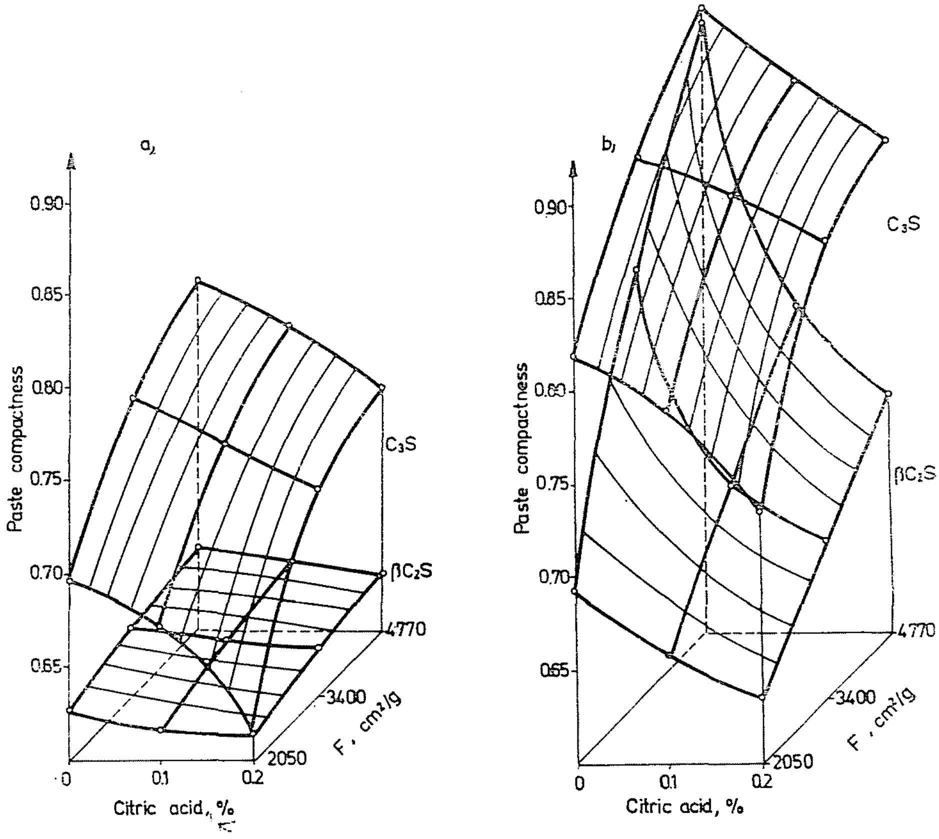

Fig. 2. Effect of citric acid on cube strength of C_3S and βC_2S pastes *a)* at 28 days; *b)* at 360 days

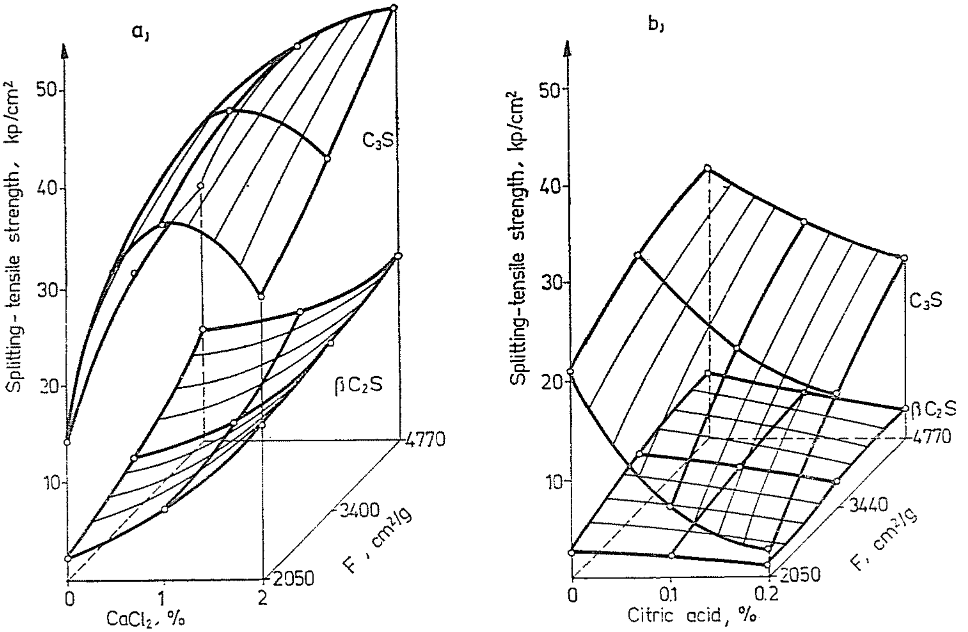

Fig. 3. 28-day splitting-tensile strength vs. clinker mineral grinding fineness and *a)* $CaCl_2$; *b)* citric acid

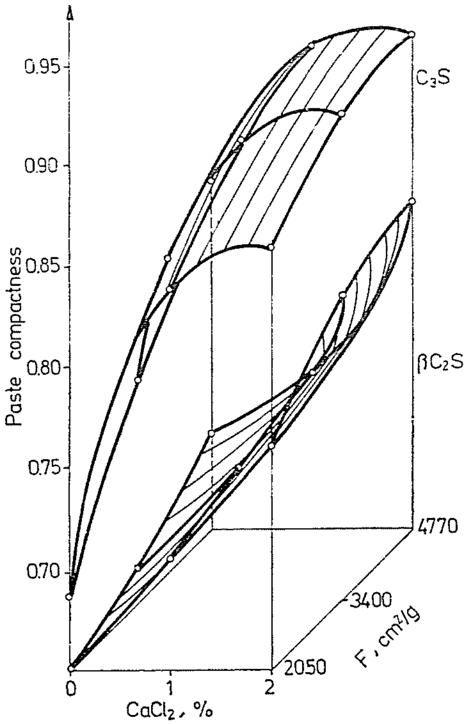

Fig. 4. 28-day compactnesses of $CaCl_2$-admixed C_3S and βC_2S pastes

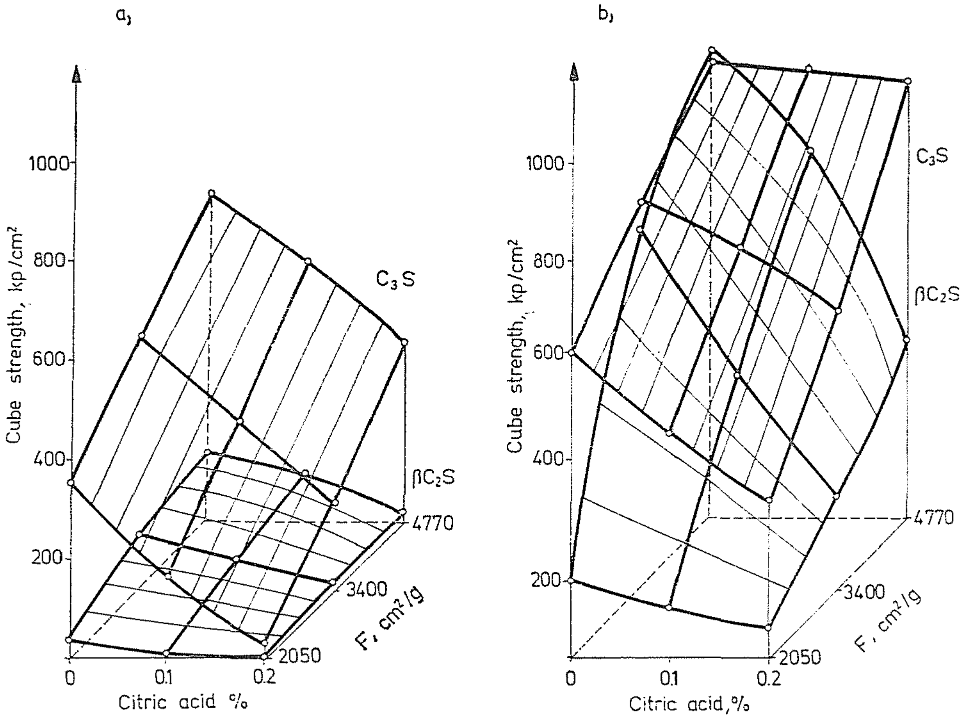

Fig. 5. Compactnesses of citric acid-admixed C_3S and βC_2S pastes at *a)* 28 days; *b)* 360 days

enhanced by the strength-reducing effect of crystalline portlandite released by C_3S hydration. Portlandite (or better $Ca(OH)_3$) released according to the reaction equation of βC_2S hydration is not crystalline. It cannot be demonstrated by thermal or X-ray methods, but — according to the recent theory by LOCHER and RICHARTZ [11] supported by our test results — it fills out the space between tobermorite whiskers of pseudohexagonal position and adds thereby to strength.

28-day (*a*) and 360-day (*b*) cube strength values of citric acid-admixed silicate pastes are seen in Fig. 2. Apparently, 28-day strength increased with that of grinding fineness and strength decrease upon citric acid admixture was much higher for C_3S pastes than for βC_2S pastes with the same characteristics. At 360 days, these differences are seen in Fig. 2*b* to be about equalized. The cube strength of C_3S pastes of high initial specific surface even hardly decreased for higher citric acid dosages as against the important losses of βC_2S pastes.

Comparison of the corresponding values in kinetic curves shows the strength loss due to higher citric acid dosage to increase with decreasing grinding fineness of C_3S and inversely with increasing grinding fineness of βC_2S.

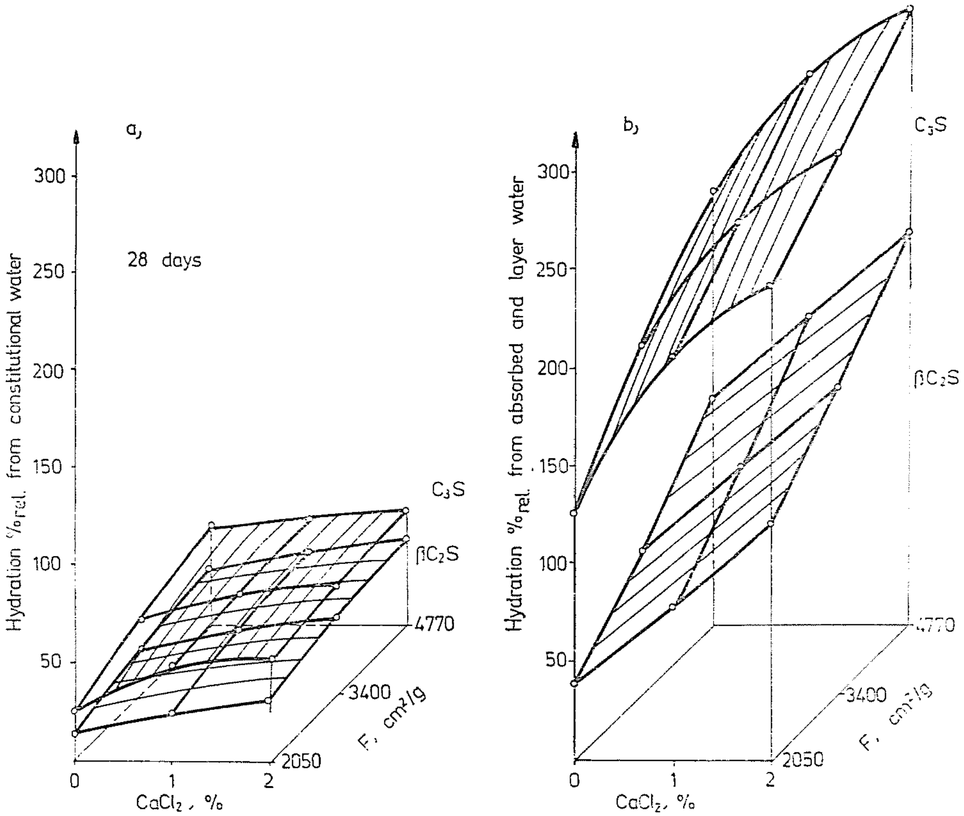

Fig. 6. 28-day hydration percentages of $CaCl_2$-admixed C_3S and βC_2S pastes computed from *a)* constitutional water content; *b)* absorption and layer water content

28-day splitting-tensile strength values of both silicate minerals have been plotted in Fig. 3 as a function of increasing grinding finenesses, of (*a*) $CaCl_2$ and (*b*) citric acid dosages. With increasing $CaCl_2$ the splitting-tensile strength of βC_2S pastes invariably grew but that of C_3S pastes only for high grinding finenesses. Fig. 3*b* points out that strength loss due to citric acid is much higher in C_3S than in βC_2S pastes, especially for high grinding finenesses.

Paste compactnesses at 28 days are seen in Fig. 4 for $CaCl_2$ admixture and in Fig. 5 for citric acid admixture, diagrams similar to those of cube strength.

Hydration of silicate minerals with admixtures is best compared by *hydration percentages*. 28-day hydration percentages computed from constitutional water content (*a*) and adsorption and layer water content (*b*) are seen in Fig. 6 as a function of $CaCl_2$ dosage and silicate mineral grinding fineness. Hydration rates of both silicate minerals are seen to develop similarly (Fig. 6*a*). Neither curve slopes differ significantly. Hence hydration mechanisms seem to be identical. Also the hydration percentage of C_3S pastes is higher than

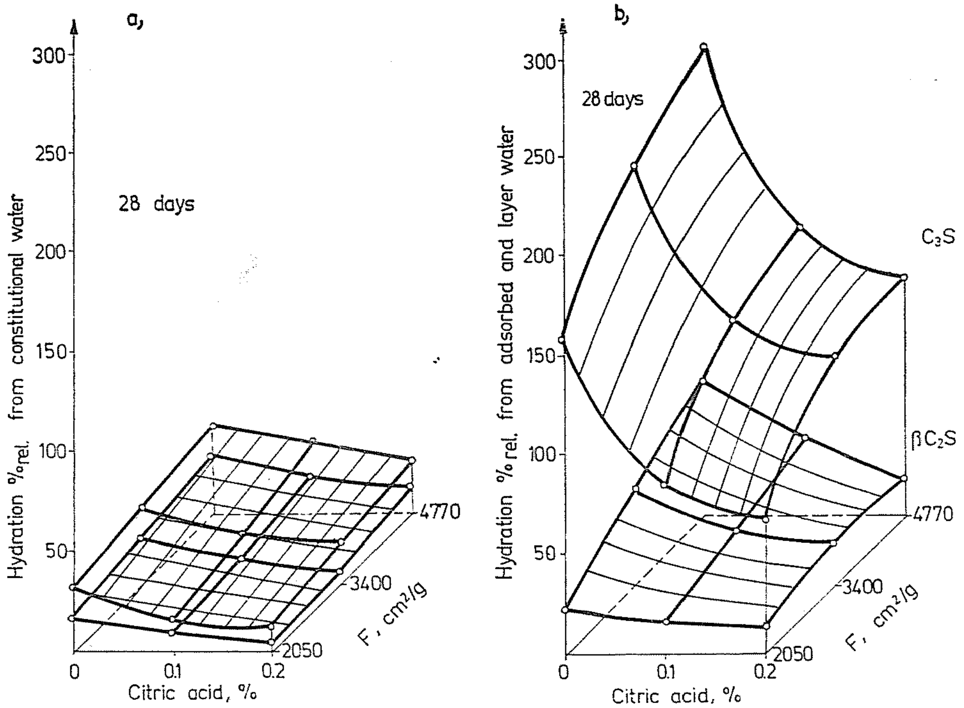

Fig. 7. Hydration percentages of citric-acid-admixed C_3S and βC_2S pastes computed from *a)* constitutional water content; *b)* adsorption and interstitial water content

that of otherwise similar βC_2S pastes achieving the former percentage as late as at 360 days. On the other hand, hydration percentages computed from adsorption and layer water (Fig. 6*b*) exhibit extreme differences between corresponding values $(\sim 120\%_{\mathrm{rel}})$, while βC_2S paste hydration percentages computed from adsorption and layer water lag far behind the corresponding values of otherwise similar C_3S pastes. This phenomenon is attributed to the initial texture compactness differences between the two silicate minerals. C_3S is of looser texture, and can adsorb more water on surface and between layers than the much compacter βC_2S.

The same is true of silicate pastes admixed with citric acid (Fig. 7) excepted that increasing the citric acid percentage reduces the hydration percentage.

Summary

Hardening and hydration kinetics of silicate minerals C_3S and βC_2S in dependence of grinding fineness and setting control admixtures ($CaCl_2$ and citric acid) were examined and seen the cube strength of both to increase upon $CaCl_2$ admixture, the increase being higher for C_3S than for βC_2S, while for increasing grinding finenesses the latter exhibited twice and even three times the strength increase of the former. More of citric acid admixture reduced the cube strength; the higher the grinding fineness of C_3S and the lower of βC_2S, the greater the loss. The tendency of splitting-tensile strength was similar to that of cube strength.

The differences between hardening kinetics of both silicate minerals are attributed partly to different initial compactnesses, and partly to different hydration product morphologies.

Irrespective of the setting control admixture, the similarity of hydration percentages of both silicate mineral pastes suggests the identity of hydration mechanisms.

Increased hydration percentage of C_3S paste computed from adsorption and interstitial water content is due to the looser texture, enabling it to adsorb more surface and layer water, irrespective of the grinding fineness, than the much compacter βC_2S paste.

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