Supporting information for:
Elastic Response of Cementitious Gels to Polycation addition

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S1. Sample preparation for adsorption measurements

Prior to the chemical analysis, part of the supernatant was filtered through 0.1 µL millipore filter and then diluted with freshly distilled water to obtain 10 mL of solution to ensure a solute concentration lower than 500 ppm. The so obtained samples were then acidified by the addition of 200 µL of orthophosphoric acid (50 % vol.) and hydrochloric acid (50 % vol.) for TOC and ICP-OES analysis, respectively. The adsorbed amounts of solutes were then deduced from subtracting the content of solutes remaining in the supernatant from the added amount of solutes in the initial suspensions. The specific surface area of C-S-H is difficult to determine properly. Instead, the adsorption were reported as a mass ratio. That is, the adsorption was defined as the amount of adsorbate, normalized by the mass of the adsorbent, as a function of its equilibrium concentration in the bulk.

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S2. Additional adsorption data

Figure S1: Adsorption isotherms for various polyactions in C-S-H suspensions (L/S = 50) at various initial calcium concentrations. (a) Linear polycations ($M_w = 4,000$ g/mol) (b) Linear polycations ($M_w = 42,000$ g/mol) (c) Linear polycations ($M_w = 400,000$ g/mol) (d) Branched polycation (Acryllic acid/Ammonium acrylate copolymer). The data points are averages obtained from three independent experiments. The full lines are best fit to the experimental data with a Langmuir equation, see the main text.
Figure S2: Evolution of the bulk calcium concentration as a function of the amount of polycations introduced. (a) Linear polycations ($M_w = 4,000$ g/mol) (b) Linear polycations ($M_w = 42,000$ g/mol) (c) Linear polycations ($M_w = 400,000$ g/mol) (d) Branched polycation (Acryllic acid/Ammonium acrylate copolymer). The data points are averages obtained from three independent experiments. The full lines are guide to the eyes.
Figure S3: Calcium (dashed line) and linear polycation (full line) adsorption on C-S-H (in millimole equivalent per mole of Si in C-S-H) as a function of the amount of linear polycation introduced ($M_w = 8500$ g/mol) at different initial concentration of Ca(OH)$_2$. Note that in the case of Ca$^{2+}$ we only report the apparent adsorption. The latter is calculated from the difference between the bulk calcium concentration at the polymer saturation (i.e. the plateau value in Figure 3, and that of without polymer.)
S3. SAXS measurements and data

The structural aspect of the C-S-H gels with and without polymer was analyzed by small X-Ray scattering (SAXS) measurements at the SWING beamline of the French synchrotron source SOLEIL (Soleil, Saint Aubin, France). Experiments were carried out at an energy of 15 keV with a sample to detector distance of 6.5 m, using the 2D AVIEX CCD detector. Data were normalized to take into account the beam decay, detector sensitivity, and sample transmission. The parasitic scattering intensity (cell windows and air) was subtracted from the total scattering intensity. The radial integration of the 2D SAXS at SWING was performed using the FOXTROT software developed at Soleil. Intensities were subsequently converted to absolute units using a sample of water as reference. SASfit\textsuperscript{S1} 0.93.3 software was used for analyzing and plotting small angle scattering curves.

![Figure S4: SAXS scattering intensity versus scattering vector for C-S-H dispersions at various Ca(OH)\textsubscript{2} concentrations. The full lines are best fit to the experimental data according to eq. 1.](image)

The obtained Intensity versus scattering vector curves, $I = f(q)$ for pure C-S-H gels are given in Figures S4 within a total $q$ range of 0.0055-0.2 nm\textsuperscript{-1}. They show similarities with
those collected in the work of Nicoleau et al.\textsuperscript{S2} That is, at small $q$ ($q < 0.02$ nm$^{-1}$), the curves exhibit a hump, which can be associated with the size of the platelets; and at large $q$ ($q > 0.02$ nm) $I$ strongly increases with decreasing $q$ indicating the presence of aggregates.

To facilitate the interpretation of the SAXS pattern, the scattering intensities were fitted with SASfit using a Beaucage model.\textsuperscript{S3,S4} The latter models both the Guinier and Porod regions with a smooth transition between them with the following function,

$$I(q) = G_l \exp \left(\frac{-q^2 R_l}{3}\right) + B \exp \left(\frac{-q^2 R_s}{3}\right) \left(\frac{\text{erf}(qkR_l/\sqrt(6))}{q}\right)^{D_l} + G_s \exp \left(\frac{-q^2 R_s}{3}\right) \left(\frac{\text{erf}(qkR_s/\sqrt(6))}{q}\right)^{D_s}$$

(1)

where subscript $s$ and $l$ stands for small and large structures, $R$ is the radius of gyration of the structures, $D$ is the scaling exponent of the power law assigned to the structures, $G$ is the Guinier prefactor, $B$ is a prefactor and $k$ is a constant.

**Table S1: Beaucage fit parameters of the SAXS patterns of the pure C-S-H dispersions at various bulk concentrations of Ca$^{2+}$**

| $c_{Ca}^{bulk}$ (mM) | $R_l$ (nm) | $D_l$ | $R_s$ (nm) | $D_s$ |
|-----------------------|------------|-------|------------|-------|
| 1.4                   | 122        | 2     | 7.8        | 3     |
| 1                     | 135        | 1.9   | 8.2        | 3     |
| 4.7                   | 145        | 2     | 4.67       | 3.4   |
| 7.1                   | 299        | 2.5   | 7.09       | 3.6   |
| 18.1                  | $> 1000$   | 2.17  | 6.6        | 4     |
| 21.3                  | $> 1000$   | 1.98  | 7.4        | 3.7   |

Although limited, the Guinier approach is enough to clearly observe the build-up of large clusters, i.e. $R_l$ increases, and their densification, i.e. small increase in $D_l$, when the
bulk concentration of Ca(OH)$_2$ is increased, see Table S1.

The SAXS patterns of the C-S-H dispersions with linear and branched polycations at high bulk concentration of Ca(OH)$_2$ and the corresponding fitting parameters and given in Figure S5 and Tables S2-S3, respectively. As it can be seen, the addition of polycation has only a small impact on the overall structure of the dispersions.

**Table S2**: Beaucage fit parameters of the SAXS patterns of C-S-H dispersions at various amounts of added polymer. The C-S-H is in equilibrium with a high bulk concentration of Ca(OH)$_2$. Polymer: PDDA ($M_w = 400000$ g.mol$^{-1}$)

| $c_{\text{add polymer}}$ (g/L) | $R_l$ (nm) | $D_l$ | $R_s$ (nm) | $D_s$ |
|-------------------------------|------------|------|------------|------|
| 1                             | > 1000     | 2.4  | 8.1        | 3.6  |
| 2                             | > 1000     | 2.3  | 8.2        | 3.6  |
| 3                             | > 1000     | 2.3  | 9.8        | 3.5  |
| 4                             | > 1000     | 2.4  | 6.7        | 3.7  |
| 5                             | > 1000     | 2.3  | 9.1        | 3.6  |

**Table S3**: Beaucage fit parameters of the SAXS patterns of C-S-H dispersions at various amounts of added polymer. The C-S-H is in equilibrium with a high bulk concentration of Ca(OH)$_2$. Polymer: BCQUAT ($M_w = 200000$ g.mol$^{-1}$)

| $c_{\text{add polymer}}$ (g/L) | $R_l$ (nm) | $D_l$ | $R_s$ (nm) | $D_s$ |
|-------------------------------|------------|------|------------|------|
| 1                             | > 1000     | 2.1  | 7.9        | 3.2  |
| 2                             | > 1000     | 2.3  | 8.3        | 3    |
| 3                             | > 1000     | 2    | 7.8        | 3.3  |
| 4                             | > 1000     | 2    | 7.7        | 3.3  |
| 5                             | > 1000     | 2    | 8.0        | 3.2  |
Figure S5: SAXS scattering intensity versus scattering vector of C-S-H dispersions for various added amounts of (a) PDDA and (b) BCQuat polymers. The dispersions are in equilibrium with a high bulk concentration of Ca(OH)$_2$. The full lines are best fit to the experimental data according to eq. 1.
S4. Model and Simulations details

Simulations were performed with a Monte Carlo method in the Canonical ensemble (constant number of particles, volume and temperature), following the Metropolis procedure.\textsuperscript{S5} The equilibrium polymer configurations in the slit were sampled via polymer translations, rotations and internal crank shaft moves, the latter effectively relaxing the internal structure of the polymers. For branched polymers, an additional rotation of the side chains around the grafting point in the backbone was implemented. Within the PM the interaction energy, \( u(r) \), between any two charges separated a distance, \( r \), is then simply given by Coulomb's law:

\[
   u(r) = \begin{cases} 
   \frac{z_i z_j e^2}{4\pi\epsilon_0 \epsilon r}, & r > d \\
   \infty, & r \leq d
   \end{cases}
\]

(2)

where \( z_i \), \( e \) and \( \epsilon_0 \) stand for the valency of species \( i \), the elementary charge and the permittivity of vacuum. \( d \) is the distance of closest approach, below which the interaction energy is infinite, i.e., the monomers are treated as hard spheres. The Coulomb interaction acts between all charges in the simulation box with the minimum image convention and periodic boundary conditions\textsuperscript{S6, S7} applied in the directions parallel to the surfaces. Beside their mutual interactions, the charges in the system also interact with the charged infinite surface.\textsuperscript{S7, S8} The charged sheet method\textsuperscript{S9} was used to treat the long-ranged contributions of the Coulomb interactions. The temperature was set to 298 K. In order to facilitate the sampling of the monomer positions close to the walls, we introduced a soft repulsive potential \( V_S \) that acts between the monomers and the surfaces, given by:

\[
   V_S = w(z) + w(h - z)
\]

(3)

\[
   w(\xi) = C \left( \frac{e^{-\left(\frac{\xi}{\tau}\right)}}{\xi^3} \right)
\]

(4)

where \( \xi \) is the distance to the wall in the \( z \)-direction. The decay length \( \tau \), was set to 1 Å, and the pre-factor \( C \) was equal to 1000 Å\(^3\)kJ/mol. The numerical values of these parameters
were arbitrarily chosen and have no pronounced effect on the results. S10

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