VI. Aging of Gel

The chemical reactions that cause gelation continue long after the gelation point, producing strengthening, stiffening and shrinkage of the network.

For different mechanisms:
(A) Polymerization

Increase in connectivity of the gel network produced by condensation reactions

\[ \equiv \text{Si-OH} + \text{HO-Si} \rightarrow \equiv \text{Si-O-Si} + \text{H}_2\text{O} \]

Producing new bridging bonds \( \Rightarrow \) stiffening and strengthening the network
(B) Syneresis
Shrinkage of the gel network resulting in expulsion of liquid from pores

-Macroscopic Syneresis (Macrodyneresis)
The whole gel network shrinks as a result of the continuous condensation.
-Microsyneresis
Phase separation in which the polymers cluster together, creating regions of free liquid.
Driving force: greater affinity of the polymer for itself than for the pore liquid.

Effects of microsyneresis on the pore size distribution of a titania gel:
   a – 0 day
   b – 1 day
   c – 9 days
   d – 45 days
(C) Coarsening or Ripening

Dissolution and reprecipitation driven by differences in solubility (referred to Ostwald mechanism)

\[ S \text{ (positive curvature)} \geq S \text{ (negative curvature)} \]

Materials dissolve from the surface of particle with positive curvature and depositive in regions with negative curvature.

Dissolution and reprecipitation Causes growth of necks between Particles, increasing the strength and stiffness of the gel.
(D) Phase Transformation

Many gels or precipitates of hydrous oxides are amorphous as formed, but aging of the solution allows reorganization of the structure, resulting in a crystalline product.

Alumina Gel

\[ \text{Al butoxide} + \text{H}_2\text{O at room T} \rightarrow \text{Amorphous gel} \rightarrow \text{Bayerite Al(OH)}_3 \]

Aging 24h

Zirconia Gel

\[ \text{ZrCl}_4 + \text{H}_2\text{O} \rightarrow \text{Amorphous ZrO}_2 \rightarrow \text{Tetragonal ZrO}_2 \]

Aging at 90-116°C

Titania Gel

\[ \text{TiCl}_4 + \text{H}_2\text{O} \rightarrow \text{Amorphous TiO}_2 \rightarrow \text{Anatase TiO}_2 \]

Aging (tetragonal)
amorphous

crystalline
Driving Force For Shrinkage

◆ Chemical Reactions (Attraction Force)
The attraction force for the solid network results from condensation reactions between M-OH groups, i.e. formation of M-O-M bonds between solids. The chemical reactions are less important for their contribution to the driving force for shrinkage than for their impact on the mechanical properties of the gel.

Condensation reaction between M-OH

Formation of M-O-M bond

Improving mechanical property of the gel network

Small driving force for Shrinkage of gel network
**Disjoining Force (Repulsive Force)**

**Double-Layer Repulsion**

**Structural-Layer Repulsion**

Liquid molecules adopt a special structure in the vicinity of a solid surface, inhibiting close approach of surface, as they resist overlapping.

Orientation of water molecules around a charged hydrophilic surface. The molecules closest to each surface exhibit a diffuse layered structure; beyond that there may be some cooperative ordering.
Osmosis Forces

![Diagram of osmosis forces with notation for pressures and concentrations.]

Osmosis is a process of diffusion driven by a chemical potential gradient.

Side 1: \[ \mu_B^1 = RT \ln P_0 + \mu_0 \]

Side 2: \[ \mu_B^2 = RT \ln P_V + \mu_0 \]

\[ \frac{P_V}{P_0} = x_B < 1 \implies \mu_B^2 < \mu_B^1 \]
To increase $\mu_B^2$, one has to raise $P$ at side 2. The increase in $P$ in side 2: $\Delta P = \pi$

$$V_m \Delta P = \pi V_m = \mu_{B}^{1} - \mu_{B}^{2}$$

$$\pi = -\left(\frac{RT}{V_m}\right) \ln(x_B)$$

$V_m$: molar volume of the solvent B

For gel

If only liquid B can permeate out of the gel, but liquid A can not permeate into the gel, Will the gel swell?
Capillary Forces (Attraction Forces)

(a) Liquid film on solid surface has two interfaces with energies $\gamma_{SL}$ and $\gamma_{LV}$

(b) Contact angle $\theta$ is determined by balance of forces at intersection of solid-vapor and liquid-vapor interfaces

The change in energy, $\Delta E$, produced by spreading of a liquid film on a solid surface is

$$\Delta E = (\gamma_{SL} - \gamma_{LV}) - \gamma_{SV}$$

$\gamma$: specific energy of an interface (surface tension)
If $\Delta E \leq 0$, liquid spreads spontaneously (Fig. (a))

If $\Delta E > 0$, result is shown in Fig. (b).

Balance of tension in Fig. (b) gives:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

0° < θ < 90°

- water intrusion

90° < θ < 180°

- Hg intrusion
Capillary Pressure ($P_C$)

Liquid in saturated portion

Unsaturated portion with $P_C$

contraction

Change in the volume of solid $\Delta V$ (a positive value)

Work done by liquid in the contraction process:

$$W = -P_C \Delta V$$

(sign “-” means work done by solid on liquid)
The energy increase of liquid due to the covering of more solid surface:

$$\Delta U = (\gamma_{SL} - \gamma_{SV}) \Delta V \left( \frac{S_p}{v_p} \right)$$

$S_p$: specific surface area

$v_p$: pore volume

Since $\Delta U = -W$,

$$P_C = - (\gamma_{SV} - \gamma_{SL}) \left( \frac{S_p}{v_p} \right) = -\gamma_{LV} \cos \theta \left( \frac{S_p}{v_p} \right)$$

For $0 < \theta < 90^\circ$, $P_C < 0$
Capillary Tube

\[ P_1 - P_2 = \Delta P = P_C < 0 \]
\[ P_1 < P_2 \]

\[ S_p = 2\pi ah \quad v_p = \pi a^2 h \quad \Rightarrow \quad P_c = -\frac{2\gamma_{LV} \cos \theta}{a} \]

![Graph showing capillary pressure vs. pore radius](image)

\[ P_{out} = 1 \text{ atm} \]

\[ P_{in} - P_{out} = P_c < 0 \]
\[ \Rightarrow P_{in} < P_{out} \]