Sol-Gel methods

The sol-gel process may be described as:

"Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid."

A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid.

A gel consists of a three dimensional continuous network, which encloses a liquid phase. In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved.

The idea behind sol-gel synthesis is to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner.

Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds.

The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, be a gelation reaction.

Enables mixing at an atomic level.

Results in small particles, which are easily sinterable.

The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. A method was needed where dust was reduced (compared to the ceramic method) and which needed a lower sintering temperature. In addition, it should be possible to do the synthesis by remote control.
One of the well known examples of a sol-gel system often cited is quick clay. Clay may form a sol (quick clay) if it is washed sufficiently to remove the counter ions. Quick clay may be gelled if enough counter ions are added, so that the colloidal particles aggregate. (exfoliation/restacking may be involved)

Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films.

If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed.

If drying is performed under supercritical conditions, the network structure may be retained and a gel with large pores may be formed. This is called an aerogel, and the density will be very low. A record is $< 0.005 \text{ g/cm}^3$. 

\textbf{Figure 4-42.} Sol-gel processing options.
Physical properties of silica aerogels

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Density</td>
<td>0.003-0.35 g/cm³</td>
<td>Most common density is ~0.1 g/cm³</td>
</tr>
<tr>
<td>Internal Surface Area</td>
<td>600-1000 m²/g</td>
<td>As determined by nitrogen adsorption/desorption</td>
</tr>
<tr>
<td>% Solids</td>
<td>0.13-15%</td>
<td>Typically 5% (95% free space)</td>
</tr>
<tr>
<td>Mean Pore Diameter</td>
<td>~20 nm</td>
<td>As determined by nitrogen adsorption/desorption (varies with density)</td>
</tr>
<tr>
<td>Primary Particle Diameter</td>
<td>2-5 nm</td>
<td>Determined by electron microscopy</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>1.0-1.05</td>
<td>Very low for a solid material</td>
</tr>
<tr>
<td>Thermal Tolerance</td>
<td>to 500 C</td>
<td>Shrinkage begins slowly at 500 C, increases with inc. temperature. Melting point is &gt;1200 C</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td>2.0-4.0 x 10⁻⁶</td>
<td>Determined using ultrasonic methods</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.2</td>
<td>Independent of density. Similar to dense silica.</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>10⁶-10⁷ N/m²</td>
<td>Very small (&lt;10⁵x) compared to dense silica</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>16 kPa</td>
<td>For density = 0.1 g/cm³.</td>
</tr>
<tr>
<td>Fracture Toughness</td>
<td>~0.8 kPa*m¹/²</td>
<td>For density = 0.1 g/cm³. Determined by 3-point bending</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>~1.1</td>
<td>For density = 0.1 g/cm³. Very low for a solid material</td>
</tr>
<tr>
<td>Sound Velocity Through the Medium</td>
<td>100 m/sec</td>
<td>For density = 0.07 g/cm³. One of the lowest velocities for a solid material</td>
</tr>
</tbody>
</table>

Applications and properties of aerogels
Example of a ceramics fiber (PZT) made from sol-gel methods

**PZT, PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3}**

There are many applications of sol-gel synthesis. The method may provide good control over stoichiometry and reduced sintering temperature. This is especially important if one of the components is volatile. May also enable production of low-temperature phases.

PZT (PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3}) is a very important material. The largest piezoelectric response is obtained for x = 0.47. The stoichiometry is difficult to control by the ceramic method, where heating at \( \approx 100^\circ C \) for several hours is needed.
**Sol**

A sol consists of a liquid with colloidal particles which are not dissolved, but do not agglomerate or sediment. Agglomeration of small particles are due to van der Waals forces and a tendency to decrease the total surface energy. Van der Waals forces are weak, and extend only for a few nanometers. In order to counter the van der Waals interactions, repulsive forces must be established. May be accomplished by:

**Electrostatic repulsion.** By adsorption of charged species onto the surface of the particles, repulsion between the particles will increase and agglomeration will be prevented. Most important for colloidal systems.

**Steric hindrance.** By adsorbing a thick layer of organic molecules, the particles are prevented from approaching each other reducing the role of the van der Waals forces. Works best in concentrated dispersions. Branched adsorbates works best. Usual for nanomaterials.

![Diagram of sol particles with organic layers](image)

**PZC, Point of zero charge**

Stabilization due to electrostatic repulsion are due to formation of a double layer at the particle. The surface of a particle is covered by ionic groups, which determines the surface potential. Counter ions in the solution will cover this layer, shielding the rest of the solution from the surface charges.

For hydroxides the surface potential will be determined by reactions with the ions $\text{H}^+$ and $\text{OH}^-$. Thus, the surface potential is pH dependent.

\[
\text{M-OH} + \text{H}^+ \rightarrow \text{M-OH}_2^+ \\
\text{M-OH} + \text{OH}^- \rightarrow \text{M-O}^- + \text{H}_2\text{O}
\]

The pH where the particle is neutral is called PZC, point of zero charge.

For $\text{pH} > \text{PZC}$ the surface is **negatively** charged

For $\text{pH} < \text{PZC}$ the surface is **positively** charged.

Typical values: $\text{MgO 12, Al}_2\text{O}_3$ 9.0, $\text{TiO}_2$ 6.0, $\text{SnO}_2$ 4.5, $\text{SiO}_2$ 2.5

Depends somewhat on the size of the particle and the degree of condensation

The size of the surface potential $\phi_0$ depends on the difference between pH and PZC.
**Double layer**

Double layer for a positively charged surface

![Diagram of electric double layer](image)

In an electric field the particle will move toward the electrode with the opposite charge. It will carry the adsorbed layer and part of the counter ions.

The “slip plane” divides the part that moves with the particle and the solution. The potential at the slip plane is called the zeta ($\zeta$) potential $\phi_\zeta$.

The pH for which $\phi_\zeta=0$ is called the isoelectrical point (IEP)

The stability of a colloid depends on $\phi_\zeta$: the larger the $\phi_\zeta$, the more stable the colloid. Should be $>30-50$ mV.

Given the same surface potential, the repulsive forces will increase with the particle size.

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**Coagulation/flocculation**

Coagulation of a sol may occur if:

The surface potential ($\phi_0$) is lowered (by changing pH)

By increasing the number of counter ions. An increase in the concentration of counter ions result in a decrease of the thickness of the double layer.

In some cases a coagulated colloid may be re-dispersed. This is called “peptizing”

This is done e.g. by removing the surplus counter ions by washing, or by adding charged ions, so that the double layer is restored.
Silicates

Silicates form gels easily because it is not very electropositive and not susceptible to nucleophilic reactions. A sol-gel process occur in several steps:

• Hydrolysis and condensation of molecules. Formation of a sol.
• Gelation (sol-gel transformation)
• Ageing.
• Drying.

Hydrolysis and condensation

The starting point for formation of a silica gel may be alkoxides or silanols. These are reacted to siloxane groups.

![Chemical structures](image)

**Figure 4-48.** Silicon–oxygen groups relevant to sol–gel processing.

\[ \equiv \text{Si–OR} + \text{H}_2\text{O} \rightarrow \equiv \text{Si–OH} + \text{ROH} \]  
Hydrolysis

\[ \equiv \text{Si–OH} + \equiv \text{Si–OR} \rightarrow \equiv \text{Si–O–Si} \equiv + \text{ROH} \]  
Condensation

\[ \equiv \text{Si–OH} + \equiv \text{Si–OH} \rightarrow \equiv \text{Si–O–Si} \equiv + \text{H}_2\text{O} \]
Silica gel

The starting materials for formation of silica gels are usually “water glass”, \( \text{Na}_2\text{SiO}_3 \), or silicon alkoxides (e.g. \( \text{Si(OMe)}_4 \)). The differences are:

- Water glass is dissolved in water while the alkoxide is dissolved in an organic solvent, usually alcohol.
- The reactive groups in water glass are silanol. In the alkoxide system, a hydrolysis reaction occurs, converting Si-OR to Si-OH. Gelation therefore starts with a change in pH (in water-based systems) or by addition of water (in alcohol-based systems).
- The alkoxide systems are more complex with more parameters. This may result in better control of the reactions.

Two reaction paths; acidic and basic environments:
At pH < PZC the species are positively charged
At pH > PZC the species are negatively charged

Reactions in acidic environments

The oxygen atom in Si-OH or Si-OR is protonated and H-OH or H-OR are good leaving groups. The electron density are shifted from the Si atom, making it more accessible for reaction with water (hydrolysis)) or silanol (condensation)

\[
\begin{align*}
\equiv \text{Si} - \text{O}X + H^+ & \rightleftharpoons \equiv \text{Si} - \text{O}^+ \text{H}^- \quad \text{X = R, H} \\
\text{Y-OH} + \equiv \text{Si} - \text{O}^+ \text{H}^- & \rightarrow \text{Y-O-Si} \equiv + \text{HOX} \\
\text{Y = H, Si} & \equiv \\
\text{hydrolysis reaction:} & \quad X = \text{R, Y = H} \\
\text{condensation reaction:} & \quad X = \text{R or H, Y = Si} \equiv
\end{align*}
\]
Reactions in basic environments

Nucleophilic attack by OH\(^-\) or Si-O\(^-\) on the central Si atom. These species are formed by dissociation of water or Si-OH. The reactions are of SN2 type where OH\(^-\) replaces OR\(^-\) (hydrolysis) or silanolate replaces OH\(^-\) or OR\(^-\) (condensation).

$$\equiv\text{Si-OX} + \text{YO}^- \rightleftharpoons \left[ \begin{array}{c} \text{OY} \\ \equiv\text{Si} \\ \text{OX} \end{array} \right] \rightleftharpoons \text{Y-O-Si} = + \text{XO}^-$$

Y = H, Si

hydrolysis reaction: X = R, Y = H
condensation reaction: X = R or H, Y = Si

Reactions are reversible

When using silicon alkoxides, acid or base must be used to catalyze the reactions

Figure 4-49. Some initial intermediates during sol–gel processing of Si(OR)\(_4\). Note that each intermediate can, in principle, undergo either hydrolysis or condensation reactions.
Condensation

The condensation process is dynamic, and may be steered in the desired direction by adjusting the proper parameters. Parameters which influences the condensation process:

- Type of precursor
- The ratio between alkoxide and water ($R_w$)
- Type of catalyst used
- Type of solvent
- Temperature
- pH
- Relative and absolute concentrations of the reactants.

The stability and reactivity of the silicon alkoxides are influenced by a steric factor. Bulky ligands slow down the hydrolysis:

Reactivity: $\text{Si(OMe)}_4 > \text{Si(OEt)}_4 > \text{Si(OnPr)}_4 > \text{Si(OiPr)}_4$

Condensation, parameters

The electron density on Si will influence the reaction rate.

$\text{Si-R} > \text{Si-OR} > \text{Si-OH} > \text{Si-O-Si}$

Acid catalyzed reaction demands high electron density
Base catalyzed reaction demands low electron density

This results in:
Acid catalyzed: more straight chains
Base catalyzed: more branched network

The water ratio, $R_w$. (OR/H₂O)

$$\text{Si(OR)}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{ROH}$$

The reaction states that a water ratio of $R_w = 2$ (OR/H₂O) is neede to convert everything to SiO₂. A water ratio of $R_w=1$ leads to complete hydrolysis but no condensation.

Increasing the water content (i.e. lower $R_w$) will reduce condensation
Reducing the water content increases the condensation
**Condensation, parameters**

**pH:** The dependence of the reaction rate with pH is different for acid and base catalyzed systems.

A minimum for hydrolysis is observed at pH = 7 and for condensation at pH = 4.5 (IEP for silica). The sol particles may be reached without an electrostatic barrier.

**Solvent:** The polarity, dipolar moment, viscosity, protolytic/non protolytic properties are important for the reactions taking place. Polar solvents stabilize polar gels by hydrogen bonding. Non-polar solvents are better for systems which are not completely hydrolyzed.

---

**The water glass system**

Three pH intervals:

**pH < 2:**
The species are positively charged and the reaction rate is proportional to [H⁺]

\[
\text{Si}-\text{OX} + \text{H}^+ \rightarrow \text{Si}-\text{O}^+\text{H}^- \quad X = R, H
\]

\[
Y-\text{OH} + \text{Si}-\text{O}^-\text{H} \rightarrow Y-\text{O}-\text{Si} \rightarrow \text{HOX}
\]

\[
Y = H, \quad \text{Si}
\]

**hydrolysis reaction:** \( X = R, Y = H \)

**condensation reaction:** \( X = R \) or \( H, Y = \text{Si} \)

**pH 2-7:**
The reaction rate is proportional to [OH⁻]

\[
\text{Si}-\text{OX} + \text{Y}^- \rightarrow \left[ \text{Si}-\text{O}^-\text{H} \right]^- \rightarrow Y-\text{O}-\text{Si} \rightarrow \text{XO}^-
\]

\[
Y = H, \quad \text{Si}
\]

**hydrolysis reaction:** \( X = R, Y = H \)

**condensation reaction:** \( X = R \) or \( H, Y = \text{Si} \)

**pH > 7:**
The re-dispersion rate is at maximum, and the solution consists of anionic species, which repels each other.
Network formation

During reaction, objects will grow. However, a gel may not form.

As the sol aggregates the viscosity will increase until a gel is formed. The sol-gel transition (gel-point) is reached when a continuous network is formed.

The gel-time is determined as the time when it is possible to turn the container upside-down. All fluid is kept in the gel, and the volume is maintained.

![Figure 4-51. Structural development of silica gels.](image)

Gel time with 0.05 mole catalyst:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Gel Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>92 h</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>106 h</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>107 h</td>
</tr>
<tr>
<td>HI</td>
<td>400 h</td>
</tr>
<tr>
<td>uten</td>
<td>1000 h</td>
</tr>
</tbody>
</table>

A gel grows by forming a network, which extends across the entire container.

Gel point

When the gel is formed, a large number of sol particles and clusters will still not have reacted. Ageing of the gel is therefore a very important stage in the process.

The gel point is not a thermodynamic event.

![Figure 4-52. Site percolation on a square lattice: (a) for p = 0.50, and (b) for p = 0.75 (p is the fraction of filled spheres).](image)
Ostwald ripening

Small particles dissolve faster than larger particles. As the process is dynamic and reversible, smaller particles may be dissolved to feed growth of the larger particles. The growth stops when the difference in solubility between the largest and smallest particle is a few ppm. It is therefore possible to prepare monodisperse silica particles from a gel.

Ageing

As the viscosity rapidly increase, the solvent is “trapped” inside the gel.

The structure may change considerably with time, depending on pH, temperature and solvent. The gel is still “alive”.

- The liquid phase still contains sol particles and agglomerates, which will continue to react, and will condense as the gel dries.
- The gel is originally flexible. Groups on neighbouring branches will condense, making the gel even more viscous. This will squeeze out the liquid from the interior of the gel, end shrinkage occur. This process will continue as long as there is flexibility in the gel.
- Hydrolysis and condensation are reversible processes, and material from thermodynamically unfavourable points will dissolve and precipitate at more favourable points. (Note the similarity to the sintering process)
Drying

When the liquid is removed from the gel several things may happen. When the liquid in the gel is replaced by air, major changes to the network structure may occur. If the structure is maintained, an aerogel is formed. If the structure collapses, a xerogel is formed.

- Normal drying of the gel leads to structural collapse due capillary forces drawing the walls of the pores together, and reducing the pore size.
- OH groups on opposite sides may react and form new bonds by condensation.
- Cracking may occur when the tension in the gel is so large that it cannot shrink anymore.
- Gas will enter the pores with a thin film of liquid on the walls. This will evaporate and only isolated spaces with liquid are left.

![Diagram](image)

Figure 4-54. Contracting surface forces in pores of different size during drying.

Metal oxides

Metals may be used for formation of gels, almost as silicon. However, many metals will form oxides when increasing pH. The water molecules of the hydrated metal ions are more acidic than for Si, and hydrolys will occur. The reactions are moved toward lower pH.

\[
\begin{align*}
\text{pH < 3} & \quad [\text{Al}(\text{H}_2\text{O})_6]^{3+} & \text{pH > 3} & \quad [\text{Al(OH)}_x(\text{H}_2\text{O})_{6-x}]^{(3-x)^+} & \text{pH >> 3} & \quad \text{Al-O-Al} \\
\end{align*}
\]

A network may be formed via two routes:

- **Olation**: Hydroxy bridges are formed by nucleophilic substitution, where an OH group attacks and water leaves. It is important that water is not coordinated too hard to the metal in order for this reaction to occur. The smaller the charge and the larger the metal ion, the larger the olation rate.
Oxolation

Oxolation is a condensation reaction where an oxo-bridge is formed. If the metal is under-coordinated, the oxolation happens by fast nucleophilic addition reactions:

\[
2 \text{M-O} \rightarrow \text{M} \begin{array}{c}
\text{O} \\
\text{M}
\end{array}
\]

Otherwise, oxolation is a two-step addition/elimination process

At basic conditions step one is catalyzed
At acidic conditions, step two is catalyzed
The reaction is slow at the isoelectric point

\[
\begin{align*}
\text{M-OH} + \text{M-OH} & \rightarrow \text{M} \begin{array}{c}
\text{O} \\
\text{M}
\end{array} \text{OH} \\
\text{M} \begin{array}{c}
\text{O} \\
\text{M}
\end{array} \text{OH} & \rightarrow \text{M} \begin{array}{c}
\text{O} \\
\text{M}
\end{array} + \text{H}_2\text{O}
\end{align*}
\]

Whether gel formation or precipitation occur depends on the reaction conditions and the kinetics. Gel formation occur when reactions are slow.

Metal oxide systems

There is a big difference between metal oxides and the silica system
Silicon are tetrahedrally coordinated to oxygen, while metals are usually octahedrally coordinated. Tetrahedra give more flexibility than octahedra.

\[
\begin{align*}
\text{Al(OH)(H}_2\text{O)}_3^{2+} + \text{Al(OH)(H}_2\text{O)}_3^{2+} & \rightarrow \text{Al} \begin{array}{c}
\text{Al}
\end{array}^{2+} \begin{array}{c}
\text{Al}
\end{array}^{2+} \text{H}_2\text{O} \\
\text{Al}_2(\text{OH})_3(\text{H}_2\text{O})_t^{3+} & \rightarrow \text{Al}_2(\text{OH})_3(\text{H}_2\text{O})_t^{3+} \\
\text{Al}_2(\text{OH})_3(\text{H}_2\text{O})_t^{3+} & \rightarrow \text{Al}_2(\text{OH})_3(\text{H}_2\text{O})_t^{3+}
\end{align*}
\]

Figure 4-55. Stereochemical possibilities for the condensation of [Al(OH)(H2O)]2+ by an olation mechanism.
Alkoxide precursors

Differences between Si(OR)₄ and M(OR)ₓ

- Metal alkoxides are stronger Lewis acids and will promote nucleophilic attack. Hydrolysis of Ti(OR)₄ is up to 10⁵ times faster than for the corresponding silicon alkoxide.
- Most metals have several stable coordination numbers or may easier expand the coordination sphere.

Hydrolysis, reactivity:
Si(OiPr)₄ <<< Sn(OiPr)₄, Ti(OiPr)₄ < Zr(OiPr)₄ < Ce(OiPr)₄

When reacting with water many metal alkoxides form precipitates. While the alkoxy silanes needs catalysts, the reaction rates must be decreased for metal alkoxides. Hydrolysis occur through an addition/elimination mechanism:

Reducing reactivity

Metal alkoxides may be polymeric (silicon alkoxides tend to be monomeric). Polymeric species react slower than monomeric. Small ligands result in faster reaction than large ligands. Bidentate ligands also slow down the hydrolysis.
**Inorganic-organic hybrid materials**

Combining properties of organic and inorganic materials. May be done as composites or using molecular building blocks.

- ORMOSILS: Organically modified silicates
- ORMOCERS: Organically modified ceramics
- CERAMERS: Ceramic polymers
- POLYCERAM: Polymeric ceramics

**Embedding organic molecules**

Forming a gel around organic molecules (Dyes, catalytically active metal complexes, sensor compounds, biomolecules)

**Incorporation of organic groups via covalent bonding**

\[ R'Si(OR)_3 + 3/2 H_2O \rightarrow R'SiO_{3/2} + 3 ROH \]
**Trialkoxysilanes**

<table>
<thead>
<tr>
<th>$RSi(OR)_{3}$</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>polymerizable group for the preparation of hybrid polymers</td>
</tr>
<tr>
<td></td>
<td>crosslinking (glossary) sites</td>
</tr>
<tr>
<td></td>
<td>group for organic polyaddition reactions; generation of hydrophilic diols by opening of the epoxide ring</td>
</tr>
<tr>
<td></td>
<td>hydrophilicity, coupling sites, coordination sites for metals</td>
</tr>
<tr>
<td></td>
<td>hydrophobicity</td>
</tr>
<tr>
<td></td>
<td>crosslinking site in thiol-ene UV cure systems, coordination site for metals</td>
</tr>
<tr>
<td></td>
<td>chromophoric substituent (non-linear optic NLO dye (glossary))</td>
</tr>
<tr>
<td></td>
<td>fluorescent substituent (pyrene derivative)</td>
</tr>
<tr>
<td></td>
<td>coordination of transition metal complexes, catalysis</td>
</tr>
</tbody>
</table>

**Scratch resistant coating**

Mixture of vinyl and mercapto substituted trialkoxysilanes.

Formation of sol coating photochemically cured

*Figure 4-63. Scratch-resistant coating on polycarbonate (left half of slide coated, right half uncoated).*
Surface modifications

Interface interaction:

\[ \gamma_{SV}: \text{energy of surface-vapour interaction} \]

\[ \gamma_{SL}: \text{energy of surface-liquid interaction} \]

\[ \gamma_{LV}: \text{energy of liquid-vapour interaction} \]

\[ \Delta E = \gamma_{SV} + \gamma_{SL} + \gamma_{LV} \]

Figure 4-64. Different wetting behavior on a surface: a) the liquid spreads easily over the surface; b) the liquid wets the surface partly; and c) the liquid does not wet the surface. Corresponding to the drawings, a water droplet on a hydrophilic (b) and a hydrophobic surface (c) is shown.