

Solvothermal synthesis

Synthesis from liquids above the boiling point at 1 bar.
(The synthesis pressure must be higher than 1 bar)



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Hydrothermal/solvothermal

Hydrothermal synthesis: H_2O , temperatures above 100°C .

Other solvents:

NH_3 , HF , HBr , Cl_2 , HCl , CO_2 , SO_2 , H_2S , CS_2 , $\text{C}_2\text{H}_5\text{OH}$, CH_3NH_2 , CH_3OH ,
 HCOOH . ++

NH_3 is a common solvent (ammonothermal)) and carbon dioxide is becoming important.

1. Hydrothermal crystallization of large crystals and gem stones
2. Hydrothermal synthesis of e.g. powder samples of oxides (e.g. zeolites)
3. Hydrothermal leaching (e.g. for treatment of ores).

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TABLE 1
Hydrothermal synthesis: dates.

Started ca. 1845

Most important for preparation of large quartz crystals.

Piezoelectric properties of quartz discovered in 1880

World production in 1985: ca. 1500 tons.

Autoclaves up to 100 liter

Year	Name	Arrangement	Comments
1845	Schafhäütl	Papin's digester	quartz microcrystals
1848	Bunsen	thick-walled glass tubes	carbonates: forerunner of visual autoclaving
1851	de Sénarmont	glass ampoules in autoclave	mineral carbonates, sulfates, sulfides, fluorides: founder of hydrothermal synthesis in geological sciences
1873	von Chrustschoff	noble metal lining	protection against corrosive solvents
1914	Morey	Morey-type autoclave	"closed" system: standard
1923	Smith, Adams	internally heated autoclave	very high pressures and temperatures: ≥ 10 kbar, $\geq 1400^\circ\text{C}$
1943	Nacken	foundation for industrial quartz growth	introduction of hydrothermal synthesis into solid state physics
1949	Tuttle	"cold seal" or test tube arrangement	external pressure regulation and measurement. More extensive working range than Morey. Standard.
1973	Capponi	modified belt apparatus	extremely high pressures and temperatures: ≥ 100 kbar, $\geq 1500^\circ\text{C}$

Quartz crystals

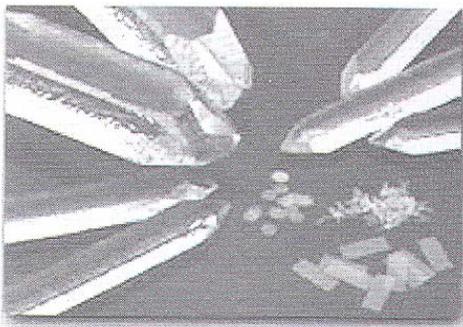
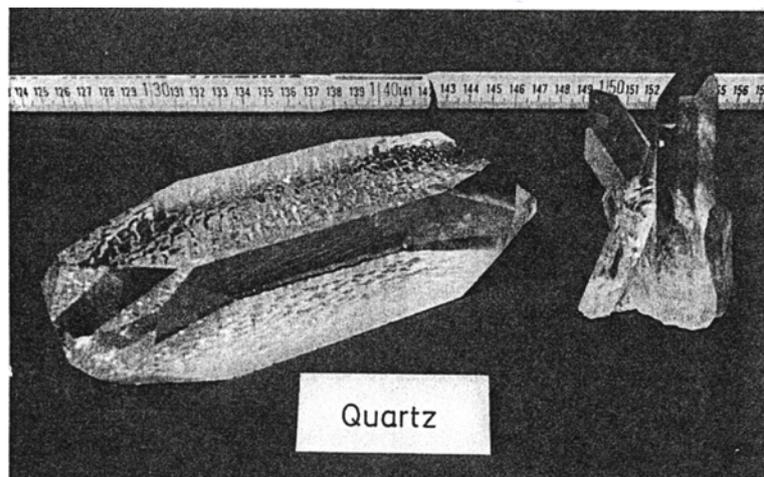


Figure 4-35. Synthetic quartz crystal (left) and rock crystal (right).



Synthetic quartz crystal (left), ca. 1 kg, with natural quartz (right).
(R. Diehl, Freiburg.)

Quartz, autoclaves

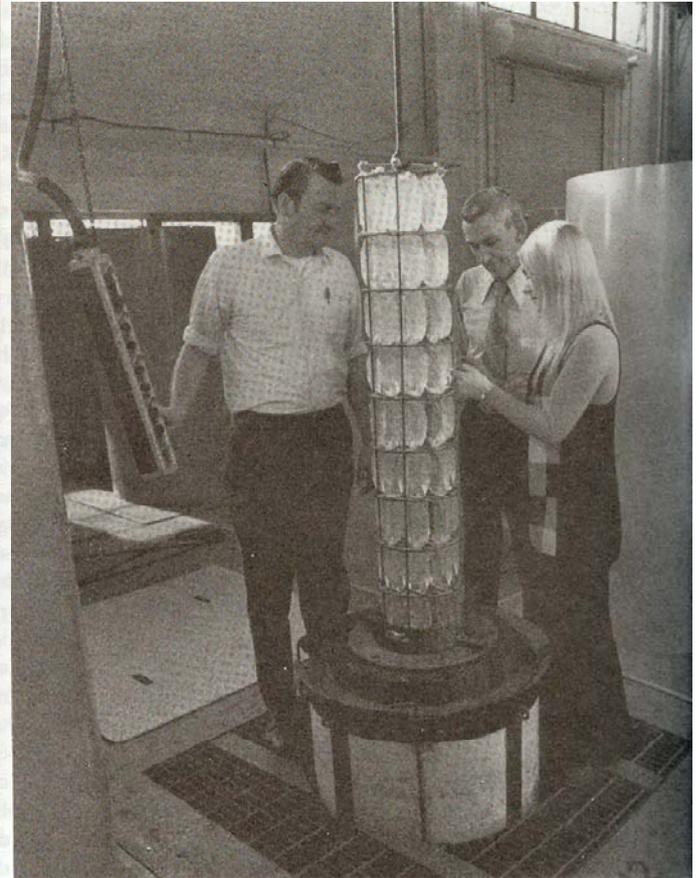


Figure 2.11. Growth of quartz crystals in the world's largest autoclave. (Photo courtesy of Dr. Taki.)

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Quartz crystals, applications

Important in electronics, watches etc. (oscillators)

Optical properties, laser windows, prisms, etc.

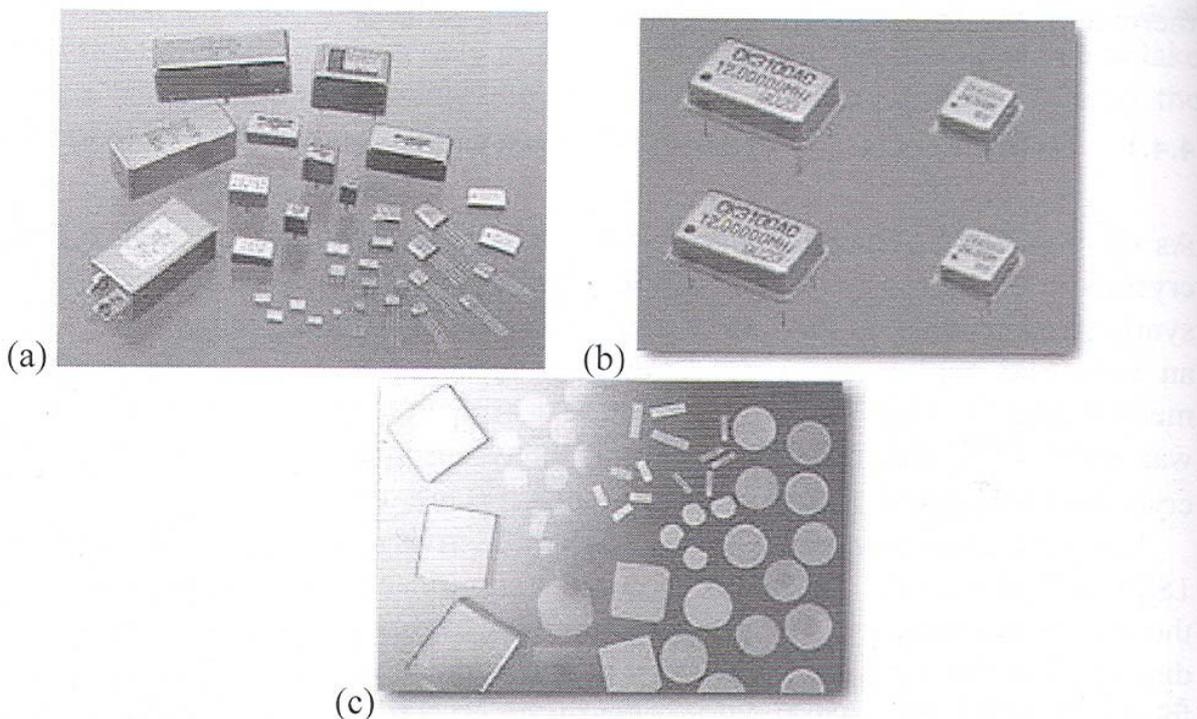


Figure 4-36. Applications of quartz crystals. (a) as filters; (b) as oscillators; and (c) as crystal wafers or blanks.

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Synthetic hydrothermal crystals



ZnO

**Emerald
(Beryl:
 $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$)**



Solvothermal, general aspects

Usually more material can be dissolved at higher temperatures

Properties of water with increasing temperature:

- Ion product increases
- Viscosity decreases
- Polarity (dielectric constant) decreases, but increases with pressure.

Synthesis usually in closed vessels, so temperature-pressure-volume considerations are crucial.

Two methods:

- **Isothermal:** Mainly for powder synthesis
- **Temperature gradient:** Generally formation of larger crystals

Sub- vs. super-critical

Closed autoclave: Autogenous pressure.

Critical point:

Critical temperature: **374.15°C**, Critical pressure: **220 bar (22.064 MPa)**

Critical density: 0.321g/cm^3

Above the critical temperature and critical pressure: supercritical, fluid phase

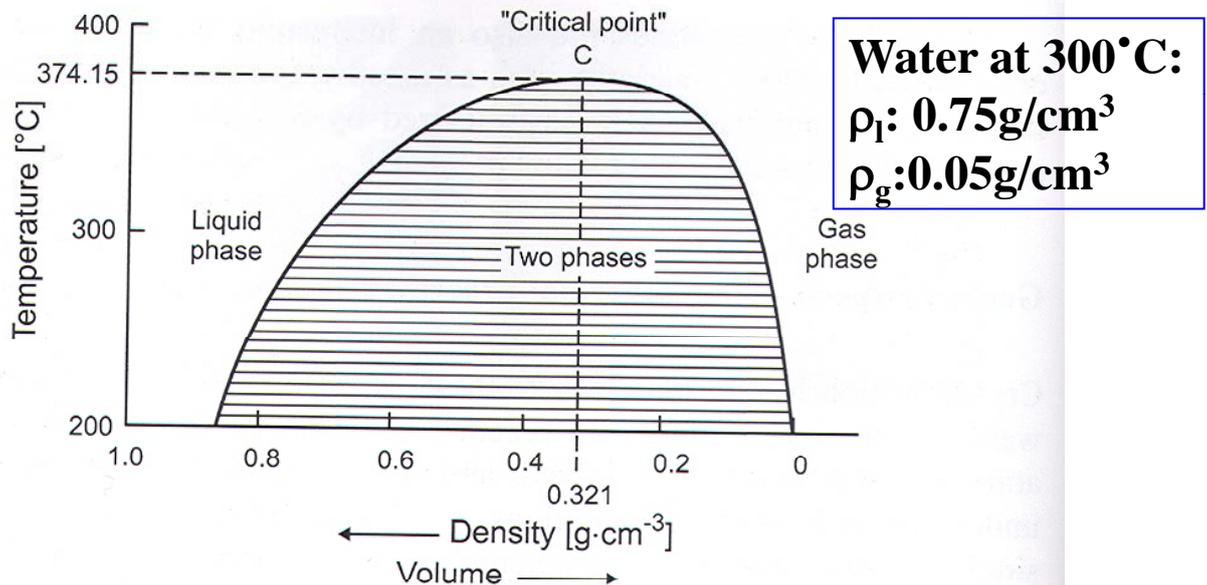


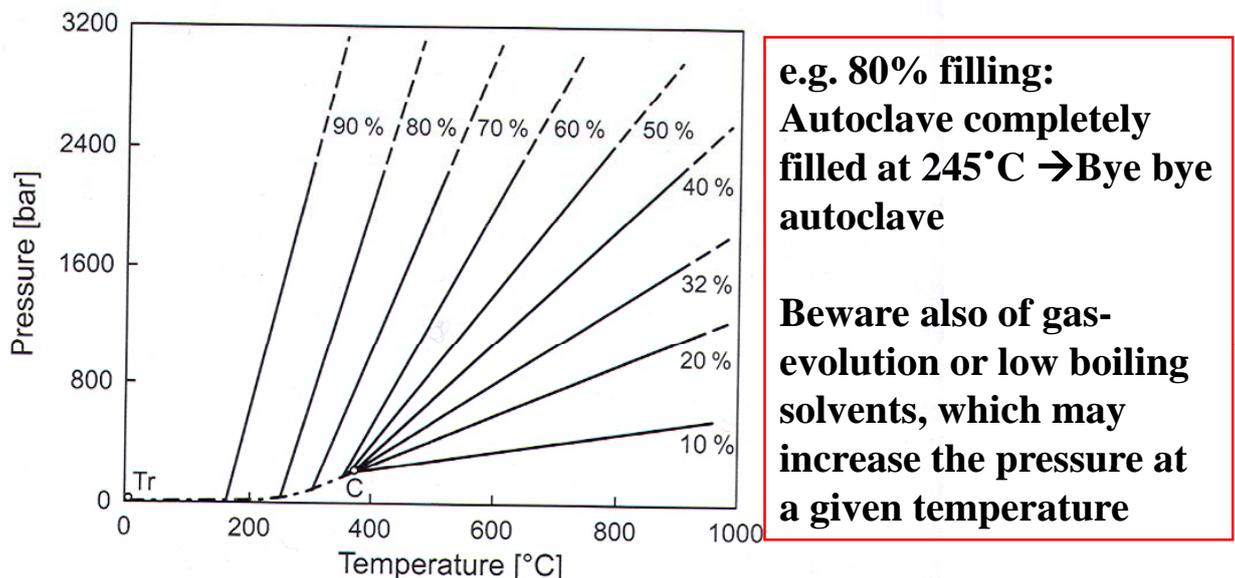
Figure 4-37. Volume (density)/temperature-dependence of water.

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P-T diagram. Importance of degree of filling of the autoclave

Autogenous pressure in a closed vessel.

At 32% filling, the water will expand to fill the autoclave at the critical temperature. At higher filling degrees, the water will expand to fill the autoclave at temperatures below the critical temperature. This will result in a steep increase in the pressure inside the autoclave, due to differences in compressibility of gas and liquid.



e.g. 80% filling:
Autoclave completely filled at 245°C → Bye bye autoclave

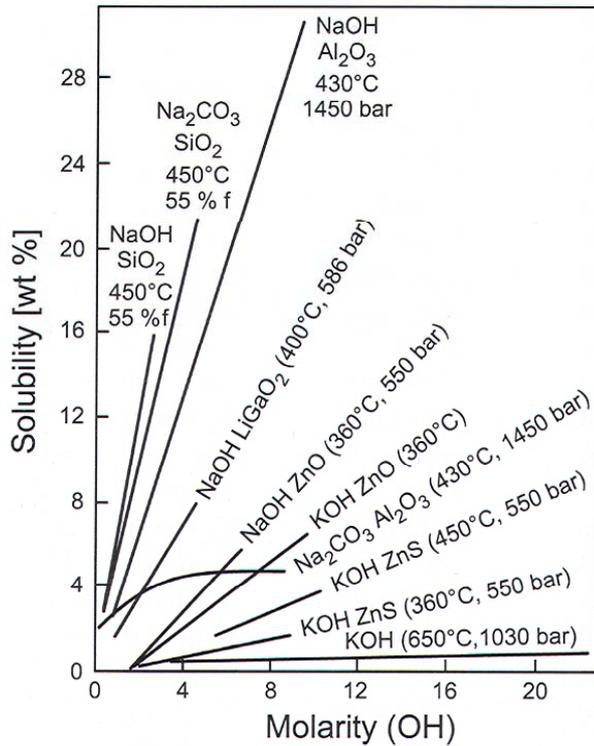
Beware also of gas-evolution or low boiling solvents, which may increase the pressure at a given temperature

Figure 4-38. Pressure/temperature dependence of water for different degrees of filling of the reaction vessel

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Mineralizers

The solubility of the materials is not always sufficient at the synthesis conditions. Mineralizers are used to increase crystallization rates.



Usually F- or OH- (alkali metal hydroxides, salts of weak acids, chlorides...)

Quartz is synthesized in a temperature gradient (400-380°C) at 1kbar. The solubility is too low for efficient crystallization at these conditions.

NaOH, Na₂CO₃, KOH, NaF may be added as mineralizers.

A solubility of 2-5 w% gives growth of ca. 1mm/day

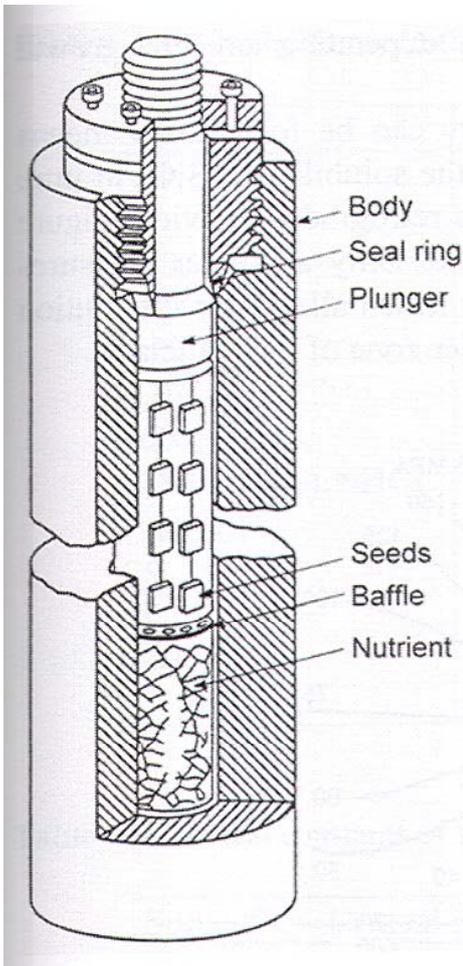
SiO₂: 0.5 M NaOH

ZnO: 6 M NaOH

Figure 4-39. Solubility as a function of the hydroxide concentration for some hydrothermal systems.

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Synthesis in a temperature gradient.



Nutrient (polycrystalline powder of starting material) is placed in the bottom. A perforated disk (baffle) separates the dissolution and growth zones (better thermal gradient), and reduces particle flow (secondary nucleation). Seed crystals with given orientation is placed in the growth zone.

T_1 The temperature in the growth zone is lower than in the dissolution zone. Convection transport the hot liquid up to the growth zone.

Typical requirements:

T_2 Some weight percent solubility
0.001 – 0.1 w% difference in solubility over 10°C

Figure 4-40. Scheme of an autoclave for hydrothermal single crystal growth.

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Retrograde solubility

Sometimes solubility decreases with increasing temperature (retrograde solubility). This is seen e.g. for SiO_2 in pure water (and in salt solutions at higher temperatures).

May be caused by properties of the compound, or properties of the solvent.

Often observed at higher temperatures where the density of water is low.

SiO_2 in pure water: retrograde behaviour above 350°C and below 6-700 bar

Also seen for e.g. halides, calcium carbonate...

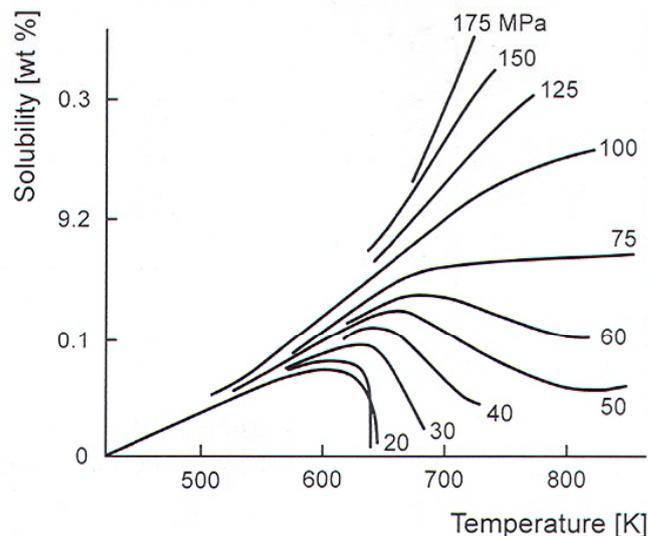


Figure 4-41. Solubility of SiO_2 in water.

Other solvents for solvothermal synthesis

Table 4-3. Examples for hydrothermal processes in non-aqueous environments.

<i>Solvent</i>	<i>Examples of synthesized compounds</i>
NH_3	nitrides, imides, amides, CsOH , Cs_2Se_2
HF	$\text{MO}_{3-x}\text{F}_x$ ($\text{M} = \text{Mo}, \text{W}$)
HCl , HBr	AuTe_2Cl , AuSeCl , AuSeBr , $\text{Mo}_3\text{S}_7\text{Cl}_4$
Br_2	SbSBr , SbSeBr , BiSBr , BiSeBr , MoOBr_3
S_2Cl_2	MoS_2Cl_3 , $\text{Mo}_3\text{S}_7\text{Cl}_4$
S_2Br_2	$\text{Mo}_3\text{S}_7\text{Br}_4$
SeBr_2	SbSeBr , BiSeBr
$\text{H}_2\text{S} + (\text{C}_2\text{H}_5)_3\text{NHCl}$	$\beta\text{-Ag}_2\text{S}$
$\text{C}_2\text{H}_5\text{OH}$	SbI_3 , BiI_3
CS_2	Monoclinic Se
CCl_4	SeCl_4 , TeCl_4
C_6H_6	Selenium
CH_3NH_2	CH_3NHLi

Critical data

Table 4-4. Critical constants of some solvents.

Solvent	Critical temperature [°C]	Critical pressure [bar]
H ₂ O	374.1	221.2
NH ₃	132.3	111.0
Cl ₂	144	77.1
HCl	51.4	83.2
CO ₂	31.3	73
SO ₂	157.8	78.7
H ₂ S	100.4	90.1
CS ₂	279	79
C ₂ H ₅ OH	243	63.8
CH ₃ NH ₂	156.9	40.7
CH ₃ OH	240	81
HCOOH	308	—

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Advantages of hydrothermal synthesis

Usually moderate temperatures 100-300°C (subcritical) at autogenous pressure.

Some advantages of hydrothermal synthesis:

- It may be possible to synthesize materials below a transformation temperature.
 - γ -CuI (transition temperature 390°C)
 - Quartz, α - β transition temperature ca. 580°C
- Transition metal compounds may be synthesized with unusual oxidation states
 - CrO₂: hydrothermal at 350°C, 440 bar:
 - $\text{Cr}_2\text{O}_3 + \text{CrO}_3 \rightarrow 3\text{CrO}_2$
 - $\text{CrO}_3 \rightarrow \text{CrO}_2 + \frac{1}{2}\text{O}_2$
- Preparation of metastable phases
 - GeO₂ with quartz type structure using quartz seeds
- Formation of zeolites and other microporous materials

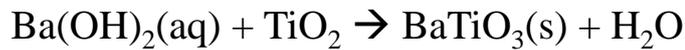
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Hydrothermal synthesis

Starting materials (solution, slurry, gel, sol) placed in a sealed autoclave
Heated to the desired reaction temperature.

Reaction and formation of product (usually by dissolution/precipitation)

Formation of barium titanate (150-250°C)



Synthesis of zeolites

Zeolites is an example of a group of naturally hydrothermally grown minerals. They were early prepared in the laboratory, and materials with natural counterparts as well as new structure types were prepared.

General composition: $\text{M}_{x/n}(\text{Al}_x\text{Si}_y\text{O}_{2(x+y)}) z\text{H}_2\text{O}$

Stability of the porous structure is obtained by the stabilizing effect of hydrated species (or templates).

May be performed also as solvothermal synthesis (using e.g. ethylene glycol)

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Comparing zeolite synthesis with biological processes

Table 4-5. Technical and biological synthesis of SiO₂-materials.

	Zeolites	Unicellular algae
Reaction time	days	shell formation within hours
Concentration of the inorganic precursor	>1 M	<0.001 M
pH	6 – 14	6 – 8
Temperature	125 – 200 °C	4 – 25 °C
Pressure	1 – 100 bar	1 bar
Structural description	compact translational repetitive microporous with uniform pores (typical: 0.3 – 2 nm)	shell hierarchical micro- and macroporous (pore diameters 5 nm to μm)

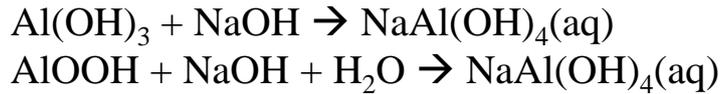
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Hydrothermal leaching

The Bayer process (patent 1888): Industrially important large-scale process for extracting high-grade aluminium hydroxide from bauxite ore.

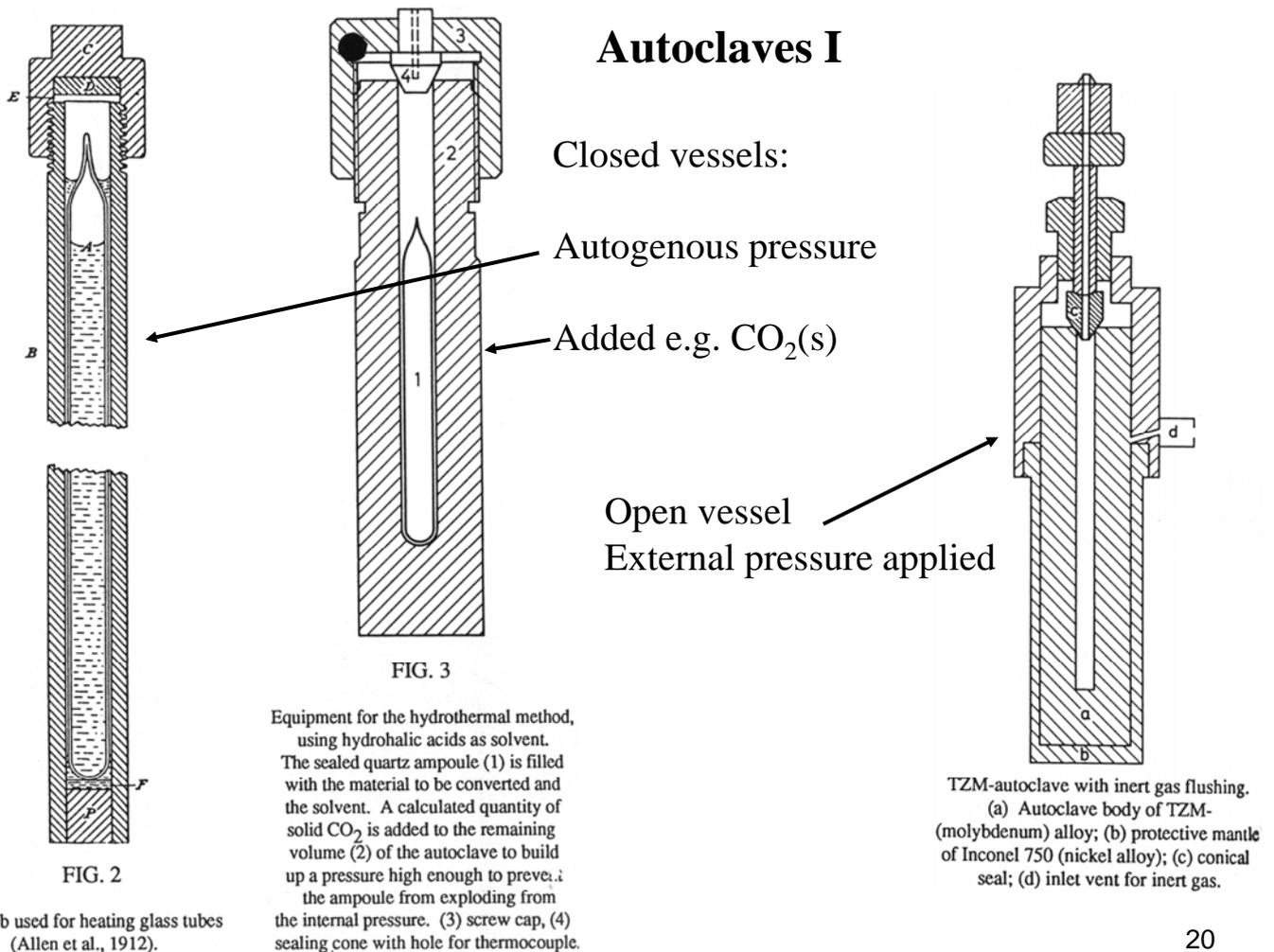
Bauxite: Mixture of $\text{Al}(\text{OH})_3$ and $\text{AlOOH} + +$ (silica, $\text{Fe}_2\text{O}_3\dots$)

Hydrothermal extraction (with concentrated sodium hydroxide solution) via reaction to a soluble aluminate complex:



$\text{Al}(\text{OH})_3$ is precipitated by cooling, diluting and seeding

Heated to corundum (for aluminium metal production)



Morey autoclave

Everything is heated
Up to ca. 400°C, 400 bar
Simple to use
Autogenous pressure

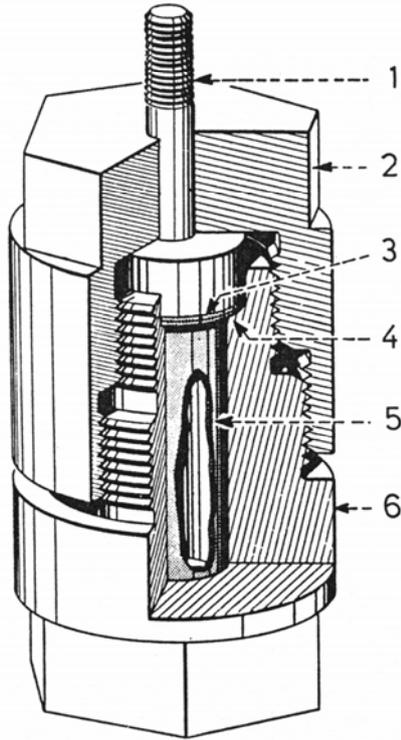


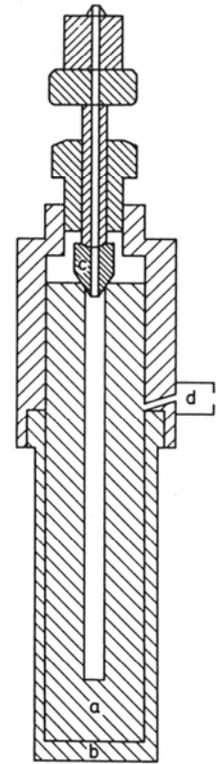
FIG. 9

Autoclaves II

Two principles

Tuttle "cold seal" autoclave

The upper part is outside the furnace (may be water cooled)
Pressure is applied from an external source.
Up to 1100°C, 5000bar



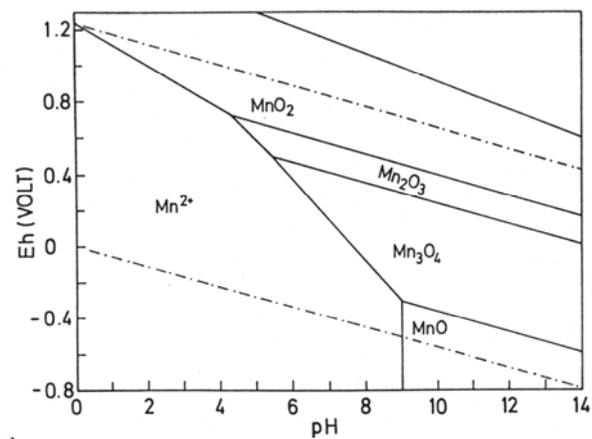
TZM-autoclave with inert gas flushing.
(a) Autoclave body of TZM-
(molybdenum) alloy; (b) protective mantle
of Inconel 750 (nickel alloy); (c) conical
seal; (d) inlet vent for inert gas.

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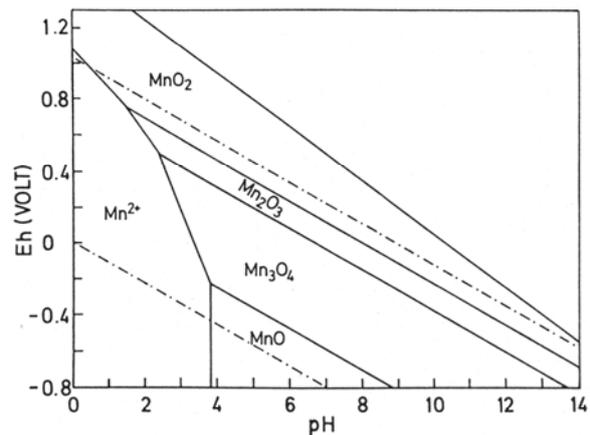
Eh-pH diagrams

By controlling the potential and the pH during hydrothermal synthesis, the oxidation state of the products may be controlled.

The Eh-pH diagrams change with temperature (and pressure)



(a)



(b)

Eh-pH diagram of the Mn-H₂O system at (1) 25°C and (b) 300°C. 22

Hydrothermal buffer systems

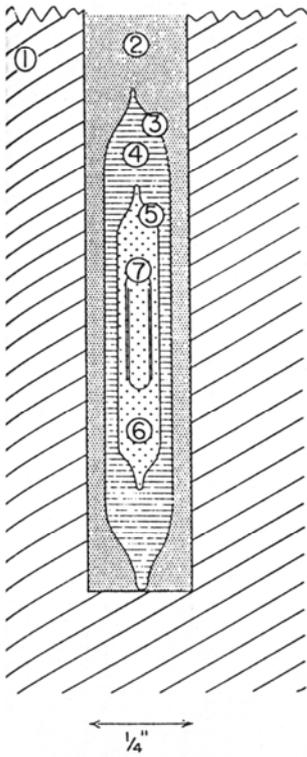


FIG. 22

Oxygen buffer assembly. (1) Pressure vessel; (2) pressure medium (H_2O); (3) sealed gold tube; (4) oxygen buffer; (5) sealed platinum tube; (6) charge.

The open silver crucible (7) protects the charge before contact with the Pt wall.

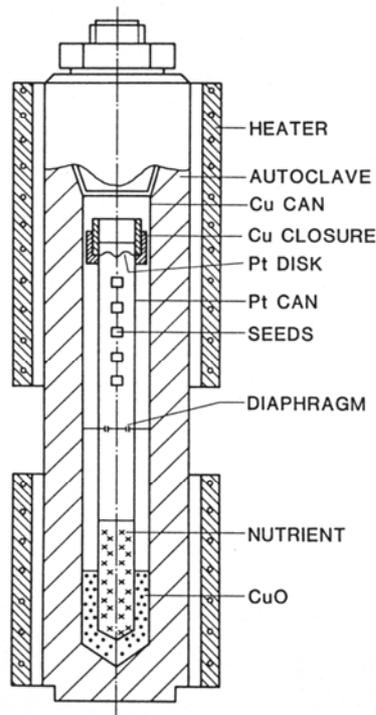


FIG. 23

Arrangement for growth of magnetic $REFe^{III}O_3$ crystals. The CuO buffer, separated from the reaction space by a hydrogen-permeable Pt partition, prevents the formation of Fe^{2+} .

By using a buffer system and e.g. hydrogen permeable membranes, the potential during hydrothermal synthesis may be controlled.

TABLE 2
Buffers.

Oxygen (H_2O)	Acid - Base
$MnO-Mn_3O_4$	Ag-AgCl
$Mn_3O_4-Mn_2O_3$	Ag-AgBr
$Mn_2O_3-MnO_2$	Ag-AgI
$Fe-Fe_{1-x}O$	Nitrogen (NH_3)
$Fe-Fe_3O_4$	Cr-CrN
$Fe_3O_4-Fe_2O_3$	Sulfur (H_2S)
Co-CoO	Ag-Ag ₂ S
Ni-NiO	$Fe_{1-x}S-FeS_2$
Cu-Cu ₂ O	
Fluorine (HF)	
$CaSiO_3 + 2HF = CaF_2 + SiO_2 + H_2O$	
$CaAl_2Si_2O_3 + 2HF = CaF_2 + Al_2SiO_5 + SiO_2 + H_2O$	