EBB 212/3

CHEMICAL SYNTHESIS OF CERAMIC POWDERS (PART 2)

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Liquid Phase/Wet Chemical Synthesis

- Precipitation
- Sol-gel
- Hydrothermal
- Nanoemulsion
- Spray drying

Advantages of LPS* over SSR**

Allow direct fabrication of coating and fibres without powder intermediates

Improved chemical homogeneity on molecular level;
(particularly when performance of powders dependant on the composition of dopants)

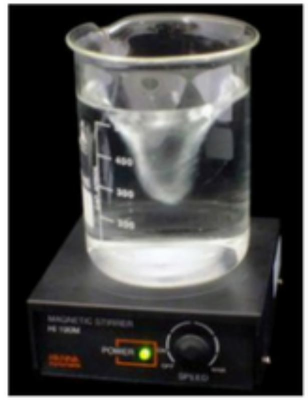
Improved mechanical properties for structural ceramics;
(fine and controlled particles size and shape)

Reduced diffusion distances on calcination;
(owing to mixing of components at molecular level that favours lower crystallization T for multicomponent ceramics)

**LPS= Liquid Phase Synthesis* ***SSR= Solid State Reaction*

Liquid Phase Synthesis (LPS)

+



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Solute + **Solvent** → **Solution**

What is (are) solvent(s) used to dissolve solute?

Water-based:
Tapped water?
Distilled water?
Deionized water?

Alcohol-based:
Acetone?
Ethanol?

Choose the right choice of water source...

Diffrences	Distilled water	Deionized water
Purity	Better than tapped water, but might still contains some organic compounds	High purity
Process	1.Thermal method or distillation. 2.Involved transfer of water in the vapour phase with its subsequent condensation	1.Reverse osmosis. 2.Based on double passage of raw water through semipermeable membrane under pressure.

Precipitation Method

Formation of a solid product from a liquid solution

Insoluble salts, i.e. hydroxides, oxides, carbonates and oxalates separate from solutions by the action of precipitant

Co-precipitation Method

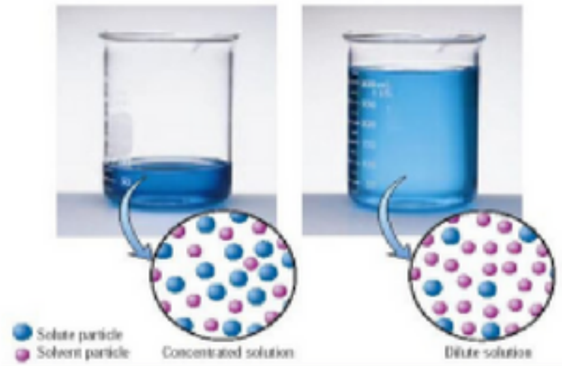
Definition...

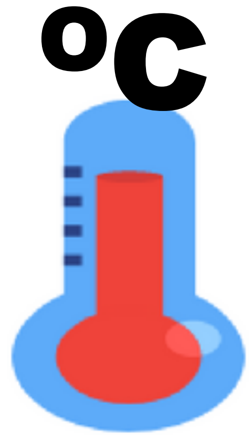
Co-precipitation: when >2 elemental species are precipitated

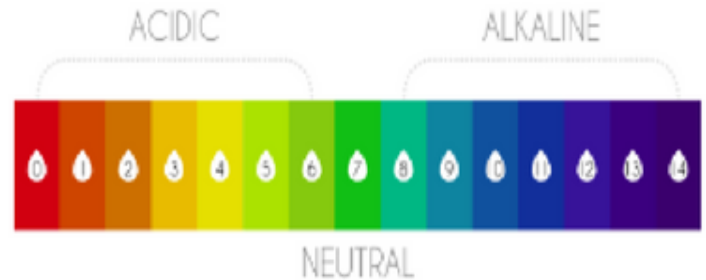
Aim...

To prepare **multi-component ceramic** products through formation of intermediate precipitates (usually hydrous oxides or oxalates), so that an intimate mixture of components is formed during precipitation, and chemical homogeneity is maintained on calcination.

Important Parameters







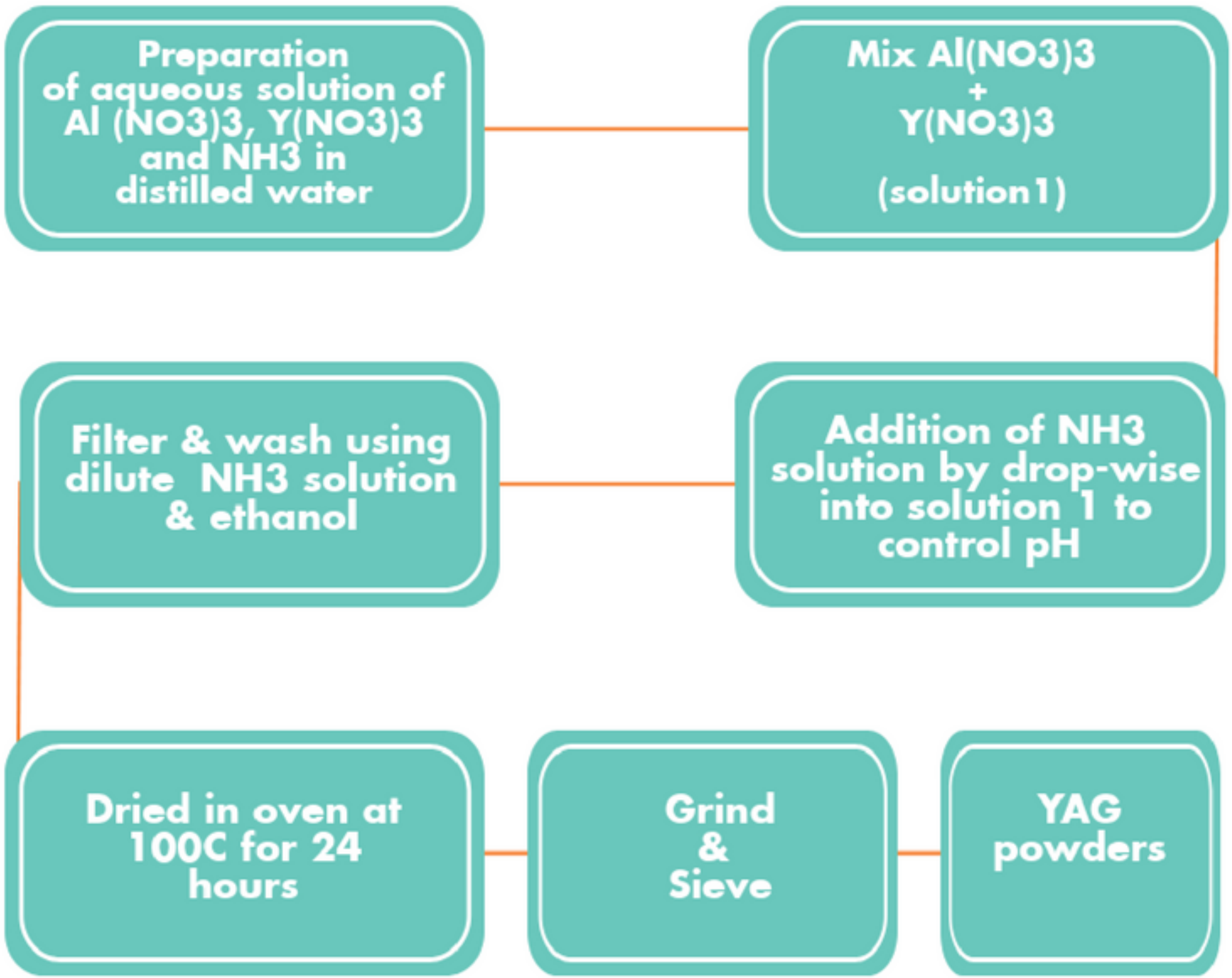
Reactant concentration

Temperature

pH

Careful control of the important parameters/solution conditions is required to precipitate the ions and thus maintain chemical homogenity on the molecular scale.

Example: Preparation of yttria aluminium garnet (YAG) powder



Sol-Gel Method

Definition...

Transformation of starting materials solution into sol or gel through chemical reaction. Then, become solid materials after drying and densification process.

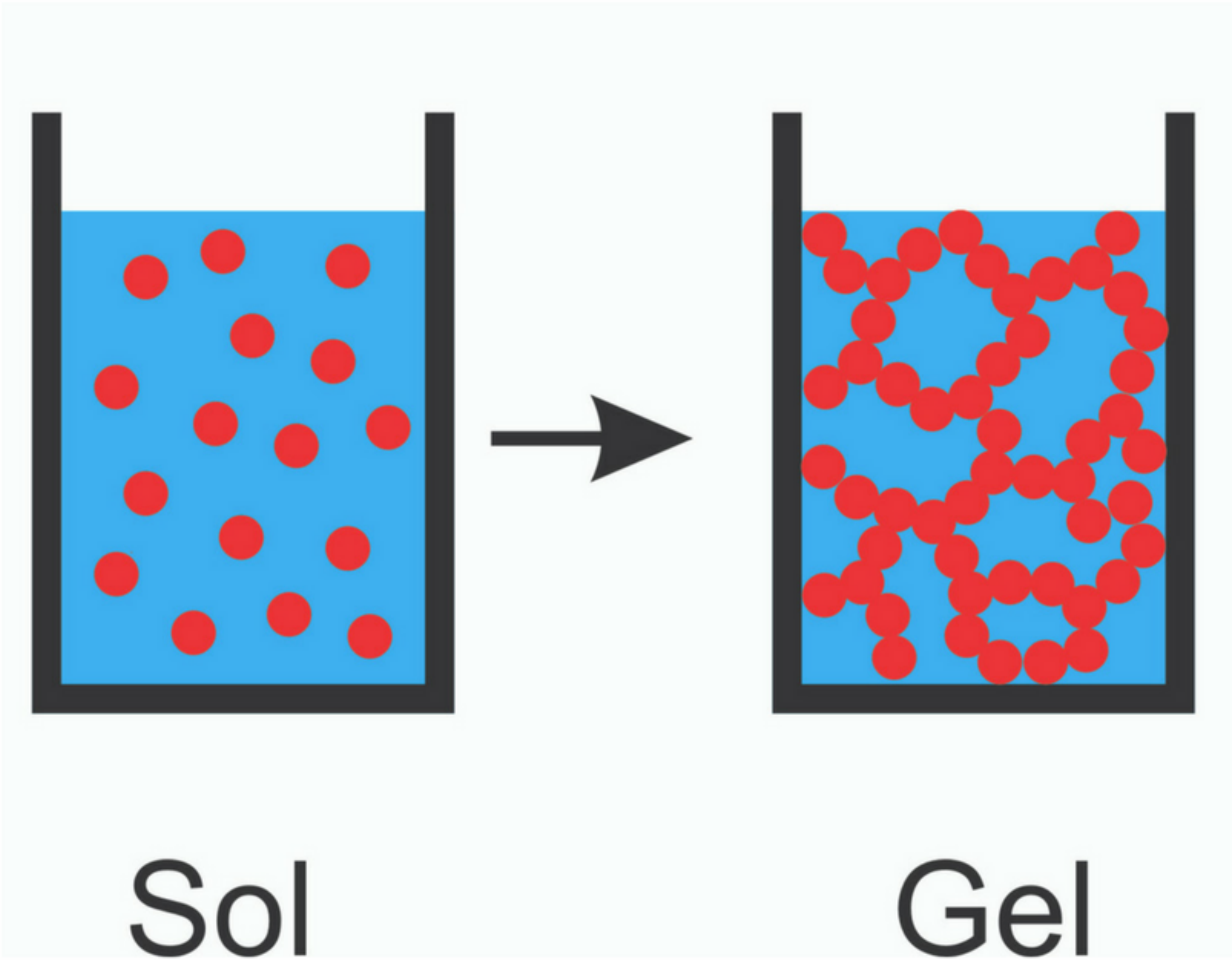
Involves the evolution of inorganic network through the formation of colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel).

Sol

Dispersion of solid particles (0.1-1μm) in a liquid.

GEL

A state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components.


Sol
Gel

Sol-Gel Method

What is colloid?

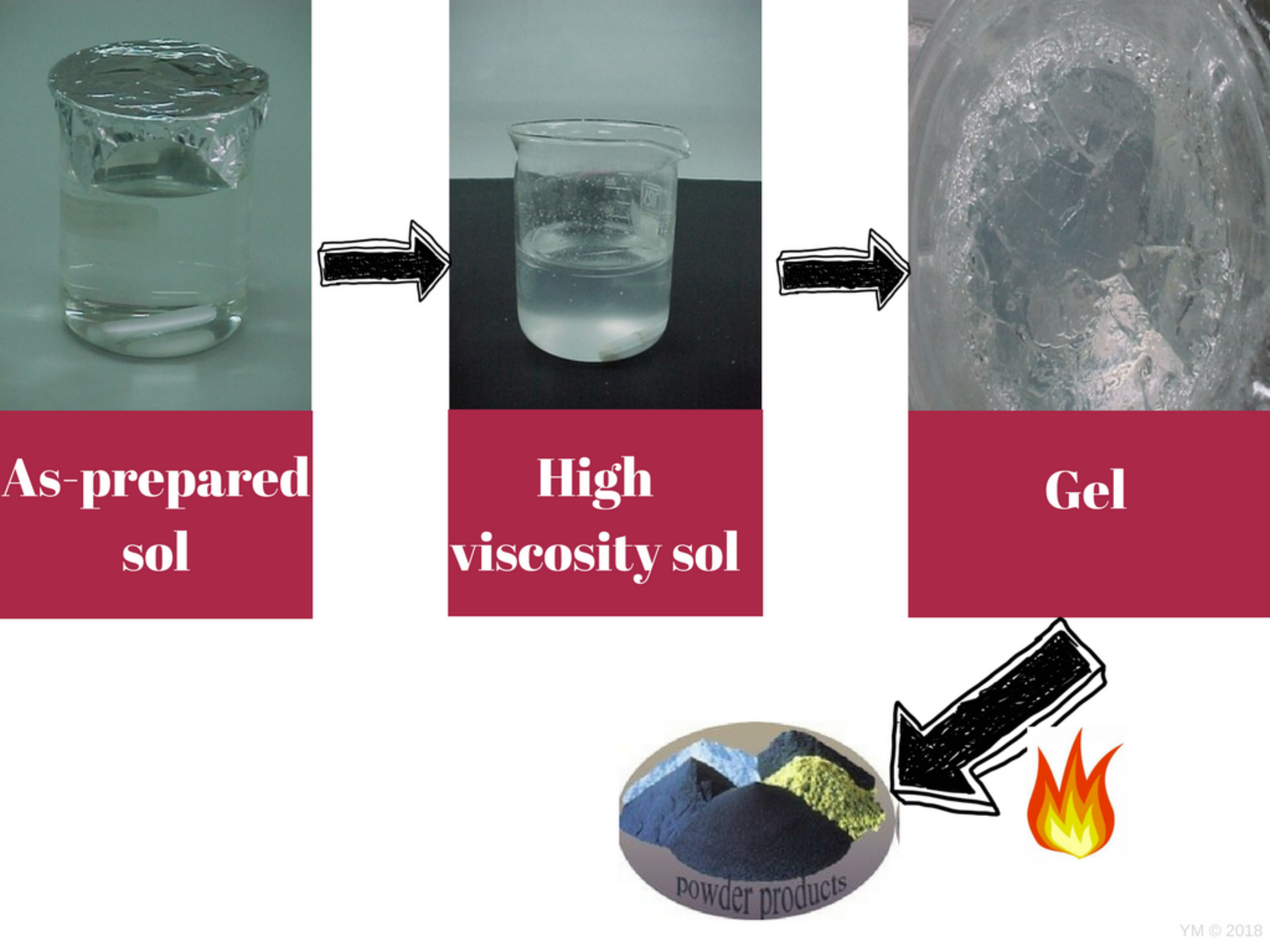
solid particles in diameter range of 10 – 1000Å, every particles consists of $10^3 - 10^9$ atoms.

Example

MILK

WATER

When light is being shined through water and milk, light is not reflected when it passed through water because it is not colloid.However, light is reflected in all directions when it passed through milk, which is colloidal.



As-prepared sol
High viscosity sol
Gel
powder products
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General Stages in Sol-Gel

1

Starting material is **converted** in a chemical process to a **dispersible oxide**, which **form a colloidal dispersion (sol)** by addition to dilute acid or water

Hydrolisis

2

Removal of water and/or anions from the **sol into stiff gel** in the form of spheres, fibres or coatings (reversible transition)

Condensation

3

Calcination of gel in the air, producing oxide powders

Drying

Categories of Sol-Gel

Alcohol-based

Starting with metal alkoxide*

M(OR)x

M = metal

R =alkyl group

x =metal valence

Aqueous-based

Starting with **metal salt solutions

water is used as reaction medium

**Alkoxide: compound where their element bonded with hydrocarbon through oxygen*

***metal acetates, nitrates, sulfates, chlorides,*

Advantages vs Disadvatages

- Homogenous
- High purity
- Low processing T
- Low processing cost

- Expensive starting materials
- Starting materials sensitive to humidity
- Long processing period

Wet chemical Synthesis

Hydrothermal Method

By Definition...

Any heterogenous chemical reactions with the present of solvent (aqueous or non-aqueous solvent) at T>RT and P> 1tam in a CLOSE SYSTEM.

Working Principle:

Typically the process is carried out in a hardened steel autoclave (which can be heated to desired temperature).

Normally the inner surfaces of the vessel are lined with a plastic (e.g. Teflon) to limit the corrosion of the vessel by the solution.

Important parameters to be considered:

Solvent

Aqueous or
Non-Aqueous

Temperature

T ≥100°C

Pressure

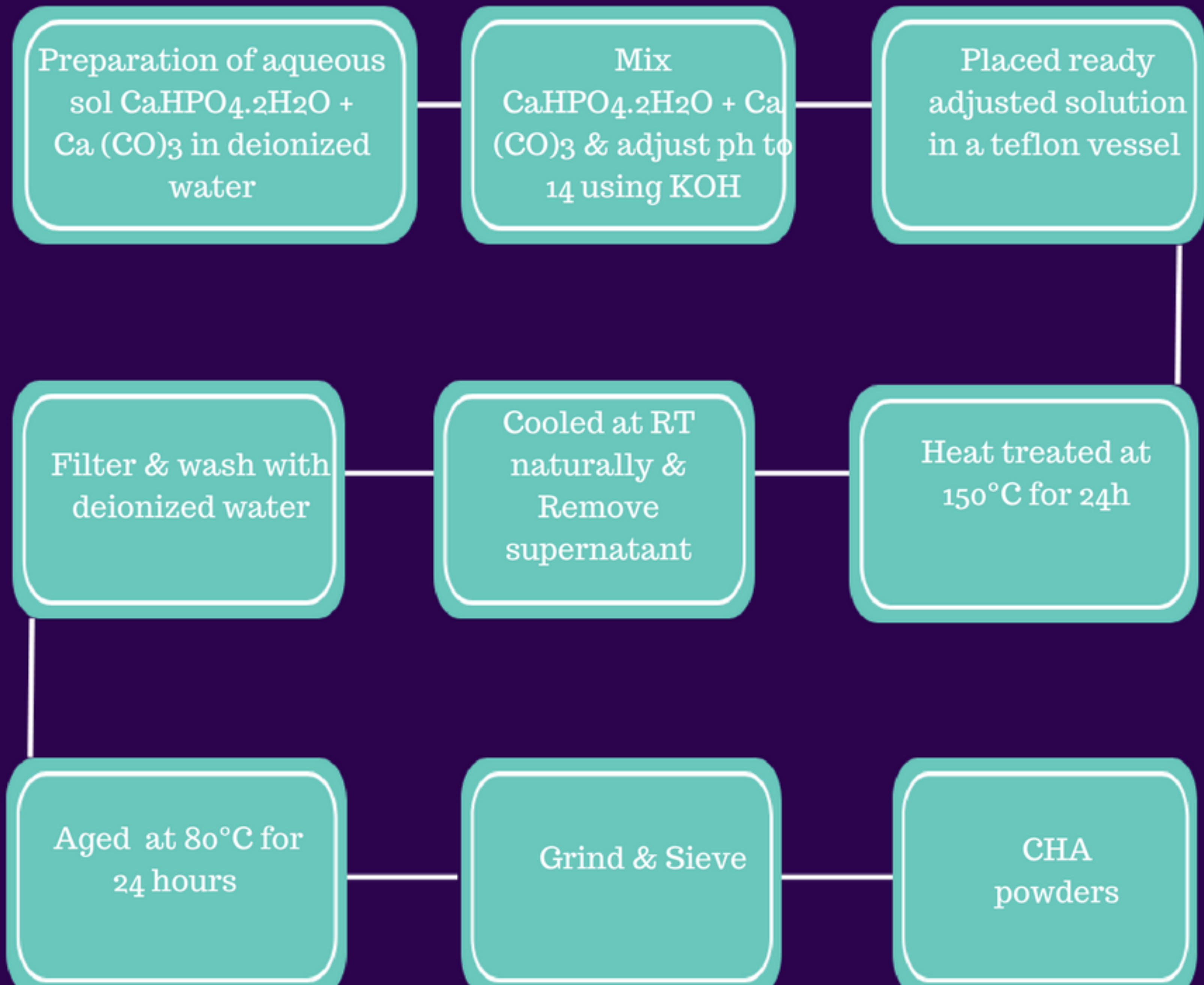
P ≥ 1 atm

Close Chamber
(Autoclave)

- ✓ High Purity
- ✓ Controlable size & shape of end product
- ✓ Able to produce fine crystal

- ✗ Processing parameters greatly influence properties of the product
- ✗ Expensive Equipment

Preparation of Carbonated HA via hydrothermal



Effect of pH & T on particle size & shape

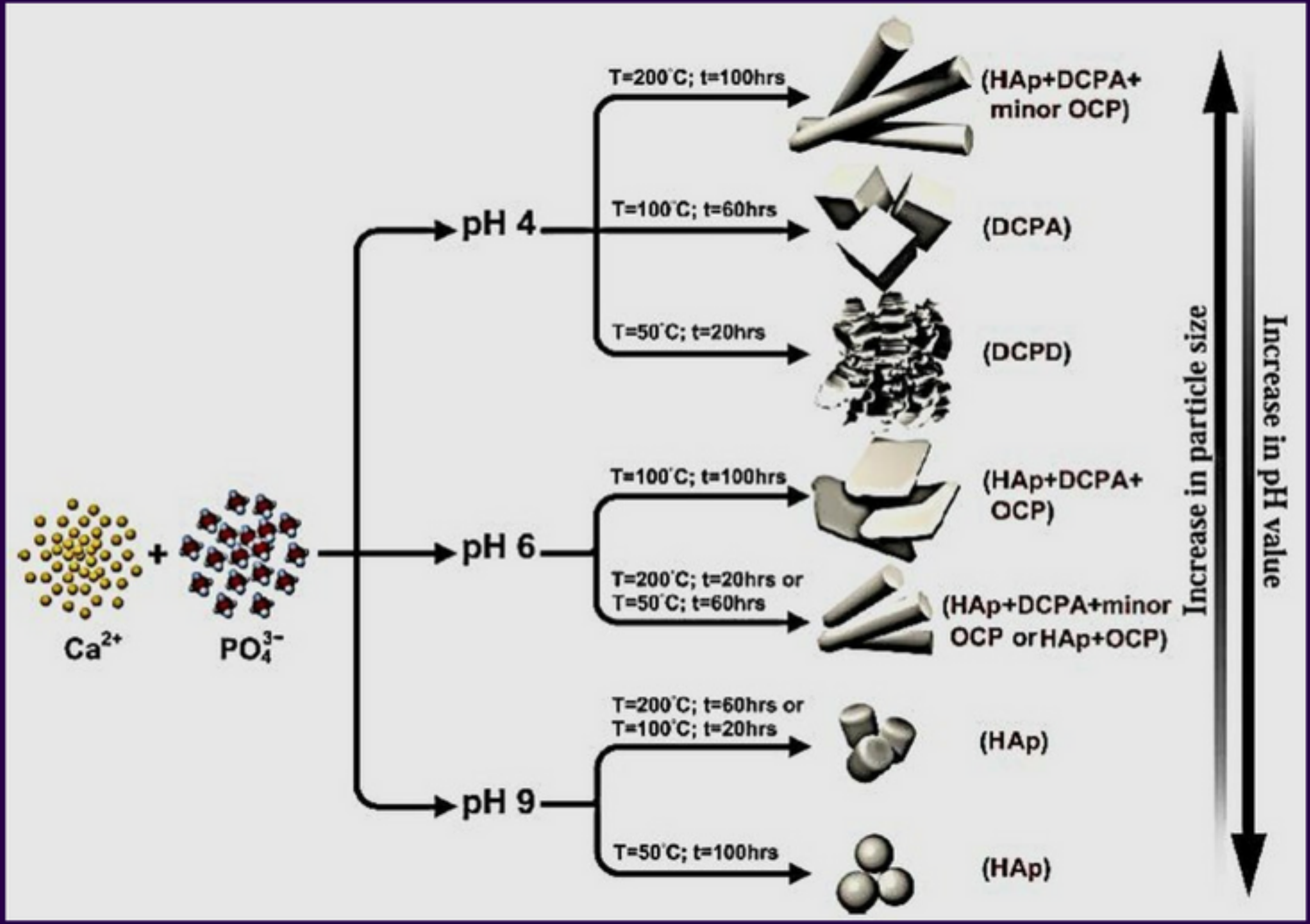


Table 4
Properties of different calcium phosphates [10,11,24,33,34].

Calcium phosphates	Abbreviations	Chemical formula
Monocalcium phosphate monohydrate	MCPM	$Ca(H_2PO_4)_2.H_2O$
Monocalcium phosphate	MCP	$Ca(H_2PO_4)_2$
Dicalcium phosphate dihydrate	DCPD	$CaHPO_4.\ 2H_2O$
Dicalcium phosphate	DCP	$CaHPO_4$
Octacalcium phosphate	OCP	$Ca_8H_2(PO_4)_6.\ 5H_2O$
α-Tricalcium phosphate	α-TCP	α-$Ca_3(PO_4)_2$
β-Tricalcium phosphate	β-TCP	β-$Ca_3(PO_4)_2$
Amorphous calcium phosphate	ACP	$Ca_3(PO_4)_2.\ nH_2O$
Calcium-deficient hydroxyapatite	CDHA	$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ $(0 < x < 1)$
Carbonated apatite	CA	$Ca_5(PO_4,CO_3)_3$
Hydroxyapatite	HA	$Ca_{10}(PO_4)_6(OH)_2$
Oxyapatite	OXA	$Ca_{10}(PO_4)_6O$
Tetracalcium phosphate	TTCP	$Ca_4O(PO_4)_2$


Emulsion
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What is EMULSION?

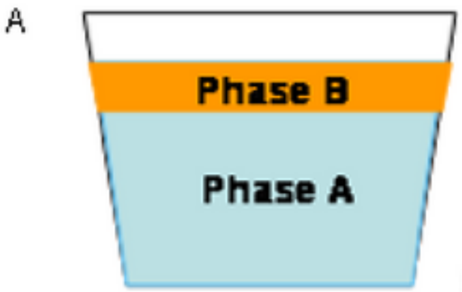
A mixture of two or more liquids that are immiscible (unblendable)

One substance (the dispersed phase) is dispersed in the other (the continuous phase)

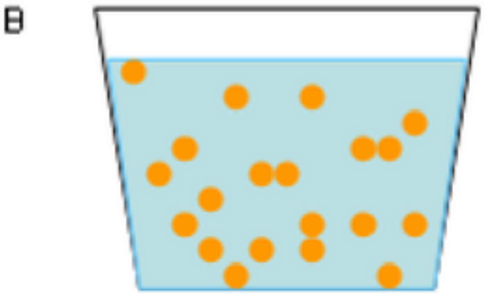
Cloudy appearance, due to many phase *interfaces -scatter light that passes through the emulsion.

*interfaces (the boundary between the phases)

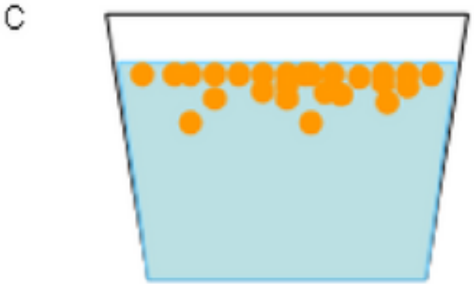
What is EMULSION?



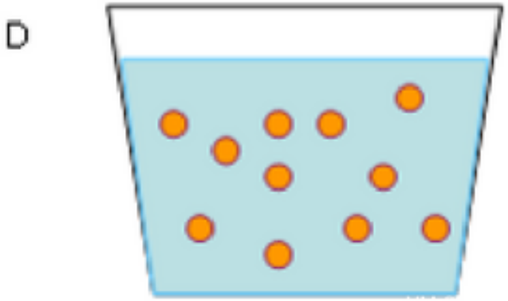
A. Two immiscible liquids, not emulsified



B. An emulsion of Phase B dispersed in Phase A



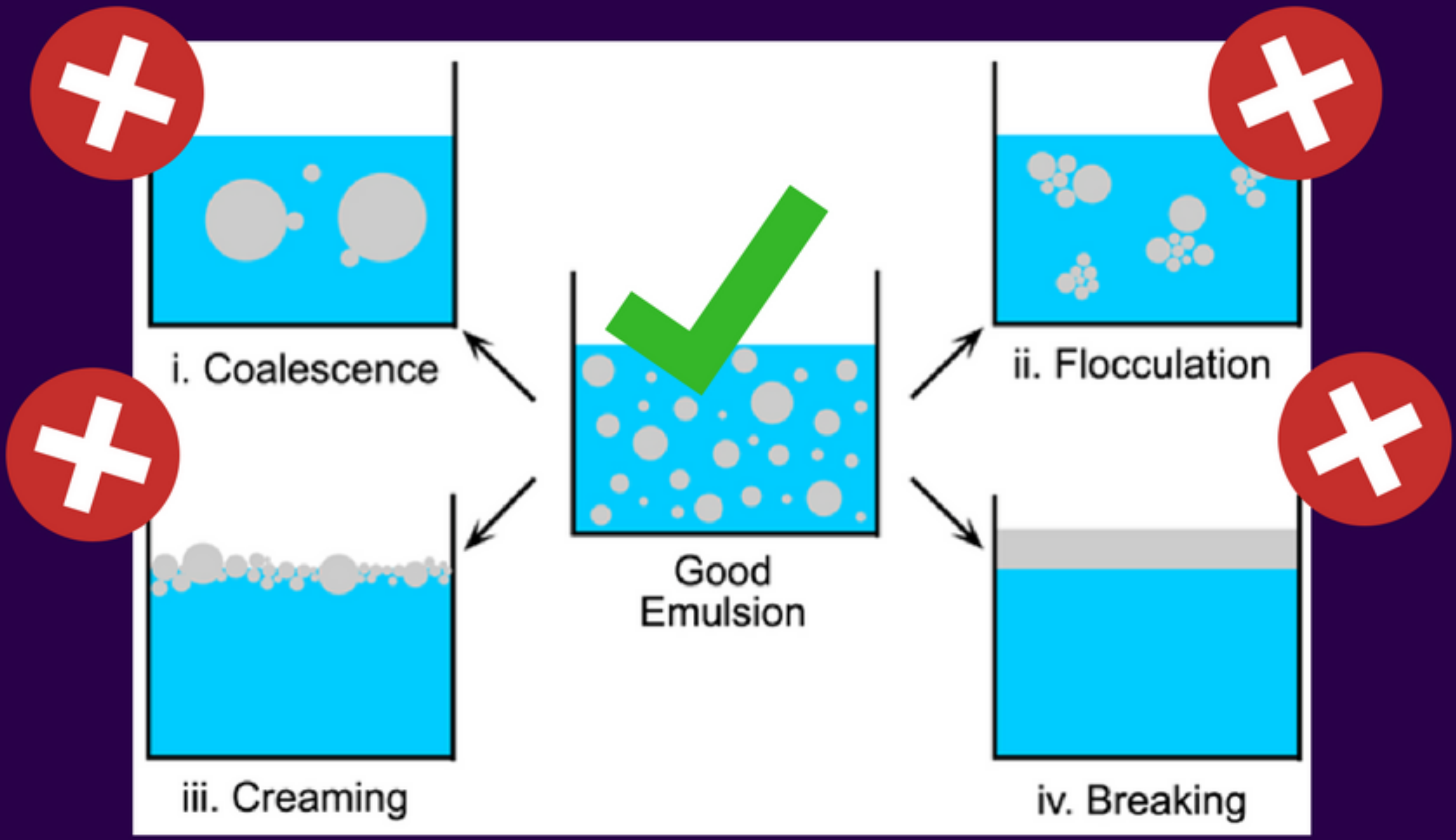
C. The unstable emulsion progressively separates



D. The *surfactant positions itself on the interfaces between Phase A and Phase B, stabilizing the emulsion

Surfactant: red outline around the particles

Possible Failure in Emulsion



How to overcome ?

Function: stabilize the immiscible liquids (such as water and organic)

Surfactant

Potentially toxic

How?
Reduce surface tension of the immiscible liquids, resulting in a dispersed phase confined to nanometer scale.

Example: nonylphenol ether (NP-5), poly (oxyethylene), Span-80

Type of Emulsion

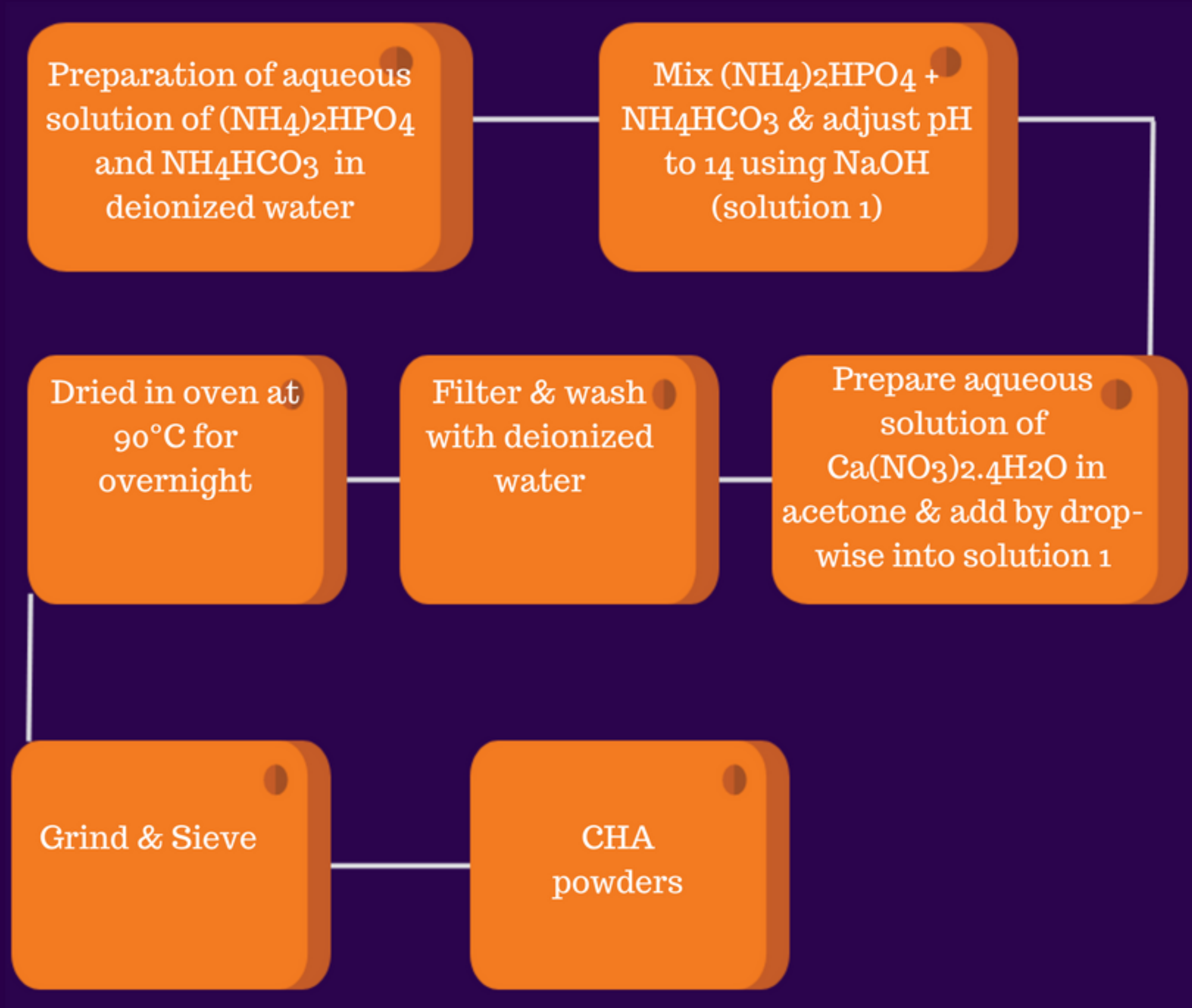
Emulsion	Microemulsion	Nanoemulsion
Thermodinamically unstable	Thermodinamically stable	Thermodinamically unstable
Cloudy	Transparent / Cloudy	Transparent/ Milky wax
Droplet size > 500nm	Droplet size ≤ 200nm	Droplet size ≤ 100nm
High viscosity	Low viscoity	Low viscoity
Low kinetically stable (Tend to sediment)	Moderate kinetically stable	High kinetically stable (Against sedimentation)
No surfactant used	Require large amount of SURFACTANT (≥ 20wt%)	No surfactant required to obtain microemulsion-like dispersion

Chemically suitable for producing Bioceramic powders

Nanoemulsion

- Use of potentially toxic components (e.g. Chlorinated solvents) can be minimized or avoided
- Reproducible nanoparticle size with a narrow size distribution can be achieved without an external energy source

Preparation of Carbonated HA by nanoemulsion



Wet Chemical Synthesis

Spray Drying Method

Understand what is Spray Drying...

Method where the solvent is evaporated.

Encourage method to produce powder with multi-component system with metal oxide based.

Working Principle

Fine droplets produced by a fluid atomizer

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Fine droplets are sprayed into a drying chamber

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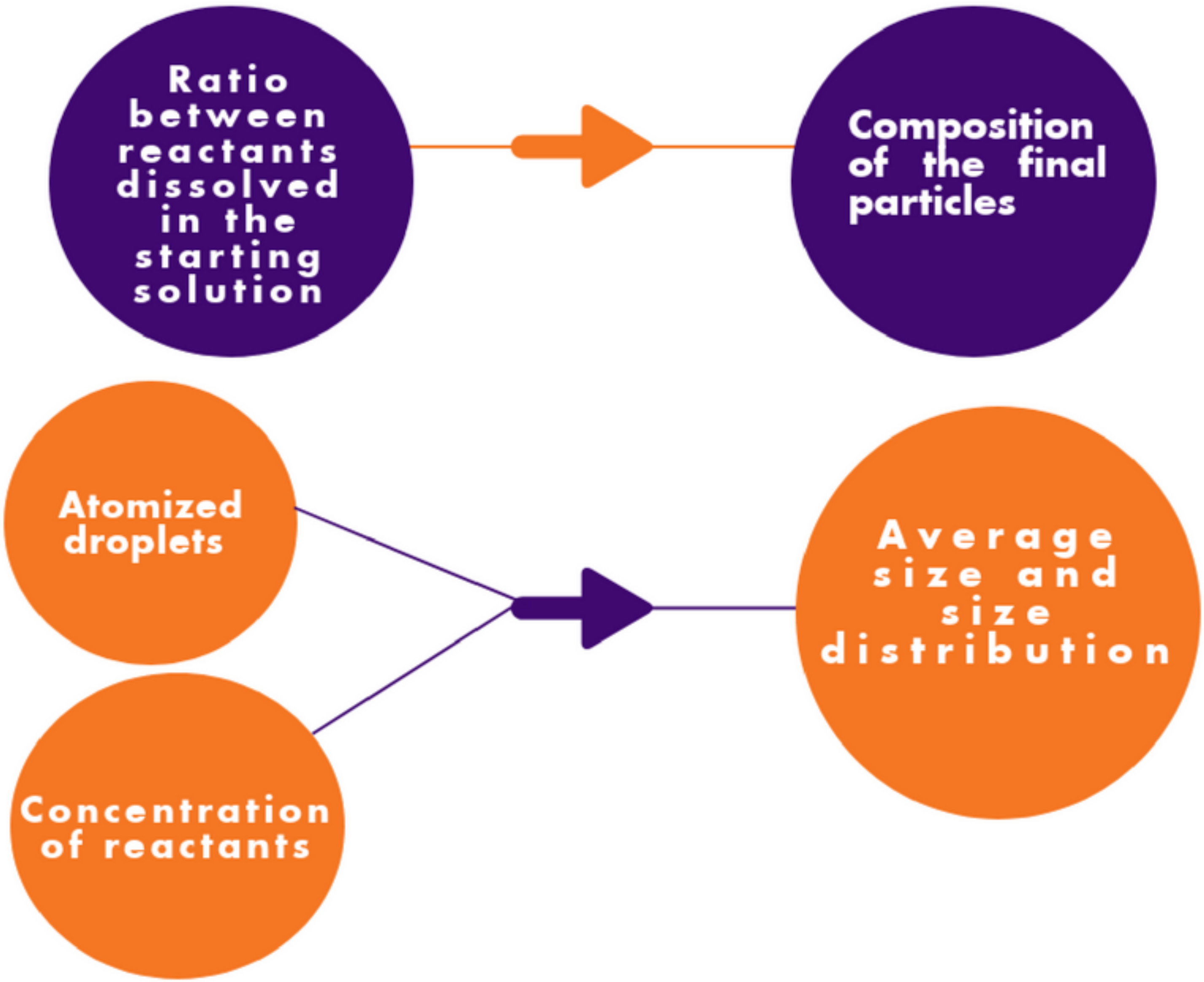
Powder is collected

Process Control

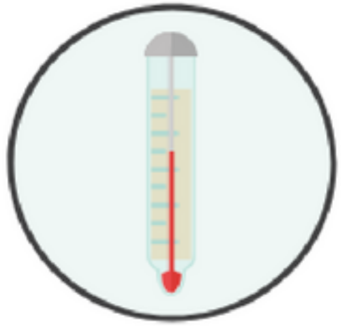


Morphology of particles and their extent of agglomeration

- Properties of precursor
- Carrier gas flow rate
- Temperature

Controllable Variables...

Size of droplets

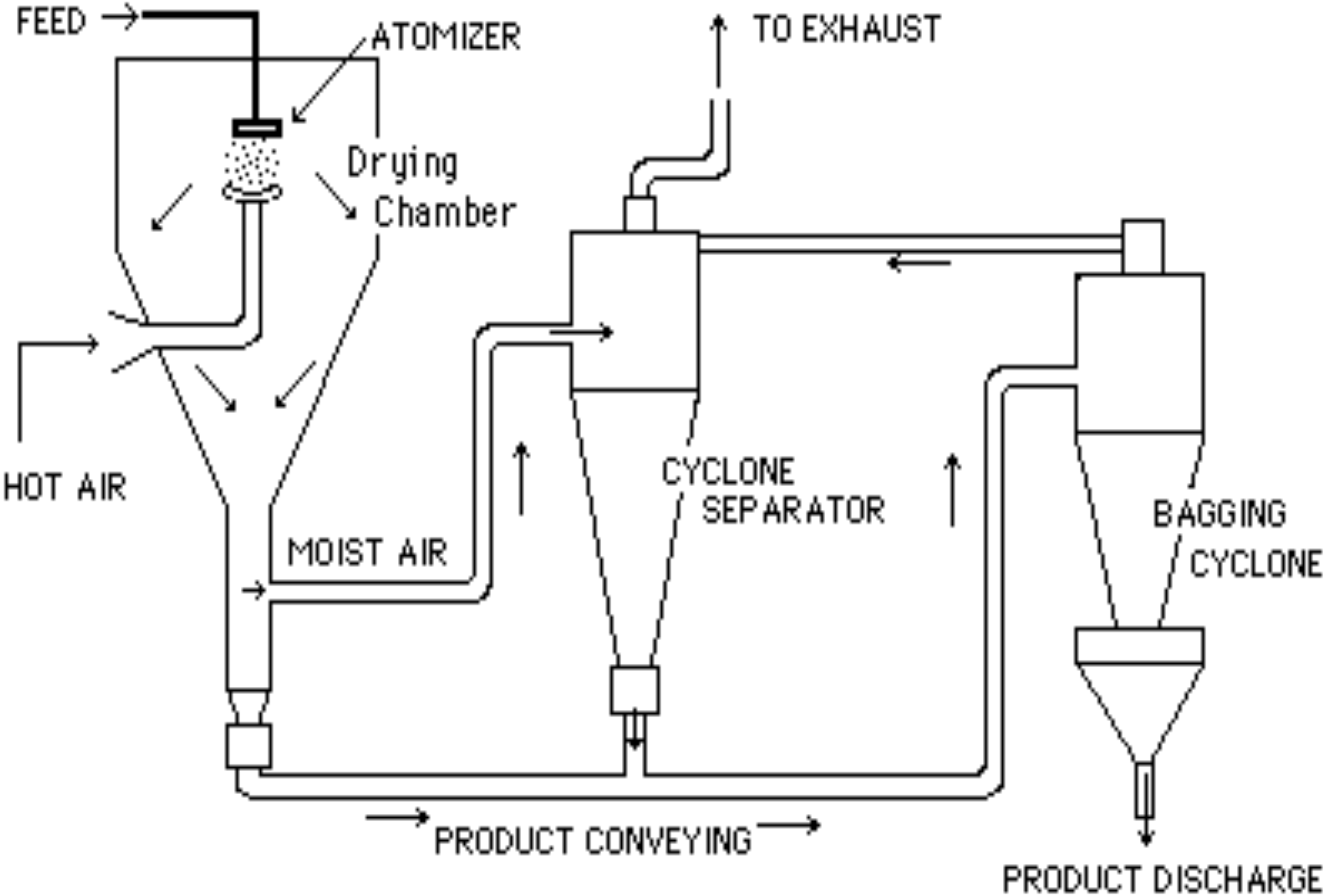


Temperature

Concentration of solutions

Design of chamber

Flow pattern of the air in the drying chamber



Cyclone Spray Dryer Schematic Diagram

Spray dryer

Nozzles

Particle Morphologies

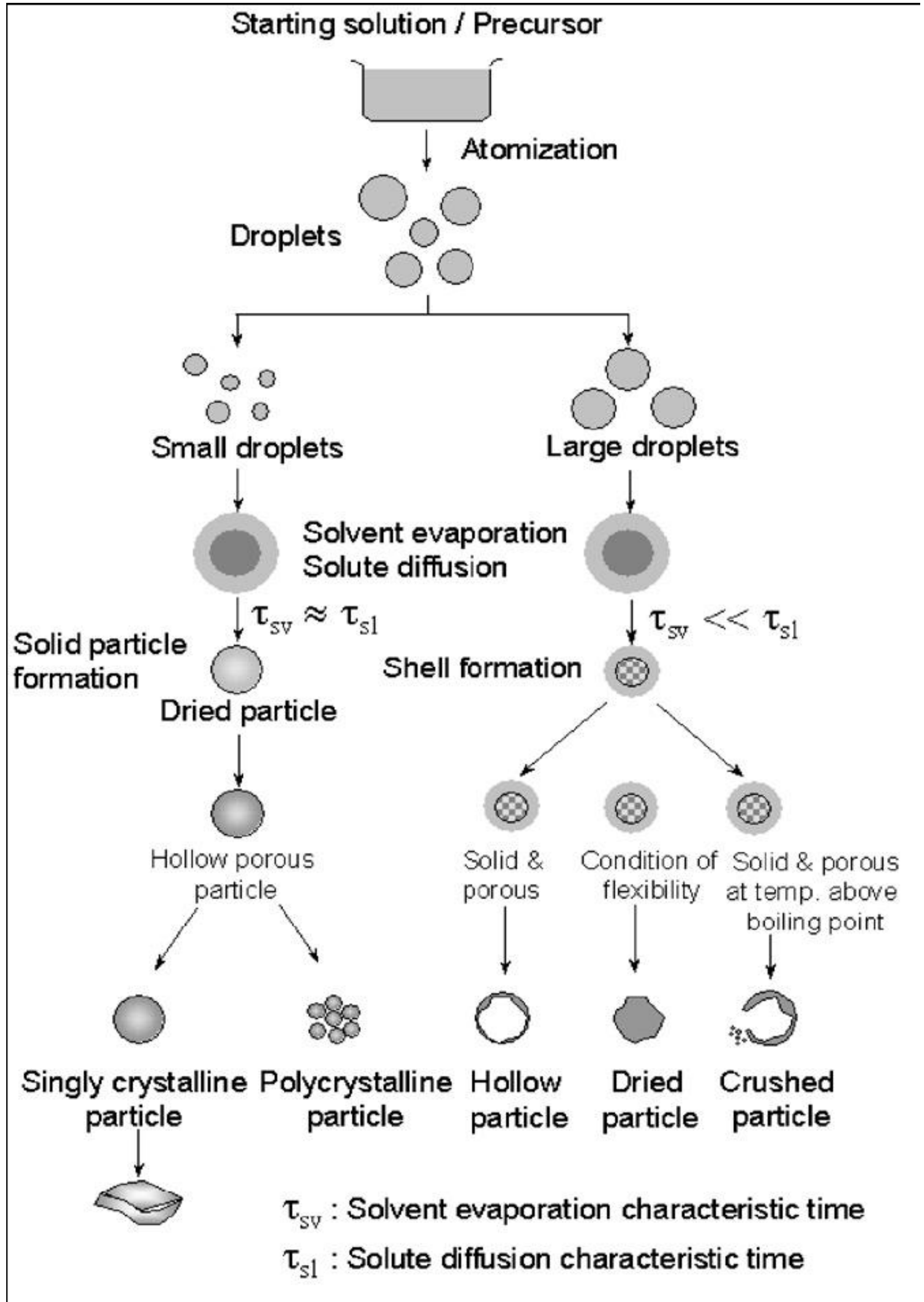
Dense

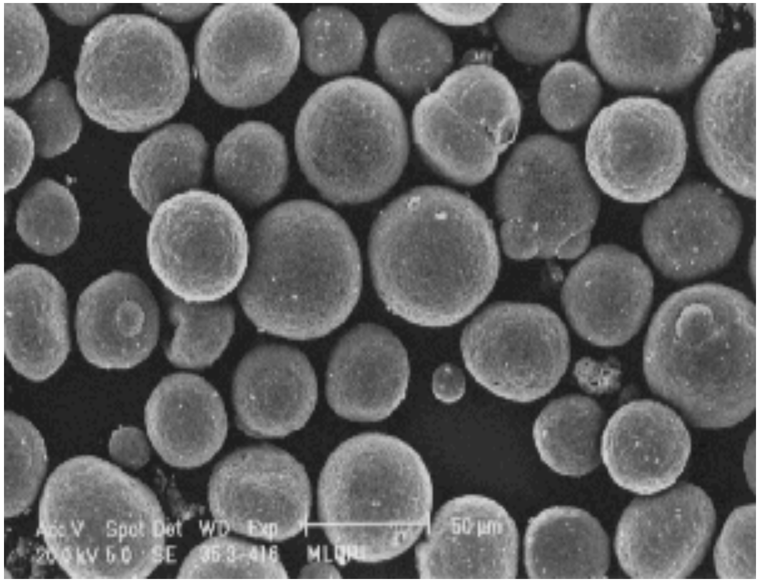
Porous

Hollow

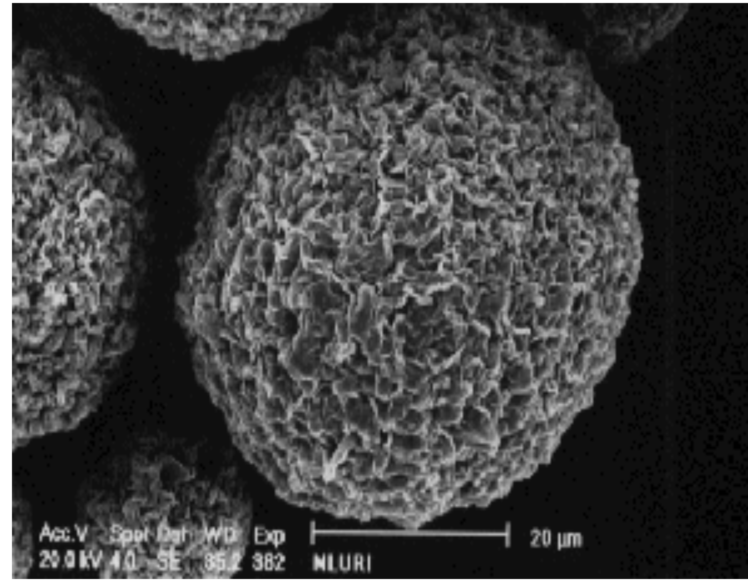
For advanced ceramics, dense particle are preferrable over those with highly porous or hollow shell-like

Morphology of particles prepared by spray method

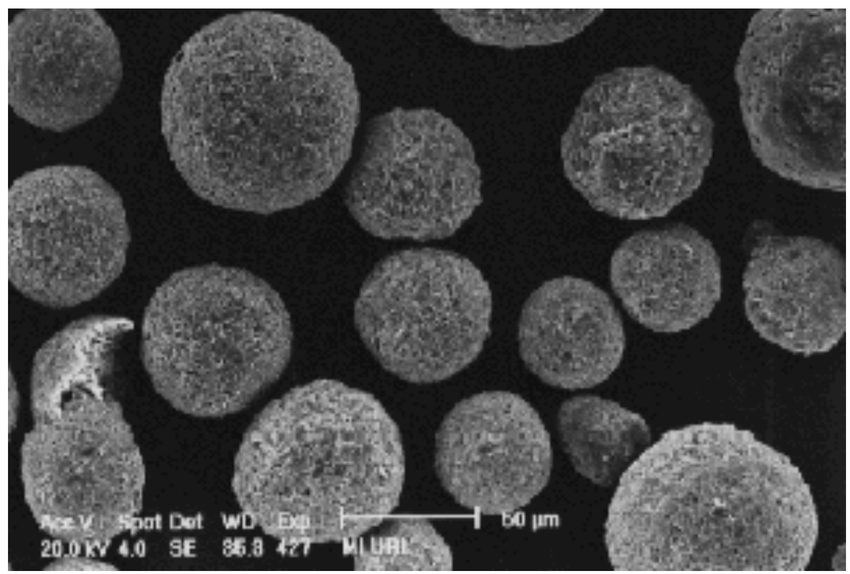




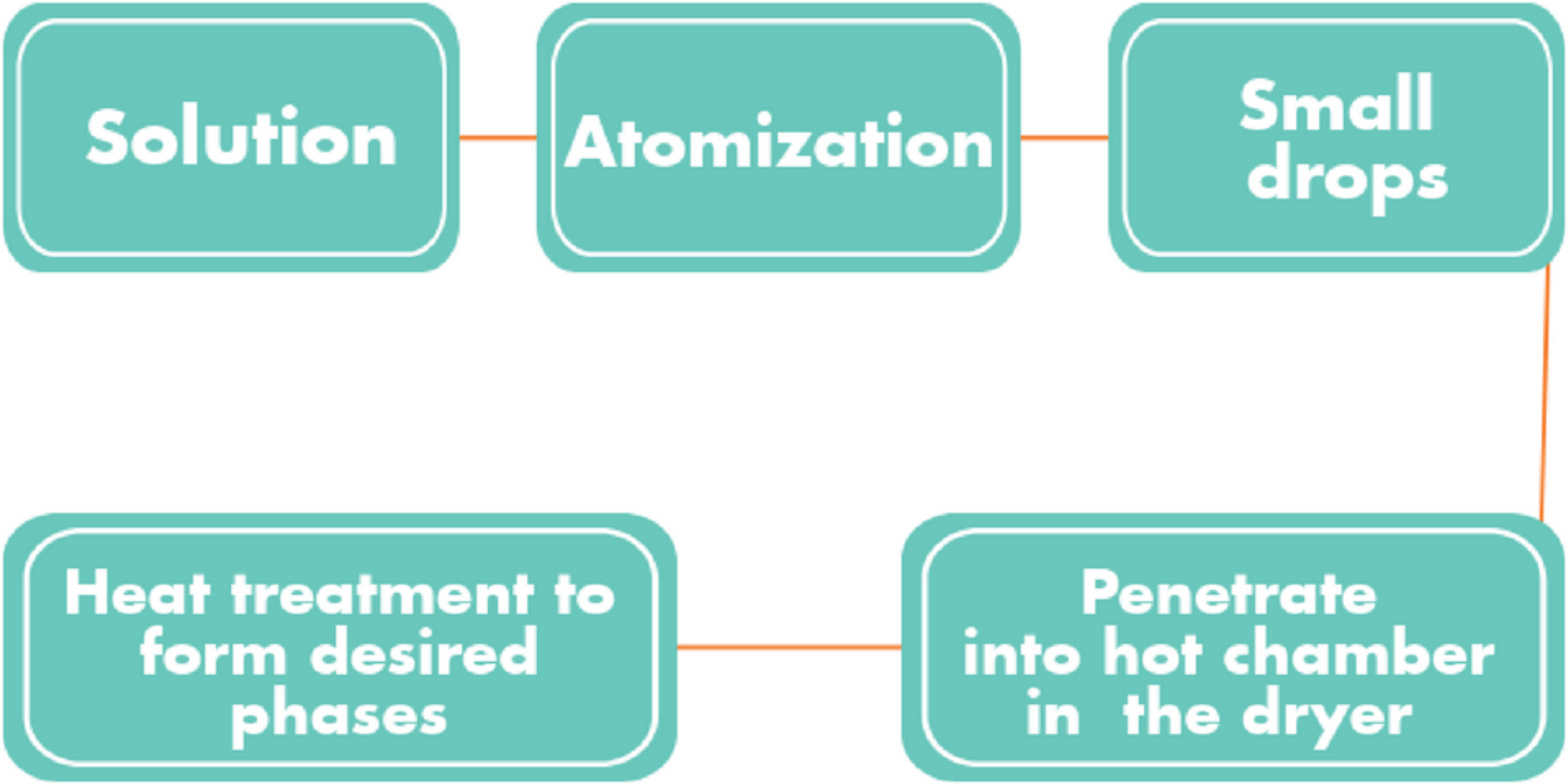
Spray dried kaolinite.



Spray dried smectite.



Spray dried muscovite


Solution
Atomization
Small drops
Penetrate into hot chamber in the dryer
Heat treatment to form desired phases

Advantages vs Disadvatages

- Able to control the particle size of powder
- Can be used from small to very high productions depending on their design
- Low cost of maintenance (small number of moving parts and the use of resistant materials)
- Purity of the product maintained (particles do not have any contact with the surface of the equipment until they are dried)
- Low bulk density of the product
- Low labor cost due to simple operating system

- Expensive equipment
- Not suitable for materials which are sensitive to heat
- Not easy to set up parameter