3. Drying and binder removal

3.0 Introduction

Drying = elimination of free and adsorbed water (including capillary water) from the as-shaped ceramic green body; mathematical modeling: heat transfer and mass transport. *Binder removal* or *debinding*, i.e. the elimination of organic binders and additives, in the prefiring stage, is a similar process. Both drying and debinding are usually accompanied by *shrinkage*.

3.1 Principles of drying

- Water content of ceramic bodies (moisture), shrinkage (linear and volumetric), contact angle (Young-Laplace equation, wetting, capillary stress), liquid permeability in porous media (Kozeny-Carman equation), humidity of air, dry and wet bulb temperature, humidity chart

- *Stages of drying:*

    - *increasing rate period – heat-up* stage: the body temperature increases from an initial value to the wet bulb value (Fourier's law, heat transfer) – for conventional drying (using convective-radiative heating) more slowly in the body interior than at the body surface,
    - *constant rate period* – constant evaporation rate; should not be too high, so that liquid loss due to evaporation at the surface (liquid-vapor meniscus) can be compensated by liquid flow driven by the concentration gradient (Fick's law, diffusion) or pressure gradient (Darcy's law, flow); ceramic body saturated with water → *shrinkage* (driven by capillary stress) until the water content in the body falls below a critical value (critical moisture),
    - *falling rate period* – meniscus radius < pore radius, liquid recedes into the body (→ further moisture transport via vapor diffusion); ceramic body unsaturated by water; the body temperature increases from the wet bulb value to the dry bulb temperature in the oven (again, for conventional drying the body interior lags behind the body surface); no shrinkage (therefore uncritical stage of drying).

3.2 Drying techniques

- *Conventional* (convective-radiative) drying: Free-room drying or drying supported by heating using infrared radiation and / or streaming hot air
- *Electroresistance* drying: Joule heating as a source term in the Fourier-Kirchhoff equation (uniform volumetric heating; useful for large bodies, e.g. large electrotechnical porcelain insulators; only possible above the percolation threshold, i.e. as long as the body has sufficient water to be conductive)
- *Microwave* drying

Microwaves (MW): electromagnetic waves with frequencies 0.3 – 300 GHz (free space wavelengths 1 m – 1 mm), typically 2.45 GHz, rarely 0.915, 28 GHz or 60 GHz; principally similar: dielectric or radio-frequency heating (1 – 100 MHz).

Interactions of materials with MW: metals reflect MW, insulators (non-lossy dielectrics, e.g. air, glass and most ceramics at room temperature) transmit MW waves; only lossy dielectrics (at room temperature e.g. water and SiC) couple to MW and the dielectric losses (dependent on temperature, frequency and porosity or moisture content) are transformed into heat → heat source term in the Fourier-Kirchhoff equation given by the MW power absorbed per unit volume. Above a critical temperature also insulators can couple with MW radiation.

Mechanisms: ionic conduction (at low frequencies), dipolar rotation (at high frequencies); penetration depth: several cm (free space wavelength 12.2 cm for 2.45 GHz MW); loss factors: high for water and for SiC.

Advantages: uniform volumetric heating, faster processing (factor 10), potential energy savings (up to a factor 10, especially in hybrid drying systems), better process control (but thermal runaway must be avoided) and improved product quality. However, for water contents > 5-10 % MW drying is too expensive (only 50 % of electrical input energy is converted to MW energy); at low water contents < 5 % MW drying becomes economical. MW heating can also be used for binder burnout and sintering (oxides, carbides, nitrides).

3.3 Drying problems

Main problem: liquid evaporation in the constant rate period should not be too fast; otherwise the liquid flow from the interior could not compensate the liquid loss and the surface would dry and shrink preferentially → stresses → *cracking* or *deformation* (warping); similar problems can arise when in the body there is a gradient in moisture or particle size.

Particular problems are posed by the *drying of gels* (hydrogels → aerogels or xerogels), due to the very small particle size or polymeric structure (→ Scherer’s theory of drying).

Method for gel drying to obtain highly porous (ϕ > 90 %) xerogels: *supercritical drying* (liquid removed above the critical point, e.g. 31 °C and 7.4 MPa for CO_2).

3.4 Binder removal (debinding)

Many ceramic shaping techniques (e.g. injection molding) involve a high amount of organic vehicles (so-called binders, including plasticizers, lubricants and other functional additives) → binder removal is an important step before sintering; three methods:

- *Extraction by capillary flow* (wicking) by heating the green body in a packed powder bed that absorbs the molten binder,
- *Solvent extraction* by immersing the body in a liquid that dissolves only one component phase of the binder, leaving an open pore structure for subsequent burnout,
- *Thermal decomposition* (very similar to drying of moist green bodies, only at higher temperatures – several hundred °C).

Complex exercise problem: Compare *microwave* drying and other drying techniques from the viewpoints of product size (small-large), geometry (simple-complex), water content and energy consumption. *Additional explicit questions:*

a.) In which cases is it useful / necessary to use combined (hybrid) techniques of drying ?
b.) How can microwave energy be used for burning out organic binders ?
c.) Can ceramics be sintered in a microwave oven ? (If yes, how ?)