# TP 2: Processing of Ceramics: Forming and Shaping

(responsable: Weitian Zhao - MXD339 – weitian.zhao@epfl.ch)

## I. INTRODUCTION

The term ceramic often refers to objects of primitive art like pottery, bricks and tiles. But the term ceramic more generally means a solid which is not a metal or a polymer. A ceramic is a solid synthetic material which often requires heat treatments for its densification. Most modern ceramics are prepared from powders consolidated (processing/shaping) and are densified by a heat treatment (sintering). Most ceramics are polycrystalline materials, i.e. having a large number of well-ordered microcrystals (grains) linked by areas less ordered grain boundaries (joints de grain) [1] as shown in figure 1.

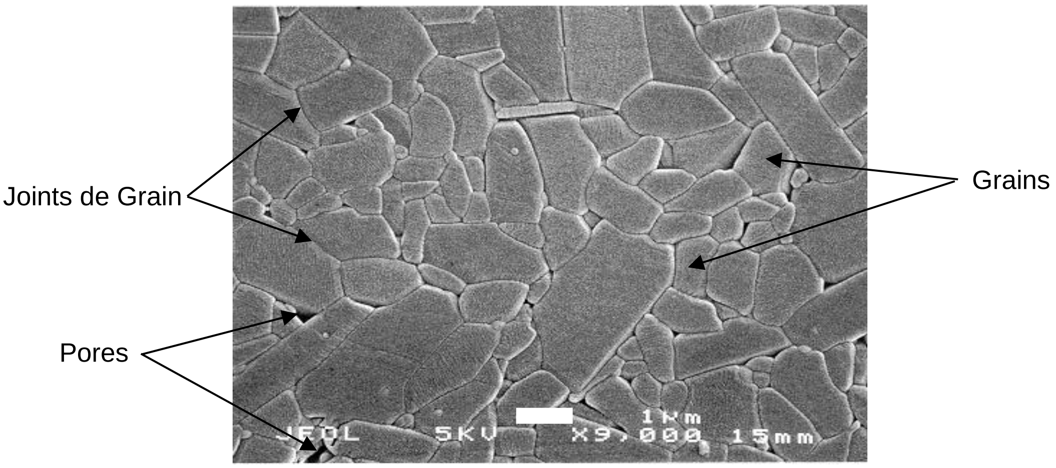

***Figure 1.*** *Typical microstructure of a polished ceramic surface that shows the single crystalline grains, grain boundaries and pores.*

The sintering transforms the compressed powder (green body) into a coherent solid through the effect of the temperature. Chemical bonds are created between particles, and holes or pores between particles are more or less filled. Temperatures which are normally applied are below the melting temperature of the main constituent. There is often a minor constituent which forms a liquid phase and makes the diffusion easier and increases the rate of sintering. The properties of sintered ceramics are strongly related to microscopic defects such as pores (incomplete sintering), clusters (due to the raw powder or the processing itself) or chemical impurities (in the raw powder, or due to contamination in the process). Current research is trying to eliminate those imperfections to achieve more homogeneous materials, with less impurities and at a reduced cost with better control of microstructure and composition of grain boundaries.

The shaping is a central theme in the manufacture of a ceramic as each application requires a precise geometry, as a vase, multilayer capacitors (thin-layer stacks of $BaTiO_3$ for example), electronic support (flat plate of $Al_2O_3$), or ball milling. The intrinsic properties of ceramics, brittleness, hardness and high melting point, do not permit the application of conventional metallurgical methods such as laminating or melt-casting. There are two main types of processing ceramics i) pressing (a dry powder) and ii) wet methods, such as slip casting or tape casting, (forming a paste or dispersion of the ceramic powder with a liquid – usually water) [2]. The choice of a method for producing a green body of powder depends on several factors including the desired properties, the geometry, its size, dimensional tolerances, surface properties, and naturally the cost and productivity. The physical chemistry of the surface of particulate materials (high surface areas 5-15 $m^2/g$) is very important for the shaping of green bodies (before heating or sintering). When using wet methods the ceramic piece has to be dried before the firing or sintering step. All methods of processing require the use of additives (usually organic) e.g. dispersants to facilitate the formation of a suspension, or binders and lubricants for compaction.[1] These organic additives must be removed before sintering, normally by pyrolysis by heating in air, this process is called debinding or binder burnout. Both steps, drying and debinding, may cause defects if the removal of liquid or additives is too fast.

This TP aims at introducing the principles of production of ceramics from powders. Figure 2 shows a flow chart of typical manufacturing processes of ceramics. The materials obtained by sintering are rarely materials in thermodynamic equilibrium. The final structure of the product is closely related to the structure of the starting material, as well as the history of manufacturing and heating during its processing from powder to sintered piece. The TP will focus on the principles and fundamental phenomena governing the shaping step in the processing of the ceramics. In this TP we will follow the steps of forming by slip casting and dry pressing. Slip casting consists of dispersing the powder into a liquid so as to obtain a concentrated suspension but very fluid, the slip. This step uses the knowledge of colloidal chemistry. [1,3,4] The slurry is then formed by casting in a mold. This usually consists of a porous material capable of absorbing excess liquid from the slurry (e.g., plaster of Paris). After the removal of excess liquid, the slurry becomes solid (green body) and can be de-molded. This technique is good to process objects of complex shapes such as dentures, Formula 1 valve engines, and also large objects like toilets and porcelain insulators for high voltage high lines and transformer stations. This type of method of wet shaping requires a drying period before the sintering step. In dry-pressing the ceramic powder is filled into a mold and pressed with a hydraulic press. After the sufficient pressure, the formed ceramic body can be de-molded. This technique is good for simple shapes and near net shape ceramic processing of simple geometries.

## II. THEORETICAL OVERVIEW

### II.1. Dispersion of powders

One of the most important steps in the slip casting is the powder suspension [4]. When you put a powder in a liquid, particles must be individually dispersed (no agglomerates), without any change in the stability of the dispersion during the processing, that is to say with a high colloidal stability preventing their agglomeration. The powders used are usually provided as dry powders in which we find most of the time some agglomerated primary particles. The cohesion of agglomerates is due to the different bonds or forces between elementary particles. The typical bonds or forces that are found in the preparation and storage of the powders are: van der Waals forces, adsorbed moisture (capillary forces), electrostatic forces and the chemical bonds. When the “agglomerates” of a powder are linked by chemical bonds they are called hard agglomerates or aggregates - that is to say something that does not normally break with a single treatment with ultrasound, but possible by grinding.

To disperse a powder, different steps are needed: a) wetting the solid, b) breaking up agglomerates, c) and stabilizing the suspension. To obtain a satisfactory dispersion one must choose a liquid, a method and duration of mechanical treatment (e.g. treatment with ultrasound or grinding) and if necessary a suitable dispersant (in the appropriate concentration).

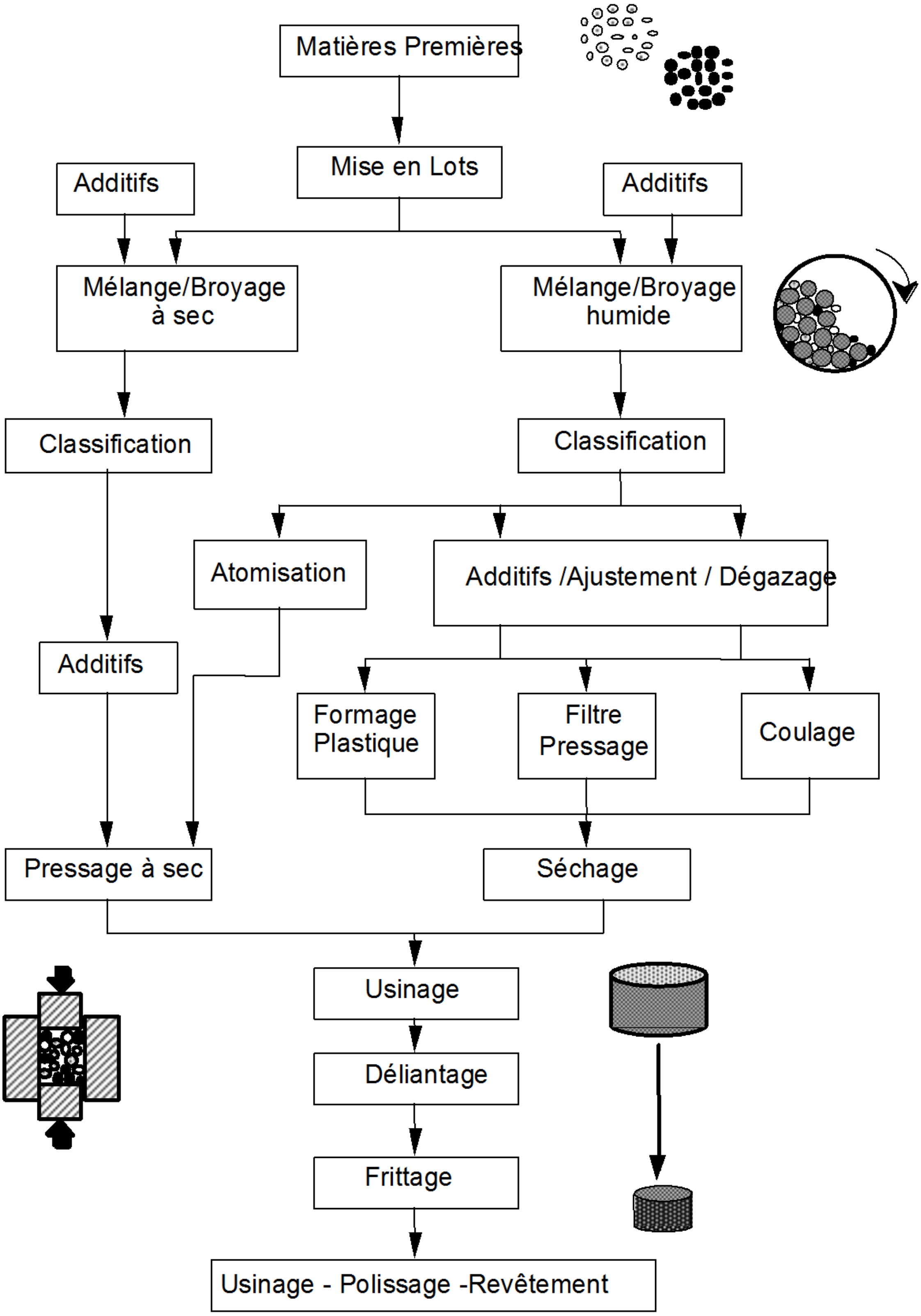

***Figure 2.*** *Organizational chart showing the various stages of ceramic processing.*

The stability of a SUSPENSION depends on the sum of the forces acting between particles, for example, electrostatic forces (repulsive for same type of particles with same surface charge), steric forces associated with a dispersant or an adsorbed polymer (usually repulsive) and the attractive dipole-dipole interactions (part of van der Waals forces), illustrated in Figure 3 (a). The electrostatic forces are due to either surface charges caused by the adsorption of ionic species (ions, or ionic surfactants) or the dissociation of surface species (Figure 3 (b)). The forces called steric (repulsive) are due to the presence of polymers or polyelectrolytes often adsorbed on the surface and create a distance between particles, or create an osmotic pressure associated with concentrations of species in the vicinity of the particle surface (Figure 3 (c)). Van der Waals force at typical distance between particles are dominated by the attractive force resulted from the interactions between instantaneous dipoles, induced by fluctuations of the charge distributions in the particles. Van der Waals forces act over very short distances and are proportional to the radius of the particle. Thus the larger the particle size the more stable they are, as the electrostatic forces are proportional to the square of the radius. The steric effects are often modeled as a barrier that limits the distance of approach between two particles and thus stabilizes the suspension (more details are given in refernce1, 3 and 4).

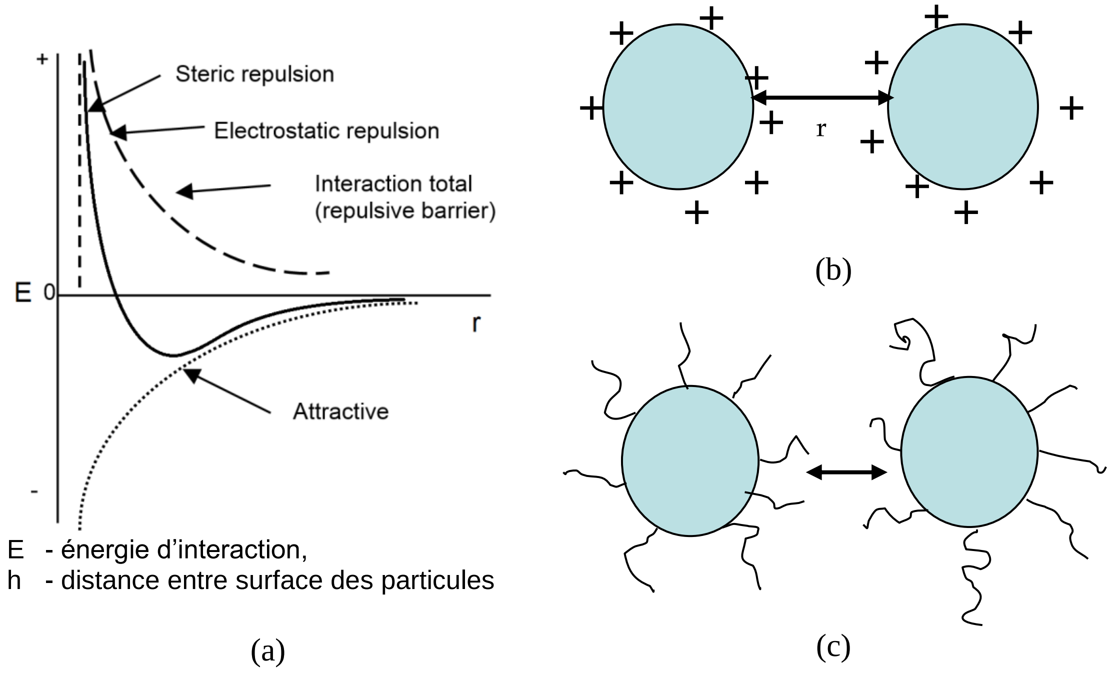

*__Figure 3.__ (a) Interactions between ceramic particles (alumina) dispersed in water with polyacrylic acid (PAA) as a dispersant. (b) Charged particles – electrostatic repulsions (c) adsorbed polymers – steric repulsions.*

A simple method to characterize the stability of a suspension is the measure of the sedimentation volume. The sedimentation volume is inversely proportional to the quality of the suspension. In other words, the stable suspensions sediment slowly, forming a dense layer, instead of agglomerated particles that form a porous structure of low density. For the slip casting of alumina ($Al_2O_3$), we measure the sedimentation volume of suspensions of different compositions and different powders and we compare these results with the density of the green body.

## II.2. Pressing

The compaction is a technique for shaping in both the traditional ceramics (manufacturing tiles) as well as in advanced ceramics (dielectric, fuel nuclear biomedical prosthesis). There are two different types of pressing techniques:

- Uniaxial pressing (pressure is applied in a direction by a piston)
- Isostatic pressing (pressure is applied in all directions through a fluid).

The quality of the compact not only influences their maneuverability but also sintering behavior and quality of finished parts. Defects in compaction will not be corrected during the sintering operation.

There are two different approaches to describe the behavior of a powder under pressure.[4] We can consider the powder as a continuous medium which applies the laws of solid mechanics. In these models, the powder is considered a rigid-plastic material. The true nature of a powder batch leads to a rather microscopic study of compaction when one is interested in mechanisms that are responsible for densification. This session would allow comparison of compaction, first of an atomized powder in the last TP and the other of a commercial granulated powder by uniaxial pressing. Once the die or mold is filled, the pressure is applied and the powder is compacted to the desired shape and size. The change in compressed density with the pressure applied generally follows three stages: I) rearrangement, II) deformation and fracture of granules, and III) densification of the granules. The different steps are usually seen on a semi-logarithmic graph of the density of compressed versus the logarithm of applied pressure (Figure 4).

The rearrangement of the non-compacted granules into a pile tapped density in the first stage of compaction takes place generally at applied pressures below 0.5 MPa. The second stage of compaction eliminates the majority of the intergranular porosity due to the plastic deformation of the granules. The final step of filling the small intergranular porosity and densification of the granules takes place at applied pressures above 250 MPa. The possibility that one or more of these mechanisms take place at the same time can not be excluded. But for compositions of granules optimized, the sequence of mechanisms explained above seems correct.

Several models [5,6,7] have been developed to attempt to describe the behavior of compaction, and most express the density of the tablet, ρ, as a function of the applied pressure. Kenkre et al. [6] proposed a model of statistical mechanics based on the volume where an activation pressure exists to enable the different phases. It means that the rearrangement takes place over a range of pressures, then deformation on another band, and finally the densification and fracture in another range again (these ranges can overlap and mechanisms may occur simultaneously). The process of rearrangement is not activated by pressure, but Other processes are, and can be represented by the following equation:

$$\rho = \frac{\rho_0}{1-\left(\frac{\rho_\infty-\rho_0}{\rho_\infty}\right)\left\{c\left[1-\exp\left(-\frac{P}{\mathrm{P_r}}\right)\right]+\left(1-c\right)\int_0^\infty dP_s g(P_s)\exp\left(\frac{-P_s}{P}\right)\right\}} \tag{7}$$

where ρ is the mass density of the tablet at the applied pressure P, $\rho_0$ the mass initial density after filling (not packed density), ρ* the theoretical density (infinite pressure), $P_r$ pressure is a fixed value characterizing the rearrangement and $P_s$ is the pressure activation for other mechanisms and $g(P_s)$ is the distribution function of pressure.

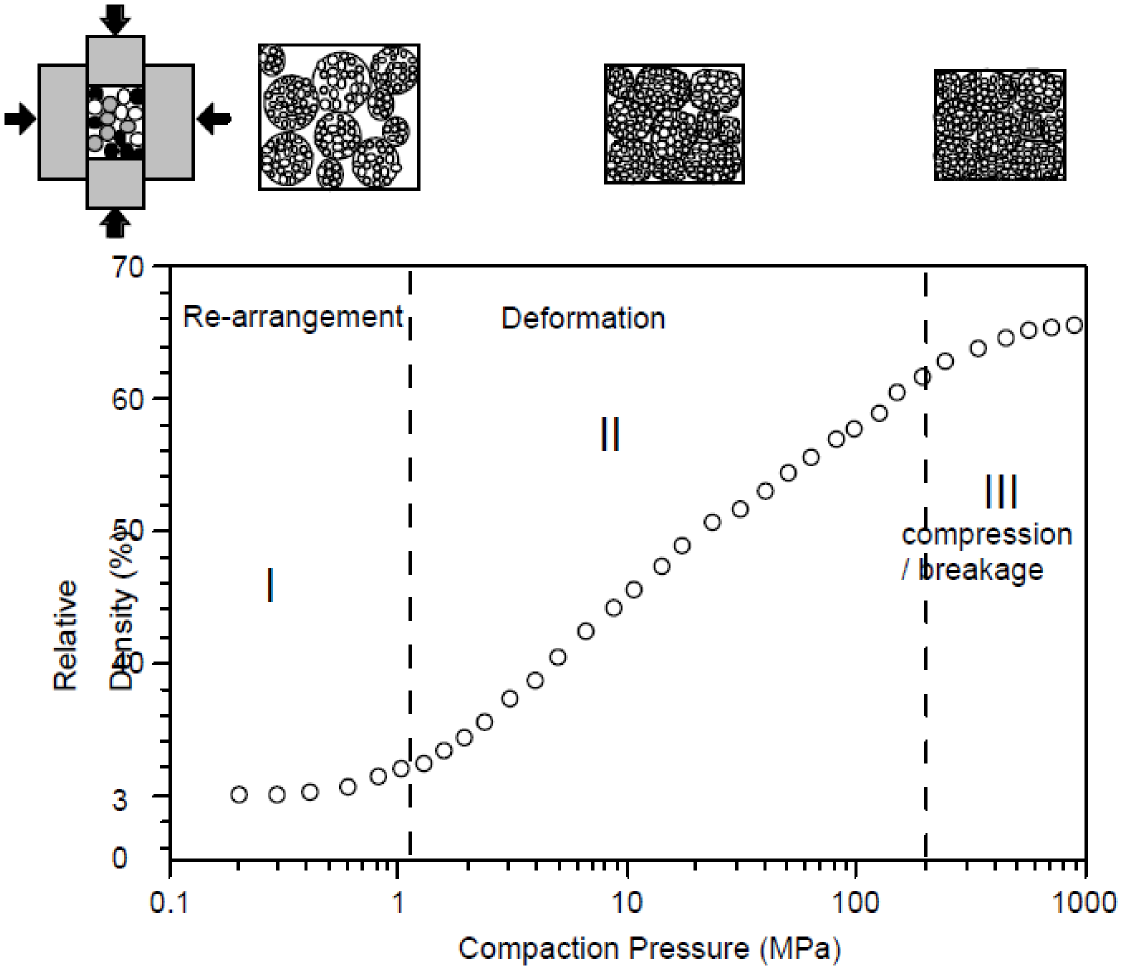

***Figure 4**. Relative density versus compaction pressure for a spray dried alumina powder showing the three regions of compaction.*

The distribution function of pressure is the possibility of a range of pressures where the different mechanisms of deformation, fracture and densification of granules can take place. This is the case when the granules are not homogeneous, or not stacked evenly. The distribution function of pressure can also result from false pressure in the transmission of pressure through a bed stacked (due to different coordination numbers in a random stacking). Kenkre et al have shown that for Alumina, granular compaction curve can be adjusted with the rearrangement term and a single pressure barrier for the activated process (where the deformation of granules of alumina is expected to dominate for lower pressures of about 150 MPa). Under these conditions, equation (7) reduces to the expression of Cooper and Eaton [5] which is limited to two regimes of pore filling, first rearrangement filling the holes of similar size to the granules and the second filling the holes and smaller intergranular porosity, either by deformation or by rupture of granule.

$$\rho = \frac{\rho_0}{1-\left(\frac{\rho_\infty-\rho_0}{\rho_\infty}\right)\left[a_1\exp\left(\frac{-k_1}{P}\right)+a_2\exp\left(\frac{-k_2}{P}\right)\right]} \tag{8}$$

Assuming that the filling of holes at low pressure is entirely due to rearrangement, the equation of Cooper and Eaton correctly describes the behavior of compaction of many granulated powders. An example of a commercial powder pellets is shown in Figure 4.

## III. EXPERIMENTAL WORK

### III.1. Sedimentation volume of an alumina powder ($Al_2O_3$)

Same alumina powders (AA04, $D_{v50}$ median diameter 550 nm) and three different dispersants will be used, which are pure water, 0.3% polyacrylic acid (PAA) solution and 0.5% PAA solution. Ammonia is added to both PAA solutions in a molar ratio of $NH_4OH$ : PAA = 3:2. The pH is determined by this ratio and is about 10.

a) Four test tubes of each 2 g (± 0.05g) of $Al_2O_3$ powder.
b) Add ~ 20 ml of liquid (water, water, 0.3% PAA, 0.5% PAA) in test tube, in a graduated glass tube (25 ml) covered with Parafilm.
c) Stir by hand for 5 seconds and then place in an ultrasonic bath for 5 minutes and agitate again for 5 seconds by hand.
d) Place the tubes in a grid so that they are in a vertical position.
e) Read the volume of the sediment.

### III.2. Determination of the liquid limit of alumina powders ($Al_2O_3$)

The following work aims at finding the optimal composition of a casting slurry consisting of alumina ($Al_2O_3$) stabilized by 0.3% or 0.5% PAA, which can ensure a fluid slip with maximum concentration of solid matter.

a) Alumina ($Al_2O_3$) powders are already in polystyrene bottles (35 ml) with the mass of powder written on the lid **(~2.0 g)**. Weigh precisely the total weight (cup + lid + powder, $\mathbf{m_1}$) using an analytical balance.
b) Using a micropipette, add **400 µL** of PAA solution and close the bottle.
c) Shake the bottle for 30 seconds on the REAX 2000 vibrator.
d) If the mixture does not look like a homogeneous liquid at the end of c), add **40 µL** of solution of PAA and repeat c). Continue until a homogeneous mixture is reached.
e) Weigh the bottle (cup + lid + powder + liquid, $\mathbf{m_2}$); calculate the liquid limit (µL /g) and (g /g), which are the volume or weight of dispersant necessary to obtain a fluid suspension of 1 g of powder. Think about which ratio is more accurate.

### III.3. Casting of alumina ($Al_2O_3$)

Use the liquid limit (for 0.5% PAA solution) from previous experiment: **X (g/g)**. Add 5% excess to allow for error.

a) Weigh separately 10 g of alumina AA04 powder and the corresponding amount of PAA 0.5%.
b) Add the powder into the liquid under magnetic stirring. Then shake the bottle on the REAX-2000 vibrator for 30 seconds.
c) Apply ultrasonic treatments if dispersion is not uniform.
d) Pour the dispersion into the cells of the mold. Cover the mold surface with a watch glass.
e) Demold previously prepared sample and observe mechanical properties.

### III.4. Uniaxial pressing

The compaction of $Al_2O_3$ powders will be performed in a simple die. The deformation and the stress during the experiment will be recorded.

Press used: Walter + Bai hydraulic press (50 t) controlled load.

Die: 20 mm steel die

Powder: Granulated alumina produced in TP1, commercial $Al_2O_3$.

1. Fill the die with 2g powder place it between pressing component.
2. Set the pressing program (loading rate 0.1 kN/s after reaching threshold pressure value, hold one minute at max. load of 40 kN, pressure unloading at same rate).
3. Initiate the program.
4. Unload and eject the tablet, measuring its dimensions and weight, notice the height of tablet does not equal the sample height at maximum loading stress.

## IV. SUMMARY

*The report should contain the following:*

- **Brief Introduction**

Goal and very brief summary of the theory necessary for understanding and interpreting the results obtained.

- **Method**

Brief description of experimental details
Do not repeat the script of the TP, but give a brief description of experiments and devices used and specifically comment on some points, if necessary:

- Error on the measurements (±)
- Sedimentation volumes
- Liquid limits

- **Results and Discussions**

Suspending

- Analysis of sedimentation volume, discussion on the effect of PAA on the colloidal stability

Slip casting

- Physical significance of liquid limit.

Pressing

- Plot the curves of $\rho$ compaction rate (%) versus log P for the test uniaxial pressing of the two powders.
- Calculate the curve $\rho$ for both powders and compare with the model $\rho$ as measured by Cooper and Eaton. Calculate the parameters $a_i$ and $k_i$ (Linear regression and error). Discuss weak points of model: Is it applicable to granulated powders? Why?

- **Conclusions**

## V. REFERENCES

[1] J. Barton, P. Bowen, C. Carry and J.M. Haussonne. *Traité des Matériaux, Volume 16, Céramiques et Verres : Principes et techniques d'élaboration*, ISBN 2-88074-605-1, Presses Polytechniques et Universitaires Romandes, 2005..

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