Relevant properties of a (liquid) powder for continuous casting of steel

R. Carli, M. Alloni, S. Casagrande

Present paper concerns noteworthy effort which has been conveyed in defining characteristics of conceptual liquid powder, more precisely a liquid casting powder. Expanding the idea of mixing properties of liquids and casting powders, a new material composed by a solid-liquid dispersion of conveniently formulated continuous casting powder in synthetic oil has been conceived. Aiming to prove that a material with higher load of solid component behaves like a liquid, few lab samples with different proportions between solid and liquid phases have been formulated and extensively characterized.

Rheological properties of this liquid casting powder samples proved those have to be considered as liquid with well-defined real-world technological properties. In particular, it has been pointed out that this material shows a specific viscosity which is connected to its solid component load through Robinson equation and its rheological behavior is described by Bingham constitutive equation.

Eventually a liquid casting powder is working as a liquid slag of a casting powder pumped at room temperature into the mold and, in comparison with natural/mineral or synthetic oil used in open steel stream, it is adding effective lubrication and control capability of heat transfer between strand and mold wall, resulting in mild homogenous cooling and in a significant increase of effective length of the mold. Indeed a tremendous improvement of general casting process quality has been observed.

KEYWORDS: MOLD FLUX, CASTING POWDER, LUBRICANT, NON-NEWTONIAN FLUID, BINGHAM, STEEL CASTING, SOLID-LIQUID DISPERSION.

INTRODUCTION

The expression *liquid powder* referred to lubrication of steel forming shell in a continuous casting machine has been used for the very first time by Prof. Alan Cramb during his plenary lecture at the 5th European Continuous Casting Conference held in Nice (F) in June 2005, when trying to stress the importance of a very innovative attitude in field of steel casting he said "we do not know what in the future... maybe a *liquid powder* for continuous casting...".

The idea of using a liquid slag to lubricate a strand in a slab caster has been studied and realized by some researchers from POSCO [1] . However, a more viable and radical solution has not yet been identified, none of existing materials correspond to the set of characteristics of a conceptual *liquid powder* or better liquid casting powder. In first approximation, such an object should be a liquid bearing some feature of a powder, more precisely in the present case an oil used for continuous casting bearing some cha-

Riccardo Carli, Marco Alloni, Simone Casagrande
Prosimet Spa, Filago, Italy, 24040

racteristics of a mold flux. A rapid survey of the attributes of a typical mold flux points to few performance carrying traits which cannot be transferred to a standard oil for continuous casting, mainly inflammability, apparent bulk density, CO2 and total Carbon contents. Moreover, it sounds really meaningless talking about melting of a liquid casting powder.
It seems that a substantial preliminary approach to possible design of a *liquid powder* compels a broader definition of its conceivable characteristics. Starting from this task, present paper deals with description of main characteristics of a theoretical liquid casting powder, consequently trying to prove that realization of an object complaining with a well-defined set of properties is actually possible, resulting in a new technological-intensive material. It will be shown that such a wonder product performs in a way not comparable with any extant standard products used in continuous casting of steel.

TECHNOLOGICAL CHARACTERISTICS OF LIQUID POWDER

Attempting to figure out what a *liquid powder* looks like in the context of steel continuous casting, one can analyse properties of existing liquids and powders used in this technological field as it follows from a Value Innovation methodological approach [2]). Thus, the exercise consists in ranking common elements of perceived quality of those products, to evidence their relative strength and weakness.
In Figure 1, results of such analysis for three different materials, are depicted.

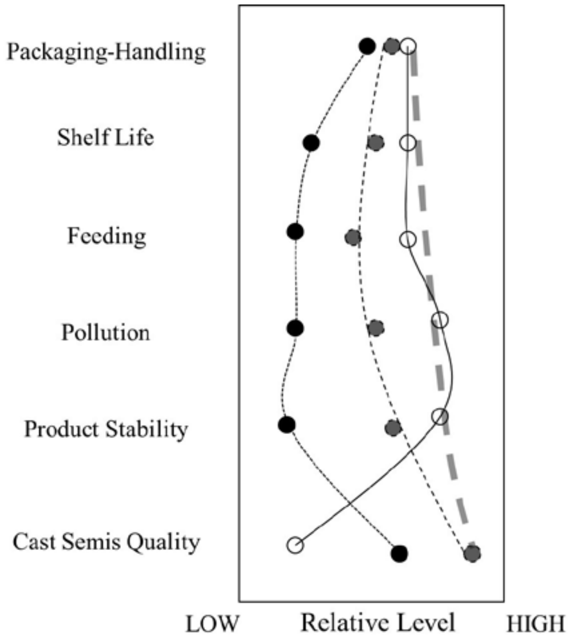

Fig.1 - Elements of perceived quality for loose powder mold flux (black dots), granular mold flux (grey dots) and oil for continuous casting (white dots).

These results are based on data collected with a simple questionnaire distributed among technical personnel of steel casting department of some steel plants, where at least two of products under scrutiny are used. It is possible to infer that a casting powder in granular form is by far showing better perceived quality than the same product in fine powder form. This is very a well-known fact in the field, somehow validating this approach. Therefore, with a reasonable degree of dependability it can be deduced that perceived quality of oil used in continuous casting is higher than the one of a casting powder for all considered elements but cast semis quality. Generally casting with oil is considered suitable only for undemanding commercial steel grades.
It seems natural to conclude that a substantial value-innovated material should exhibit whole set of perceived quality elements laying on dashed bold line in Figure 1, conceptually drawn simply *mixing* quality of casting powder and oil.
Expanding this idea of mixing, a new product, composed by a solid-liquid dispersion of conveniently formulated continuous casting powder in synthetic oil based on fatty acids glyceric esters, has been conceived. Aim of this attempt is the realization of a product featuring characteristics of both oil and continuous casting powder, to be used as lubricant

in steel casting process.

EXPERIMENTAL

Following the method described elsewhere [3,4]), some samples based on specific raw materials have been prepared. Namely, Al_2O_3 (Nabalox® 104RA, alpha- Al_2O_3 98%, Al_2O_3 99.8%), CaF_2 (Fluospar, Acid Grade, CaF_2 > 95, ISO5439, structure controlled by XRD, Brüker D2 PHASER), $CaSiO_3$ (Wollastonite, Industrial Grade, CaO 44÷45 %, structure controlled by XRD, Brüker D2 PHASER), Na_2CO_3 (Sigma-Aldrich, anhydrous, free-flowing, Redi-Dri™, ACS reagent, Na_2CO_3 ≥99.5%), have been selected. These materials have been ball-milled for 30 min in twin agate mortars with a bench mechanical orbiting device (Philips, MINIMILL) or for 15 min in a Titanium Carbide eccentric mechanical mill (Hertzog HSM100H), then sieved with mechanical vibrating sieving system (Retsch AS200), collecting fraction below 60µm.

Few hundred grams of Powder Component, PC, has been prepared with these milled and sieved raw materials simply by mixing for two hours in a rotatory drum bench mixer. Final composition of the mix has been determined by XRF analysis (performed with Brüker S8 TIGER) and it's reported in Table 1.

Tab.1 - Chemical analyses of Powder Component.

	Weight %
CaO	38.0
SiO2	44.0
Na2O+K2O	6.5
Al2O3	1.2
F	5.5
Basicity	0.9
Bulk Density‡	1.94 ±0.06 (kg/l)

Bulk Density, BD, is marked with "‡" symbol to indicate that parameter poses quite an issue in evaluation for a mixture of different solids. Value reported is the measured density of a high pressure casted pill of PC. This value has been then validated by calculating molar fraction weighted sum of all mineral components N as $BD‡=\sum_i^N \rho_i \frac{n_i}{n_{TOT}}$.

Different amounts of PC have been dispersed in a poly-α-olefin oil, PAO, (Mobil SHC 500) with lab scale high peripheral speed colloidal mill (IKA, MK2000/05) for 5 min. 5 different samples have been prepared with different PC load, A: 60% wt./wt., B: 50% wt./wt., C: 40% wt./wt., D: 30% wt./wt., E: 20% wt./wt..

Bearing in mind that hypothetical limit to consider a liquid as a *liquid powder* can be a mix with at least 50% wt./wt. PC load preserving suitable fluidity for effective and stable pumping, rheology of these samples has been fully characterized by research rheometer Anton-Paar MCR302. Measurements were performed @ 298 K, consistently with standard procedure ASTM D2196-15 [5]). Raw data processing was executed with Anton-Paar RHEOCompass software. Further number crunching has been performed by in-house-developed Python routines.

PHYSICAL-CHEMICAL CHARACTERISTICS OF LIQUID POWDER

Viscosity

As stated above, it has been essential to study parameters affecting viscosity of dispersions trying to obtain a liquid with suitable properties, in particular fluidity. Investigation on complexity of solid-liquid dispersion systems requires in depth theoretical interpretation of all relevant interaction forces affecting status of dispersed particles [6]). It has been pointed out that most essential elements in describing the system are: kinematic viscosity of liquid medium η_0, volume concentration of dispersed particles or solid volume fraction $\varphi=C_M/\rho_p$, where C_M is mass concentration of solid and ρ_p is bulk density of dispersed particles (BD‡) and void fraction $1-\varphi/\varphi_m$, where φ_m is maximum volumetric fraction of solid. See Figure 2.

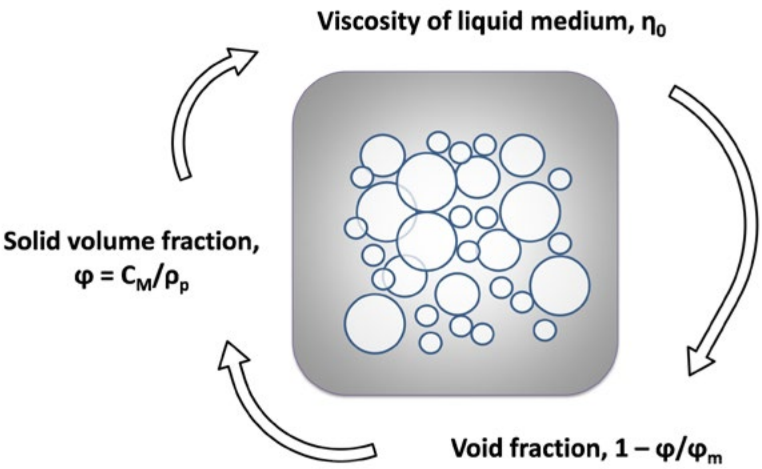

Fig.2 - Elements describing solid-liquid dispersion system.

Based on these quantities semi-empirical correlations for relative viscosity, $\eta_r=\eta/\eta_0$, of hard-spheres suspensions have been developed in the past. Krieger-Dougherty equation has shown considerable applicability in wide range of real suspensions reasonably described by a model of non-interacting hard-sphere solid-liquid dispersion [7]. However, in case of liquid casting powder here described, the Krieger-Dougherty equation has shown some deviation for higher φ, probably because implemented correlation considers only trend of void fraction $1-\varphi/\varphi_m$. Indeed, better results were obtained with Robinson equation 7), Eq.1, where ratio between volume concentration of dispersed particles φ and void fraction $1-\varphi/\varphi_m$ is taken into account.

$$\eta_r = 1 + \frac{[\eta]\varphi}{\left\{1 - \left(\frac{\varphi}{\varphi_m}\right)\right\}} \quad \mathbf{1)}$$

In Eq.1, term [η] is the intrinsic viscosity or the crowding factor as described by M.Mooney [8]. This quantity is a constant for a specific system and is generally derived along with φ_m as a curve fitting parameter. Experimental data fitting for measured relative viscosities of A-E samples is reported in Figure 3, where best fitting is also represented.

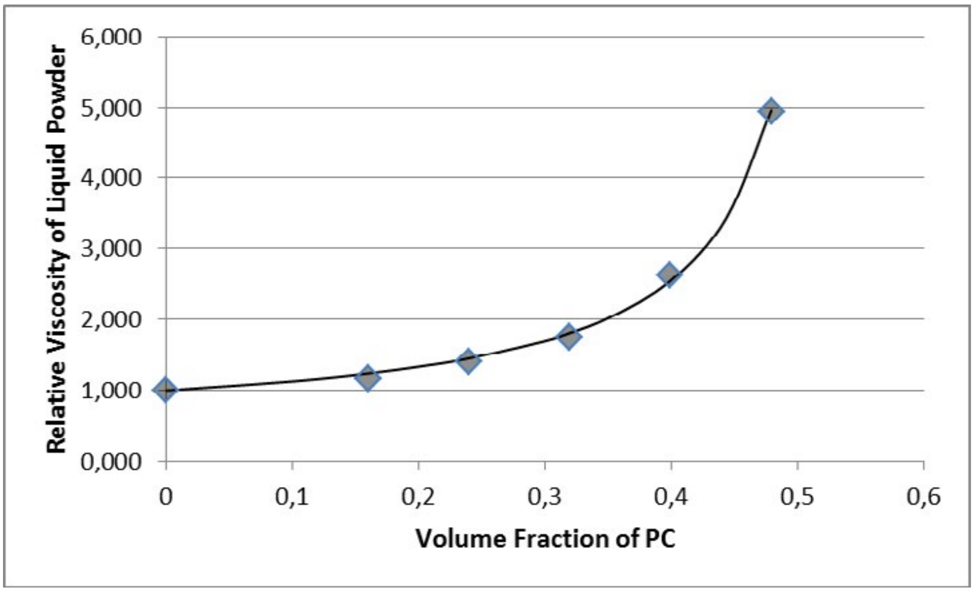

Fig.3 - Fitting of experimental data (grey dots) by Robinson equation (line).

It's interesting to note that fitted parameters for data depicted in Figure 3 shown values of [η] = 1.059 and φ_m = 0.549 which are similar to same parameters reported for different suspensions of poly-dispersed minerals [9]). Further, value of φ_m = 0.585 is very close to theoretical random close packing fraction of uniform hard spheres φ^*_m = 0.63 proving effectiveness of packing of poly-dispersed solid particles in liquid powder.

Rheological model

In studying rheological properties of liquid casting powder, very first observation was the shear-thinning nature of this suspension which is indeed quite common characteristic of real non-Newtonian fluids. This characteristic has been clearly observed for all samples A through E. Therefore, knowing viscosity for a specific range of working conditions will not be enough to define technological properties of a liquid casting powder. Indeed, a more accurate rheological methodology needs to be taken up in evaluating factors which actually affect behaviour of a liquid casting powder. Particularly, an equation relating stress, strain, time and sometimes other variables such as temperature (constitutive equation), is needed to describe the rheological behaviour of non-Newtonian fluids [9]).

Then, aiming to define a suitable constitutive equation for the liquid casting powder, first approach was to interpolate experimental data of shear stress measured in a relatively wide range of shear rates where Bingham model generally applies, see Eq.2.

$$\tau = \tau_0 + \eta_P \times \dot{\gamma} \qquad 2)$$

Where τ_0 is the stress yield (Pa), the limiting stress below which the fluid is stagnant or gives an elastic response [10]), η_P is the plastic viscosity (Pa*s) accounting for the excess of the shear stress over the stress yield divided by the shear rate [11]) and γ is the shear rate (s^{-1}).

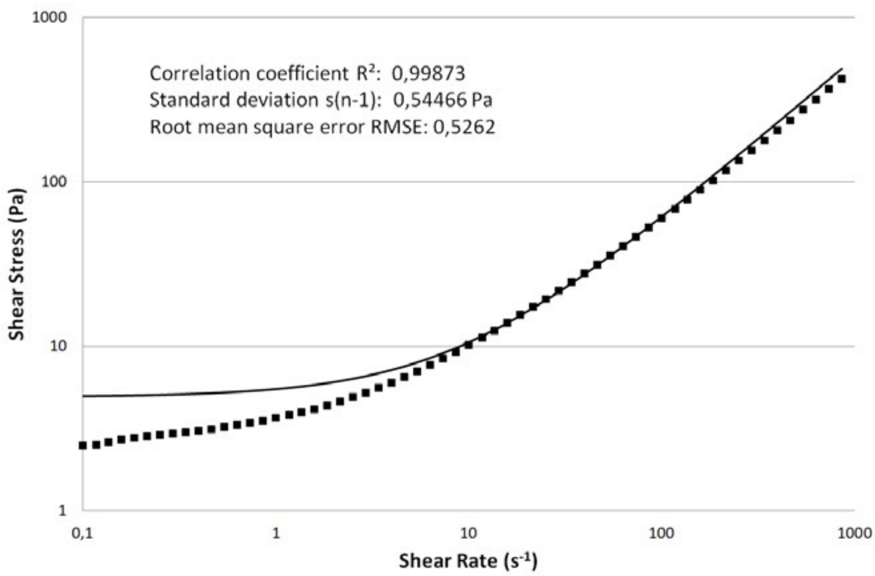

Fig.4 - Bingham fitting of liquid casting powder sample.

Although results of measurement are reasonably fitted in the shear rate range reported as typical for stirring, mixing and pipeline flowing (10^0-10^3 s^{-1})[6]) (see Figure 4), parameters of stress yield τ_0 and plastic viscosity η_P are strongly dependent on interpolating range, indeed it seems that, for a specific values interval, a different constitutive equation better fits experimental data [12]). In spite of that, final criterion to establish appropriate behaviour of a sample of liquid casting powder has to be defined as suitable balance between relative viscosity, η (relative to kinematic viscosity of liquid medium η_0 measured @ reference temperature in present case 298 K), stress yield τ_0 and plastic viscosity η_P from Bingham model.

It has been stated above that an eligible liquid casting powder has to be composed by at least 50% or more of PC, then deeming very first acceptable composition among samples A-E, namely sample B, it has to be clarified in which sense this is a liquid. Considering possible application of a liquid casting powder, liquid means a product bearing *main features* of an oil used in continuous casting, as illustrated in a previous paragraph. Therefore, attention has to be focused on what has been accounted as *feeding*, in other words the possibility to feed the product to a continuous casting machine during normal operations as oil is pumped through pipes to the casting mold.

Sample B has characteristic values as follows: η=2.619 @ 298 K and γ = 4.6 s^{-1}), stress yield τ_0 = 4.922 Pa and plastic viscosity η_P = 0.5637 Pa.s from Bingham model, then question is how these factors are affecting fundamental technological characteristics of this liquid casting powder such as flow through pipes.

Flow through cylindrical pipes

Generally, selected pumping system has to be appropriately sized matching characteristics of pipes required in transferring the liquid powder from a reservoir vessel to a casting mold. Therefore, piping and pumping systems have to be designed based on knowledge of head pressure requirement for a given transfer duty. Clearly, the scope is to maintain stable flow of the liquid powder to a mold.

Limiting present discussion to laminar flow regime, it can be shown that for Newtonian fluids Hagen-Poiseuille equation holds:

$$Q = \frac{\pi D^4}{128\eta L}\Delta P \qquad 3)$$

Where η is fluid kinematic viscosity, D and L are respectively diameter and length of pipe and ΔP is pressure requirement. Equation, Eq.3, in case of a non-Newtonian fluid assumes a specific form which is corrected by a function of parameters of relative constitutive equation or rheological model and $\tau W = \frac{\Delta P * D}{4 * L}$, defined as shear stress at pipe wall. In the case of liquid casting powder which is in first approximation a Bingham fluid as discussed above, Eq.3 becomes [13]):

$$Q = \frac{\pi D^4}{128\eta_P L}\Delta P\left(1 - \frac{4}{3}\phi + \frac{1}{3}\phi^4\right) \qquad 4)$$

Where $\phi = \frac{\tau_0}{\tau_W}$.

Equation, Eq.4, effectively establishes pressure required for a given transfer duty in case of a Bingham fluid, thus for a liquid casting powder sample, explicitly sample B.

In a functional example, for a specific feeding interval of 40÷70 g/min and a linear pressure drop of 3000÷5000 Pa*m^{-1}, it is possible to define a given working space which is fairly crossed by only two equations, EQ.3, plotted for pipe diameters of 12 and 13 mm (approximately ½ inch). See synopsis in Figure 5.

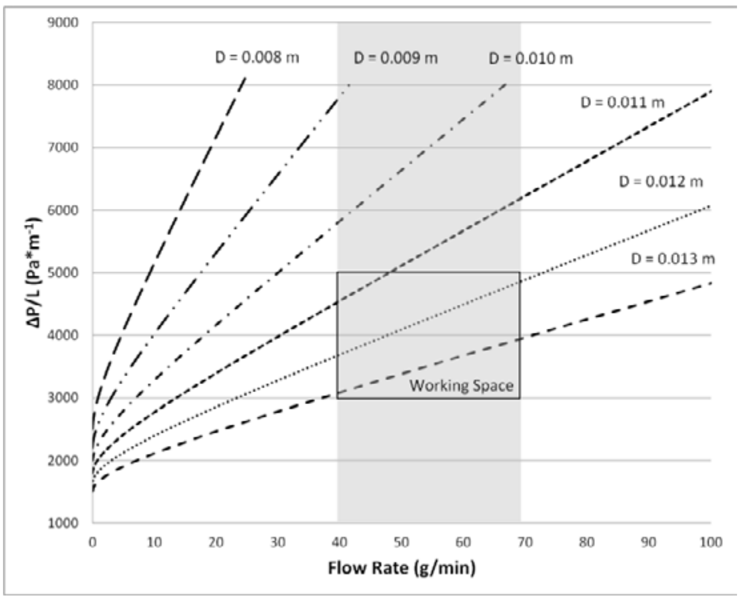

Fig.5 - Definition of actual working space for real application of a liquid casting powder.

At this point of present discussion, it can be concluded that first eligible sample to be classified as liquid casting powder, namely sample B, has to be considered a *liquid* in all pondered aspects, in particular it has been pointed out that this material shows a specific viscosity which is connected to its PC load through a Robinson equation (Eq.1) and its rheological behavior is described by a Bingham constitutive equation (Eq.2). Remaining subject concerns the performance of this material when used in a continuous casting process. Is it *actually* a liquid casting powder?

LIQUID CASTING POWDER HOW IT WORKS

Based on plant results presented elsewhere [14-16]), it is possible to depict the behaviour of a liquid casting powder in a real working environment. It has been observed that solid component, PC, of this solid-liquid dispersion is melting very rapidly at the expenses of heat produced by burning-off of liquid medium. This feature is perfectly matching normal operations of continuous casting of long products in open steel stream, where thermal insulation of liquid steel bath is not an issue. The advantage resides in the fact that a liquid powder is not a compromise like oil, which is burning in contact with liquid steel. Liquid powder actually provides a liquid slag with all known properties of commercial casting powder for continuous casting in close steel stream. Change introduced by such a product in present technology is by any perspective a radical one. As depicted in simple scheme of Figure 6, the liquid powder is fed through a tip especially designed to fit specific mold size and shape.

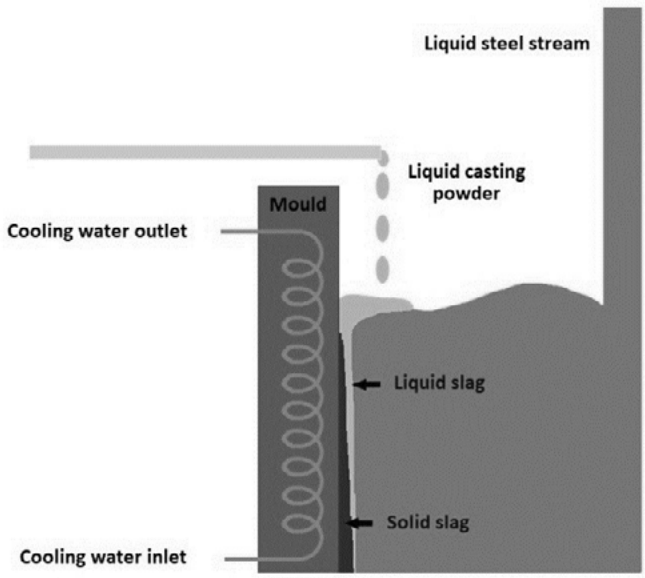

Fig.6 - scheme of liquid powder functioning in mold.

Liquid casting powder in contact with liquid steel is spreading across the entire surface laying entirely close to meniscus area. This effect is a result of pressure produce by first impact wave of steel stream which push slag toward mold wall and some specific characteristics of slag. In particular, slag surface tension and viscosity have to be carefully balanced to endow proper wettability and spreadability, avoiding potential slag entrapment. It has been observed as a general consequence that feeding rate set below a critical limit does not give any interference with liquid steel stream, dumping possible slag entrapment.

In spite of all important operational advantages, nothing is comparable with tremendous improvement of general casting process quality due to infiltration of liquid slag into gap between strand shell and mold wall, when the liquid casting powder starts working as a standard casting powder used for continuous casting in close steel stream.

In comparison with common natural or synthetic oil used in open steel stream, liquid powder is surely adding effective lubrication and, more important, control capability of heat transfer between strand and mold wall, resulting in mild homogenous cooling and in a significant increase of effective length of the mold.

Consequence of this situation is a large tide of benefits pointed out in operations and semis quality during extensive plant trials, such as strong rombohedricity reduction, considerable drop in scale formation and major increase of casting speed [17]).

CONCLUSIONS

Significant effort has been conveyed in defining characteristics of conceptual *liquid powder*, more precisely a liquid

casting powder. Based on expanding idea of mixing, borrowed from *Value Innovation* methodological approach to elements of perceived quality by end-user of this conceptual product, a new material composed by a solid-liquid dispersion of conveniently formulated continuous casting powder in synthetic oil based on fatty acids glyceric esters, has been formulated, in samples with different proportion between solid and liquid phases.
Extensive characterization of rheological properties of this liquid casting powder samples proved those have to be considered as liquid with well-defined real-world technological practical properties. Indeed, this product is working as a liquid slag of a casting powder pumped at room temperature into the mold and in comparison with standard natural/mineral or synthetic oil used in open steel stream, it is adding effective lubrication and control capability of heat transfer between strand e mold wall, resulting in mild homogenous cooling and in a significant increase of effective length of the mold.

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