Digital printing of glass-ceramic glazes

D.Boccaccini

Tecnoitalia Srl

Miembro de: RCAI – “Comisión de Ciencias Agrarias, Ingeniería y de Materiales”

15 de junio 2018 – Cooperazione Universitaria Argentina - Italia

RCAI www.rcai.it - Red de Científicos Argentinos en Italia

Interdisciplinary team

M. Cannio, V. Riva, M. Hanuskova, M. Romagnoli
Dipartimento di Ingegneria Enzo Ferrari, Università di Modena e Reggio Emilia

UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

D.N. Boccaccini
Tecnoitalia S.r.l., Sassuolo (Italy)

R. Taurino, F. Bondioli
Dipartimento di Ingegneria e Architettura, Università di Parma

UNIVERSITÀ DI PARMA

M. Tognetti
Daxel S.r.l., Rubiera RE (Italy)

M. Cicconi, T. Fey
Institute of Glass and Ceramics, Department of Materials Science and Engineering, University of Erlangen- ... any

FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

V. Novaresio
ALLOVIS Engineering, Torino, (Italy)

ALLOVIS Engineering

A. R. Boccaccini
Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Erlangen,

FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

Aim of the work

1. To understand outstanding versatility showed by Inkjet printing in ceramic tile decoration: Drop On Demand system (DOD) and Continuous Ink Jet (CIJ) based on electro valves .

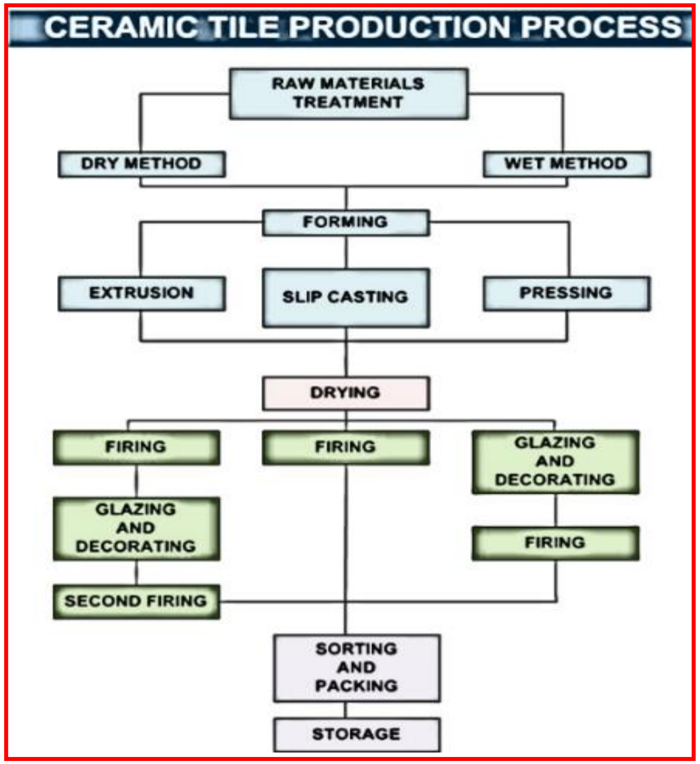
2. To investigate rheological and fluid dynamic characteristics of the glazes and the process parameters required for an optimum deposition on ceramic tile

3. To design semi-empirical printability fluid region using Reynolds number and Ohnesorge number

Outline

1. Digital printing of glazes
2. DigiGlaze: properties
3. Case study: 7 commercial glazes
4. Analysis of defects: «mountain waves» on fired tiles
5. Experimental section
6. Design of printability fluid region
7. Computational Fluid Dynamics (CFD) simulation

Why digital printing of glazes?



Glazing process: One of the most critical processing stage in the production of ceramic tiles; material losses of up to 40% (glaze, fluidising agents & binders to the atmosphere).

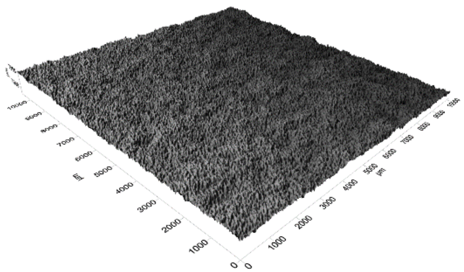
Digital printing of glazes with solvent or water based suspensions based on high frequency (not piezo) valves:

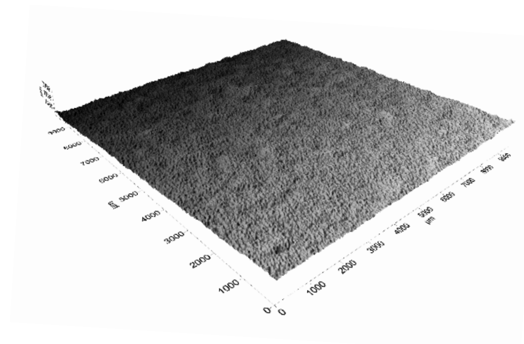
- decrease of glaze waste up to 40%
- possibility to work with water based suspensions
- better tactile impression, reduced ink consumption
- roughness decrease compared to standard methods

Why digital printing of glazes?

Printed green, roughness 41-59 um | Printed sintered, roughness 43 um

Digital technology

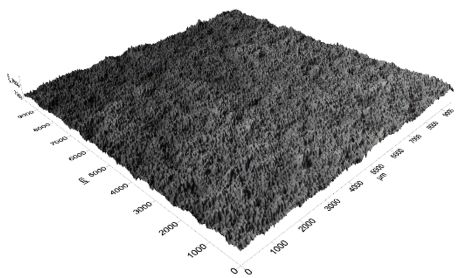


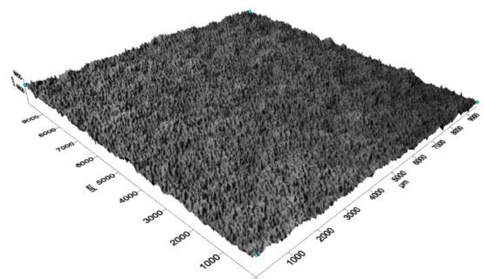


lower roughness

Printed green, roughness 84 um | Printed sintered, roughness 77 um

Spraying technology





higher roughness

Profilometry analyses of green and sintered glass frits deposited by spraying and digital printing

UNIMORE

Inkjet technology: case study

- Production speed up to 65 m/min
- Application of **glazes, engobes, smaltobbio** (both white and coloured) and **protective glazes**
- Pressure < 2 bar
- Flow from 0.4 up 1.25g/s

Inkjet technology

Continuous mode → Microsolenoid valve

Drop on demand mode → Thermal, Piezoelectric, Microsolenoid valve

DigiGlaze

Tecnoitalia srl., Sassu

15 de junio 2018 – Cooperazione Universitaria Argentina - Italia

Overview of the study

Analysis 7 commercial glazes

Glaze formulation:

- Rietveld analysis: phases, cristalline/ amorphous ratio
- EDS: Chemical analysis
- Granulometric analysis: size particle distribution

Physical chemical properties:

- Apparent viscosity
- Surface tension
- Contact angle
- Zeta Potential

- Nozzle step 3 mm
- Manufacturing line speed: 20-30m/min
- Nozzle diameter: 350µm
- Pressure: from 0.4 to 1.2 bar
- Flow jetting speed: 5-9m/s
- Frequency DOD mode: 200-600Hz

Process parameter/ machine
(nozzle diameter, flow pressure, step between nozzle)

Fluodynamic charcaterization
(N° Reynolds, Weber, Ohnesorge)

Printability diagram definition

Rheological conditions | **Process parameters** → **Efficient Printing**

15 de junio 2018 – Cooperazione Universitaria Argentina - Italia

Digital printing of glass-ceramic glazes

15 de junio 2018 – Cooperazione Universitaria Argentina - Italia

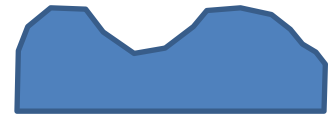
Critical points

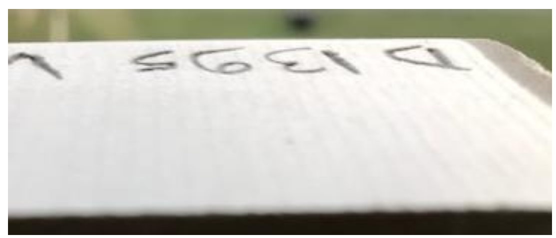
Defects: presence of lines on support

Type: «mountain wave»

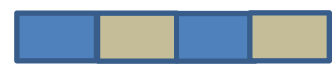
Viscosity decrease

Separation amorphous-cristalline phases





Find the suitable rheological conditions

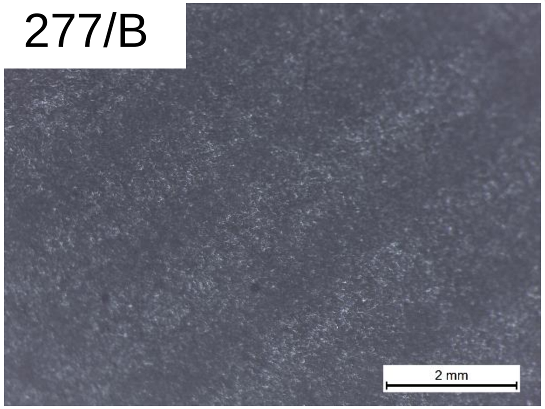


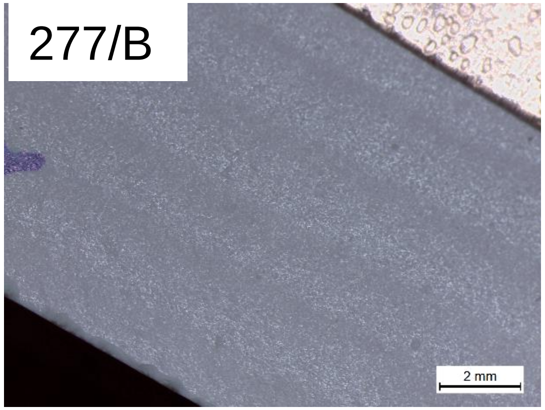
15 de junio 2018 – Cooperazione Universitaria Argentina - Italia

15 de junio 2018 – Cooperazione Universitaria Argentina - Italia

Materials

Sample	Digital printing quality parameter Continuous jet printing mode	Digital printing quality parameter Drop on demand mode
	From 0-10 (10 excellent; <5 low performance)	
554 white	10	10
EN48 white	9	10
3293 white+Zr	8	10
SL 711 coloured	6	9
M490 black	5	9
277/B white Bentonite	4	9
277/A alumina white	4	9





Light microscopy results

Digital printing of glass-ceramic glazes

Materials: physical and chemical characterization

Real density of powder samples by He pycnometer	
Sample	Density g/cm^3
554	3.0275±0.0035
EN48	2.8462±0.0038
3293	3.0534±0.0021
SL 711	2.9072±0.0007
M490	2.9648±0.0027
277B	2.9339±0.0020
277A	3.0204±0.0025

- No significant difference in real density
- Higher amount of CaO in M490, 277B, 277A
- Higher amount of amorphous phase and silica

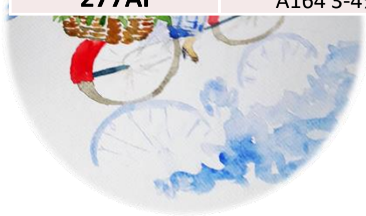
Decrease in digital printing quality parameter

Chemical analysis (EDS) wt%

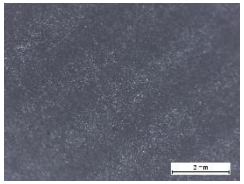
Sample	Additive	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	ZrO_2
554	A164 5%	3.06	17.74	57.62	1.4		20.18
EN 48	A164 9.5%	4.05	21.79	63.63	2.2		8.34
3293	A164 9.5%	3.07	20.97	51.73	1.76		22.47
SL711	A3 3%-Oil 5359 6%	3.35	21.93	60.2	2.31		12.21
M490	A164 3-4%	2.16	11.53	67.19	1.42	5.4	12.3
277B	A164 3-4%	2.42	13.49	63.6	1.5	5.67	13.32
277Al	A164 3-4%		18.53	59.65	1.61	5.54	14.67

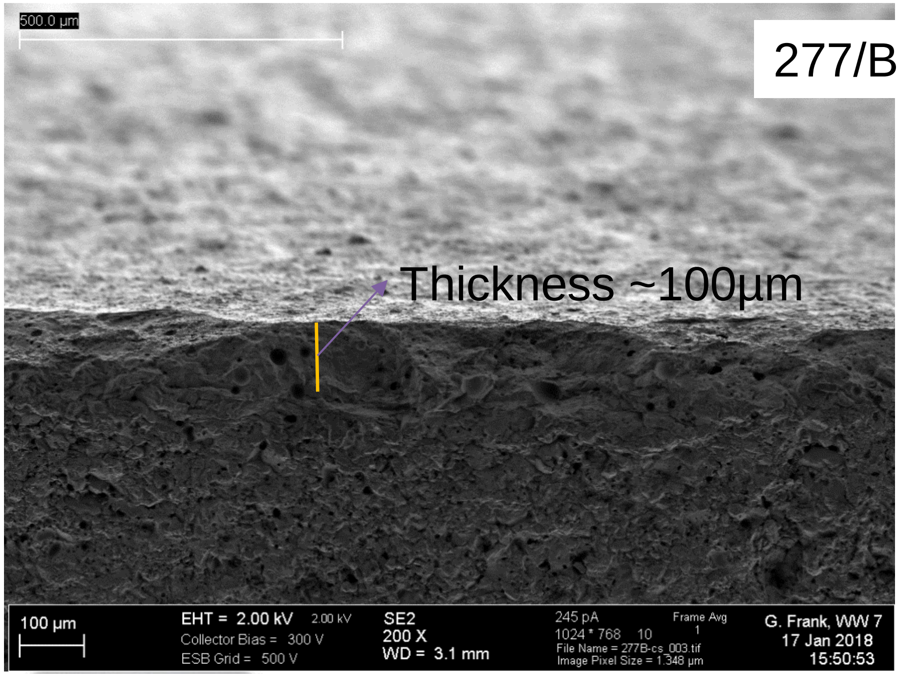
Data from quantitative Rietveld wt%

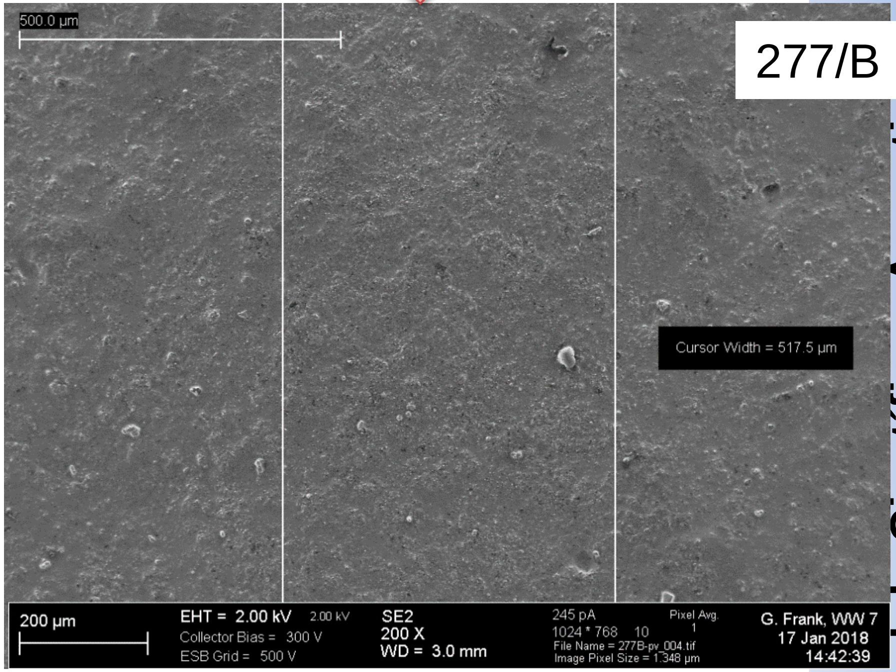
Sample	Quarz	Illite	Zirconia	Kaolin	Allumina	Albite	Dolomite	Wollastonite	Amorphous
554	13.6	3.27	18.75	13.18		25.42	0.51		25.26
EN 48	22.91	6.14	9.76	22.79		11.38			26.99
3293	17.48	5.08	14.22	9.89	6.29	5.32			41.68
SL711	20.21	5.51	9.85	14.7		10.06	1.44		38.19
M490	34.37	5.9	11.27	4.44	9.13	1.33			33.54
277B	40.97	5.27	12.94	4.27					36.54
277Al	27.55		10.65	3.55	12.87			0.96	44.38



Defects: morphology analysis







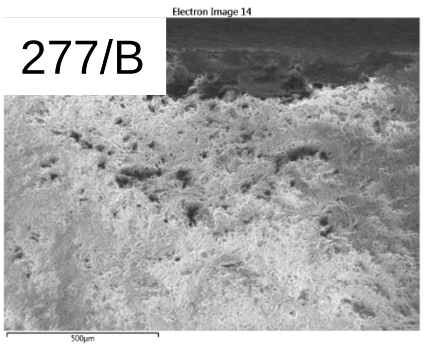
No significant difference in morphology

Chemical characterization

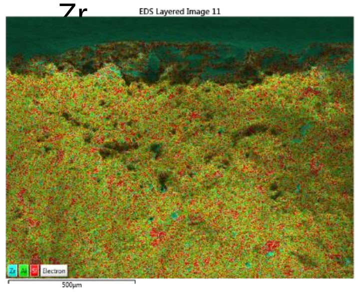
Presence of higher Zr content in the glaze than in the substrate

Sample cross section

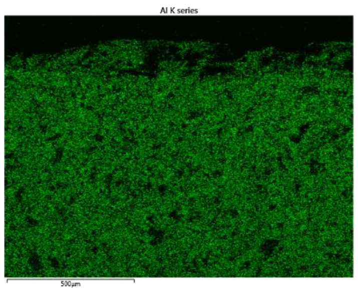
277/B



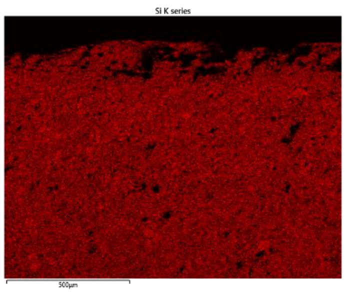
Si, Al, Zr



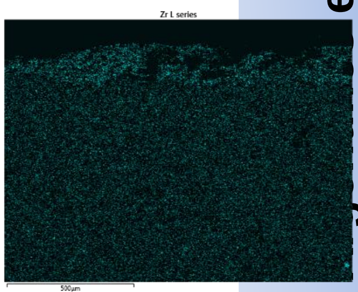
Al



Si



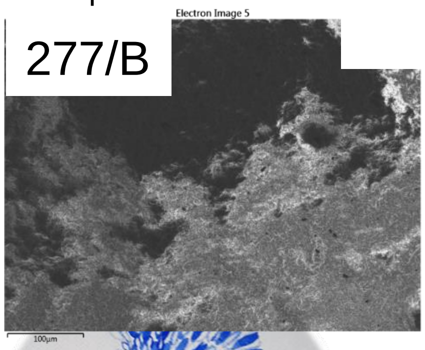
Zr

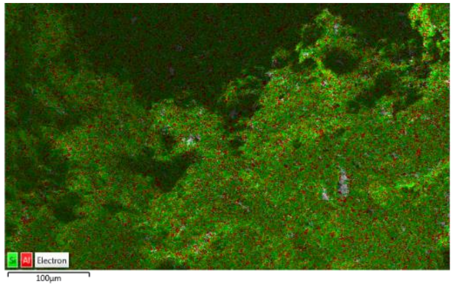


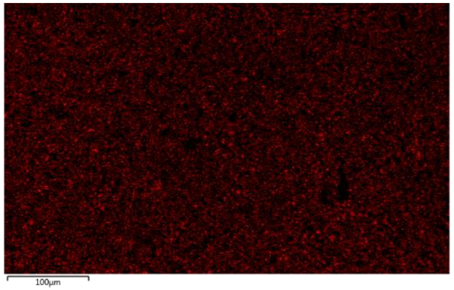
No variations of chemical composition on the surface between rough and smooth areas

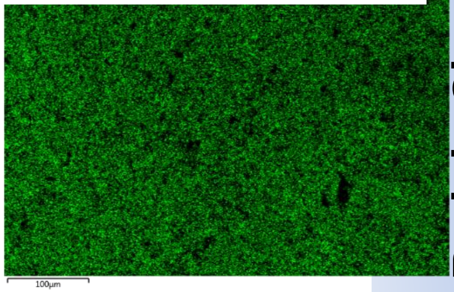
Sample surface

277/B







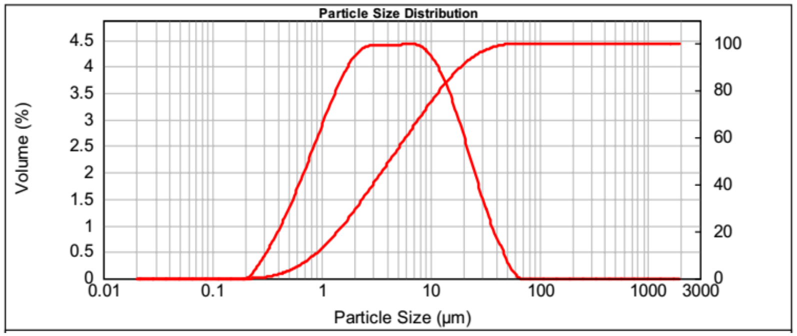


EDS phase Maps results of fired glazed tiles: cross section and surface

Particle size distribution

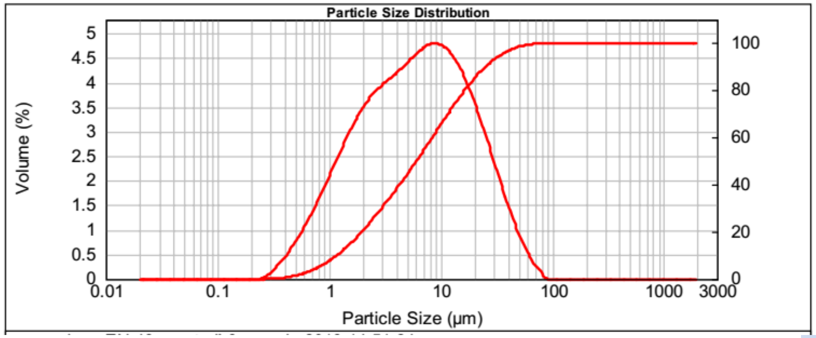
554

d(0.1): 0.865 um d(0.5): 4.208 um d(0.9): 18.880 um



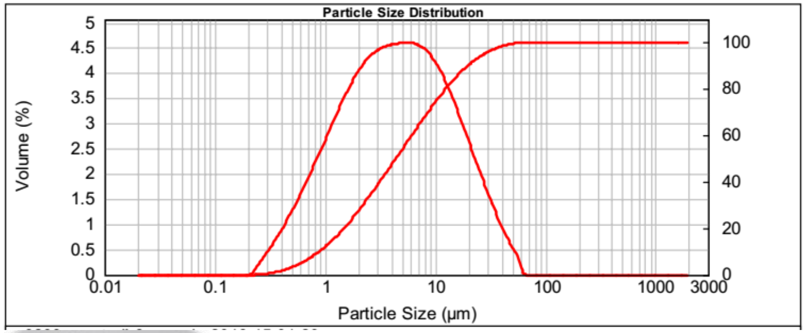
EN48

d(0.1): 1.167 um d(0.5): 6.063 um d(0.9): 25.153 um



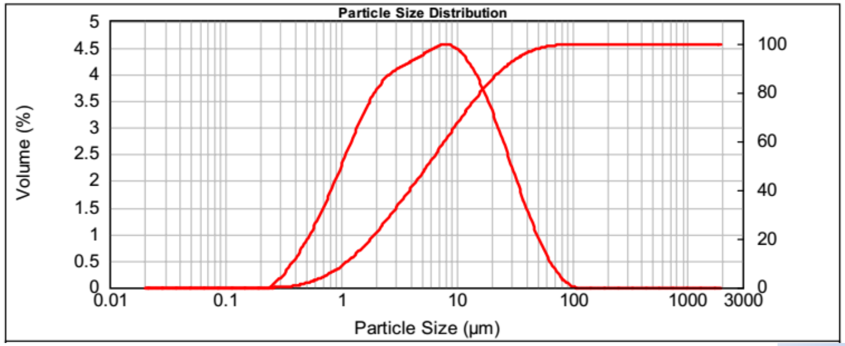
3293

d(0.1): 0.881 um d(0.5): 4.379 um d(0.9): 19.642 um

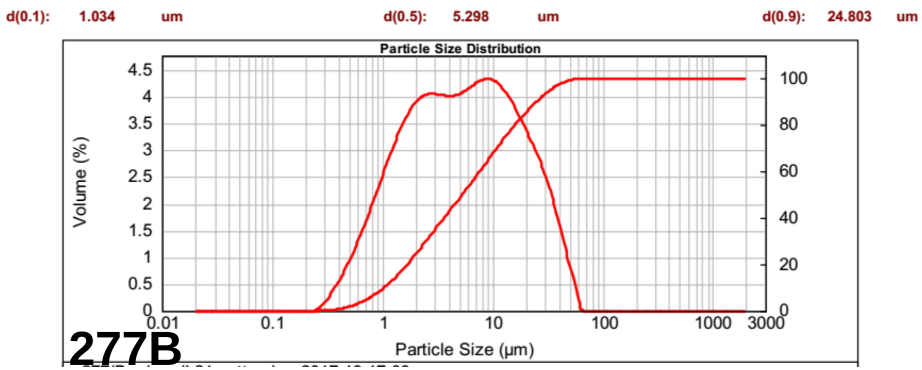


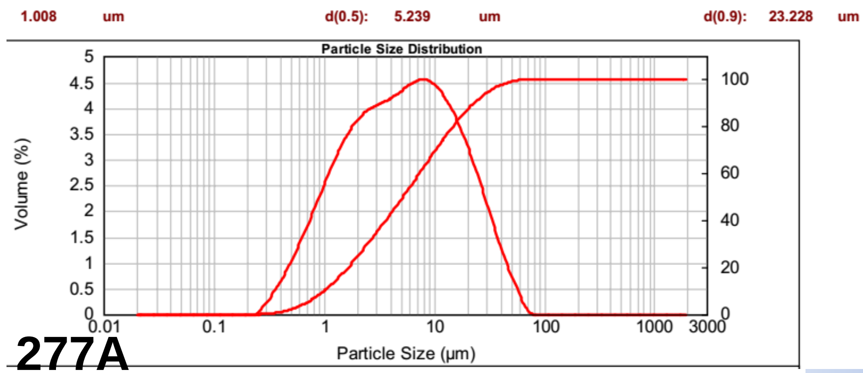
SL711

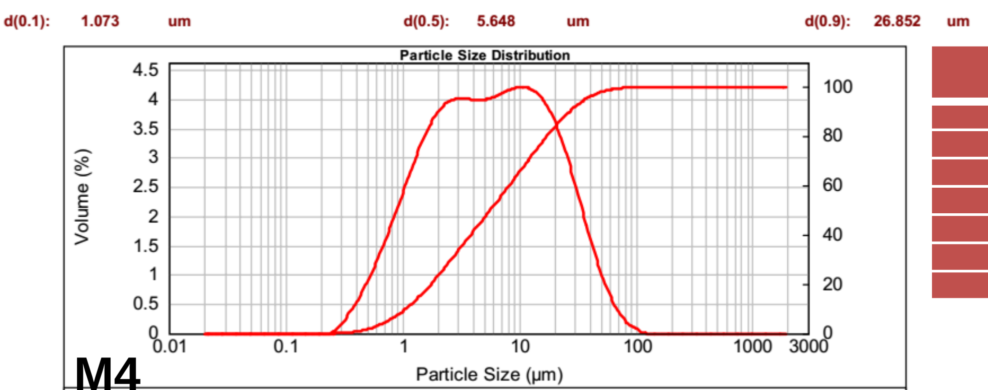
d(0.1): 1.092 um d(0.5): 5.600 um d(0.9): 25.293 um



Particle size distribution







Sample	d(0.1) µm	d(0.5) µm	d(0.9) µm
554	0.865	4.208	18.880
EN48	1.167	6.063	25.153
3293	0.881	4.379	19.642
SL 711	1.092	5.6	25.293
M490	1.073	5.648	26.852
277/B	1.034	5.298	24.803
277/Al	1.008	5.239	23.228

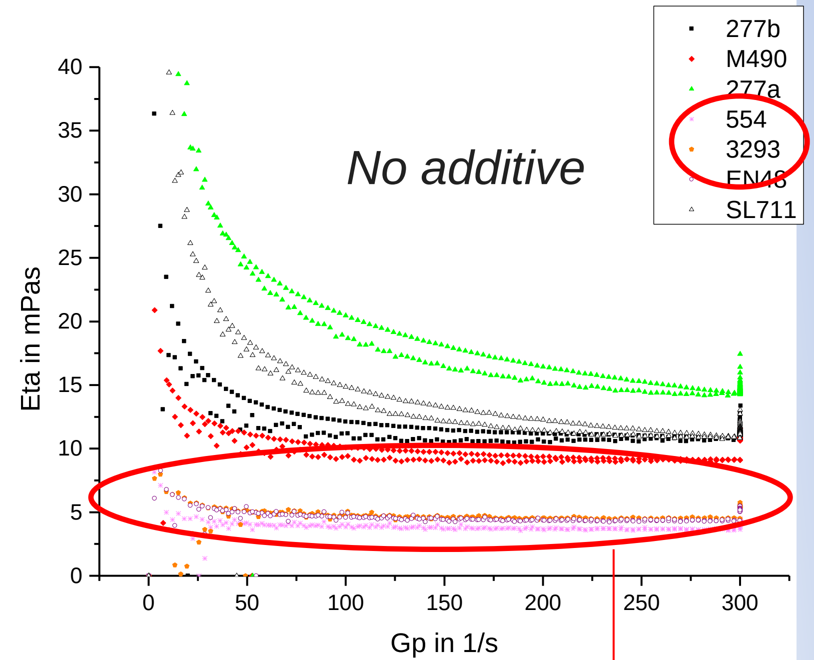
No significant difference in particle size distribution

Rheological characterization

Sample	Digital printing quality parameter Continuous jet printing mode	Digital printing quality parameter Drop on demand mode
	From 0-10 (10 excellent; <5 low performance)	
554 white	10	10
EN48 white	9	10
3293 white+Zr	8	10
SL 711 coloured	6	9
M490 black	5	9
277/B white Bentonite	4	9
277/A alumina white	4	9

Rheological measurement conditions by CS Rheometer

Step	Properties/method
1	CR 300 s^{-1} Time: 30 s
2	CR 0 s^{-1} Time: 60 s
3	CR from 0 to 300/2500s^{-1} Time: 300 s
4	CR from 300/2500s^{-1} to 0 Time: 300 s



Best performance in continuous ink jet printing

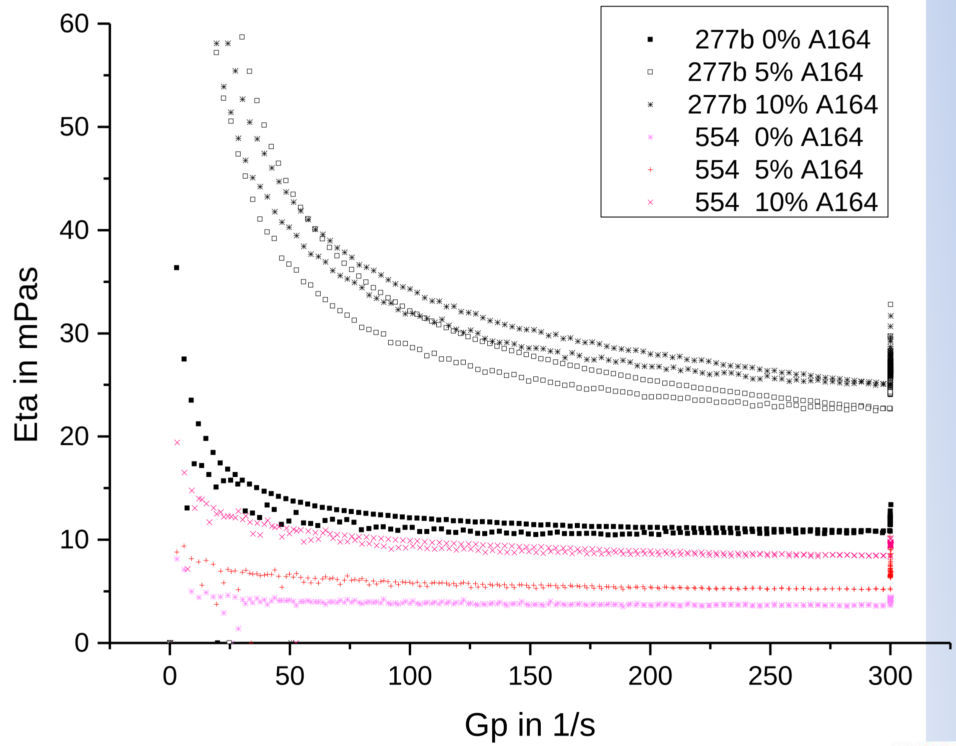
Rheological characterization

Printing quality parameter

Sample	Continuous jet printing mode From 0-10 (10 excellent; <5 low performance)
554	10
277/B	4

Increase in additive concentration does not give an increase of performance for 277 B

Influence of additive concentration

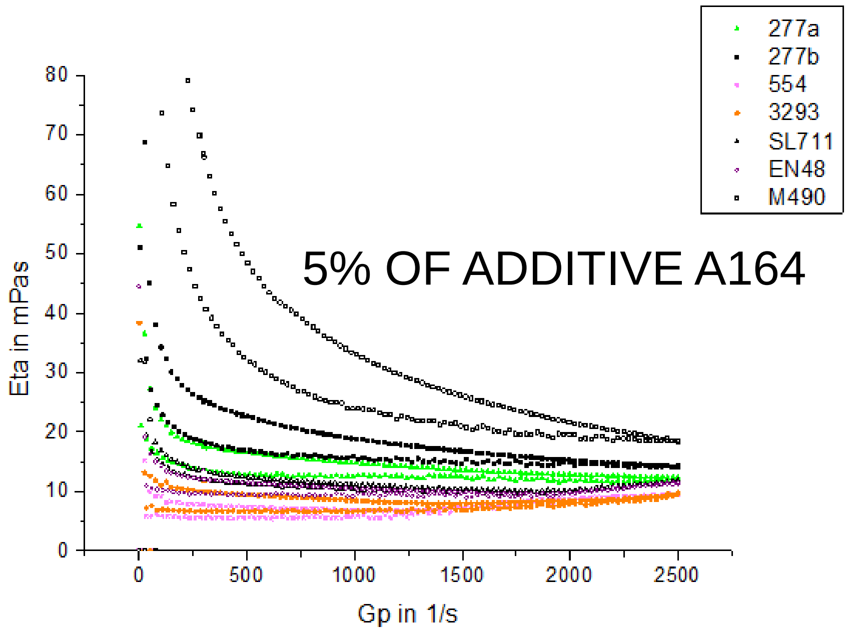


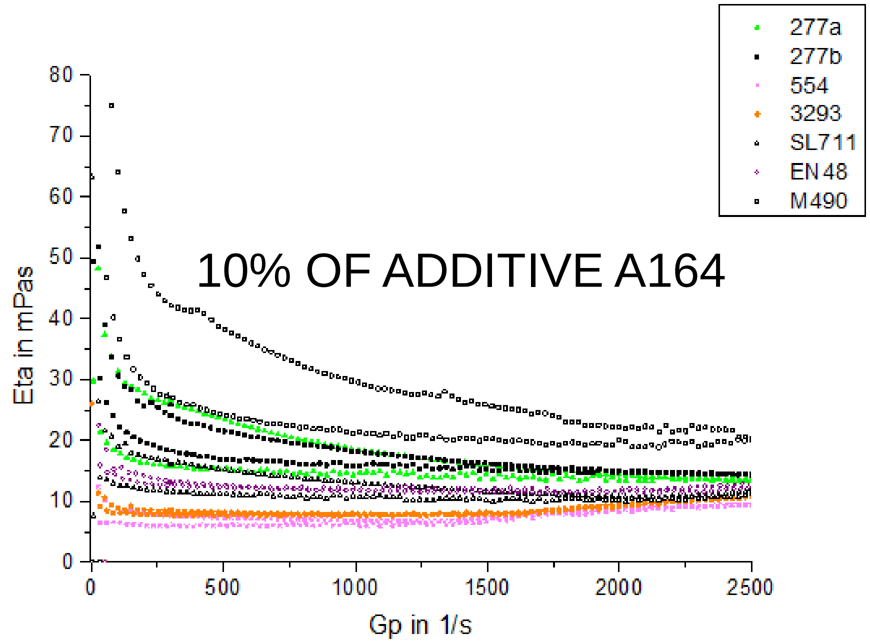
Digital printing of glass-ceramic glazes

15 de junio 2018 – Cooperazione Universitaria Argentina - Italia

Rheological characterization

Influence of additive concentration at high values of Gp

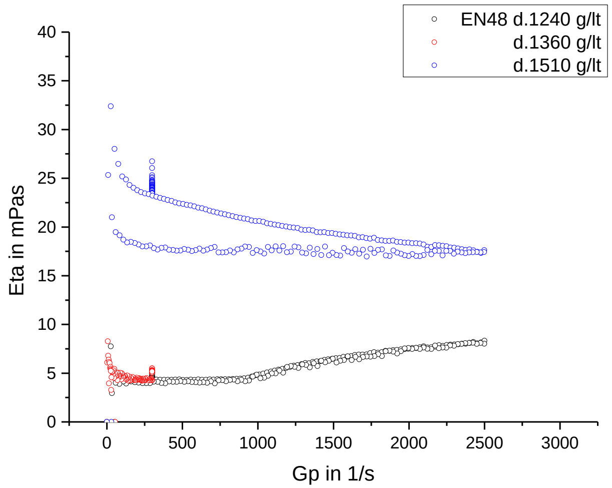


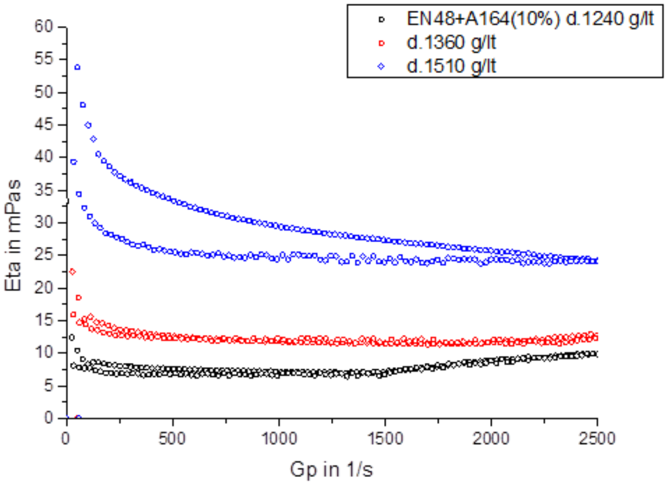


No significant difference in rheological trend up to 1500 s^{-1}

Rheological characterization

Influence of density at high values of Gp





Gp in 1/s

Improvement of the viscosity trend due to the additive addition

also at high values of density

Contact angle and Surface tension

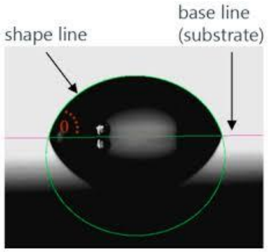
Continuous jet printing mode

OCA 20 Apparatus

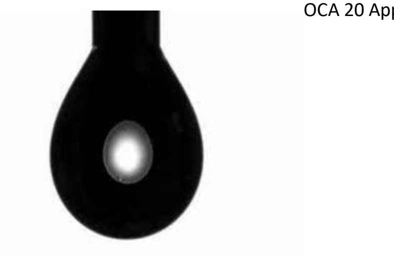
Static contact angle (θs) and surface tension (ϒ) of as received glazes at density of 1.36 g/cm^3 (Sessile, pendant drop method)

Sample	θs (°)	ϒ (mN/m)
554	26.2±5.1	69.1±0.4
EN48	41.3±3.2	72.3±0.6
3293	30.2±5.2	71.2±1.1
SL711	45.8±0,2	62.0±0.8
M490	74.8±3.1	66.1±0.5
277B	51.2±4.3	65.2±0.7
277A	42.1±5.6	66.5±1.1

No additive



Sessile drop method

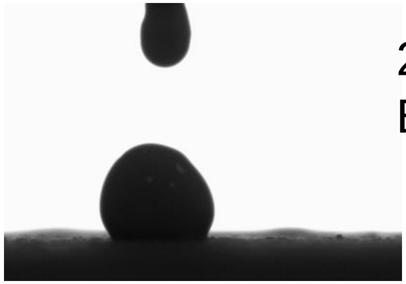


Pendant drop method

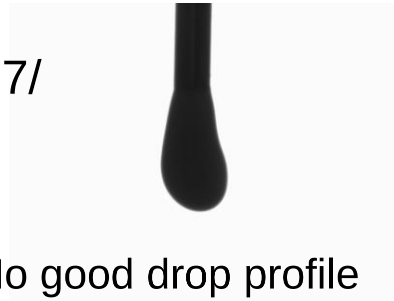
Static contact angle (θs) and surface tension (ϒ) of glazes with 10 wt% A164 of 1.36 g/cm^3 (Sessile, pendant drop method)

Sample	θs (°)	ϒ (mN/m)
554	43.9±2.3	47.6±1.1
EN48	53.9±1.1	45.7±1.1
3293	34.2±2.2	46.3±0.7
SL711	45.85±0.2	49.9±0.5
M490	56.2±2.7	69.1±0.7
277B	108.9±5.6	19.6±0.6*
277A	112.1±4.7	22.9±0.5*

10wt% of additive



277/B



No good drop profile

*45 and 44 mN/m respectively when measured with Force Tensiometer

UNIMORE

Stability and zeta potential

no additive

↓

Phase separation after 2hours

with additive

↓

Good stability up to 8 hours

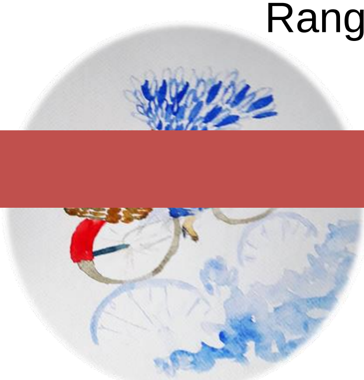
10 min → 2 h → 8 h

Sample	Z mV No Additive	Z mV Additive al 10%
M490	-45.8 ± 11.2	-54.6 ± 11.2
3293	-41.4± 9.7	-55.8 ± 9.2
SL711	-33.2 ± 10,2	-58.2 ± 8.8
277B	-30.8 ± 8.6	-54.6 ± 9.2
277A	-38.5 ± 8.1	-63.8 ± 9.5
EN48	-43.2± 9.8	-56.8 ± 5.7
554	-34.1 ± 7.1	-62.3 ± 6.2

Zeta potential strong enough

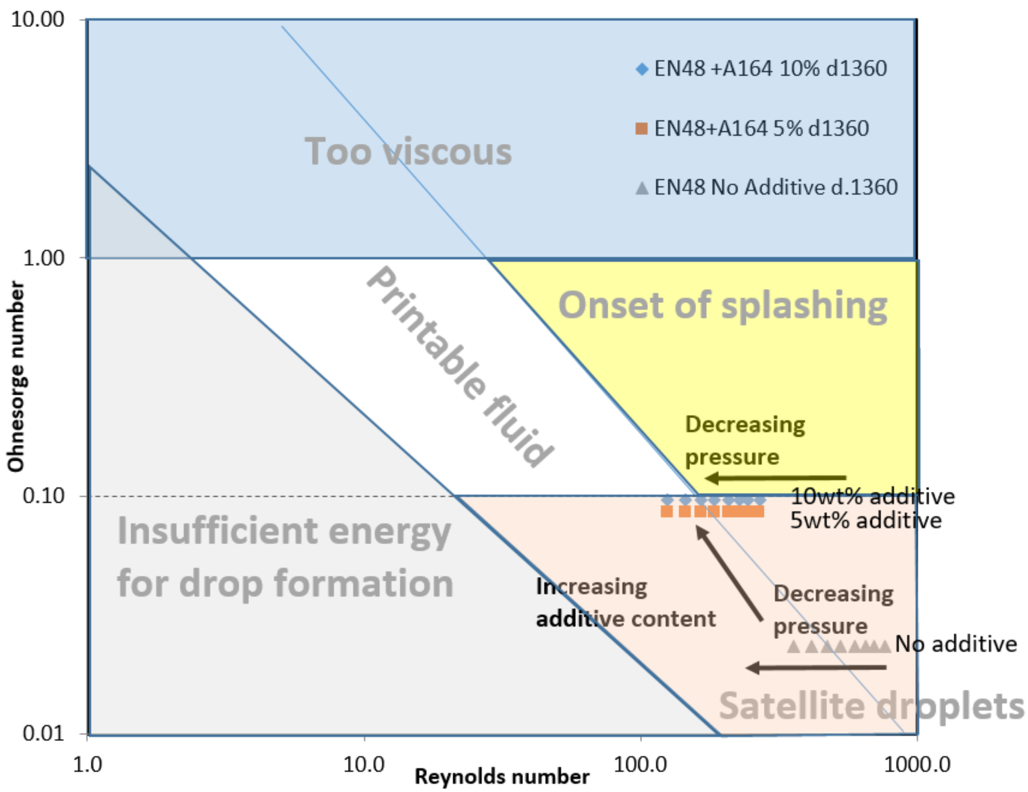
Range: from -30.8 to -45.8   No additive

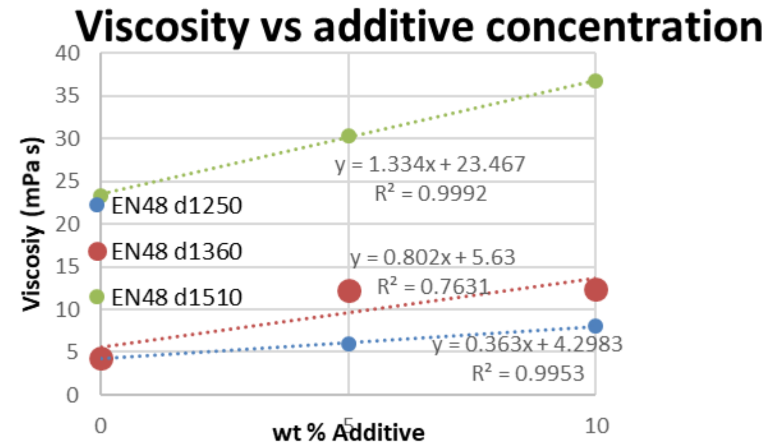
Range: from -54.6 to -63.8 With additive

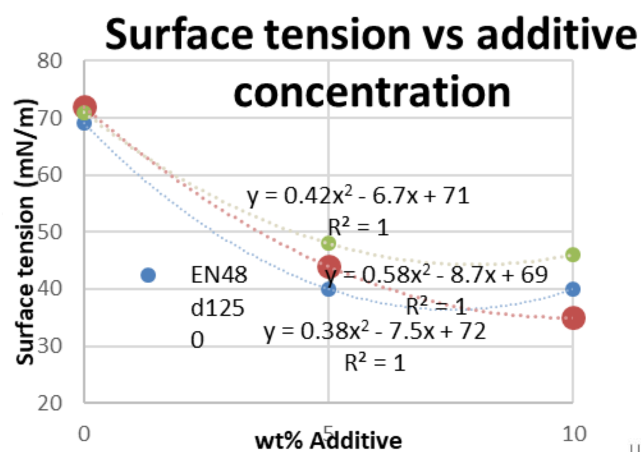


Design of printability fluid region in DOD mode

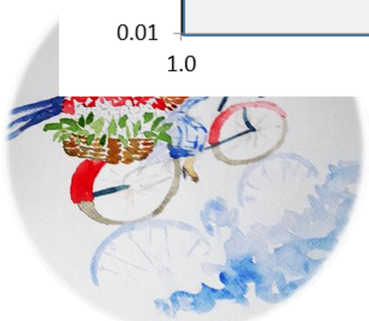
Semi-empirical model; EN48 at different concentration of additive and pressure





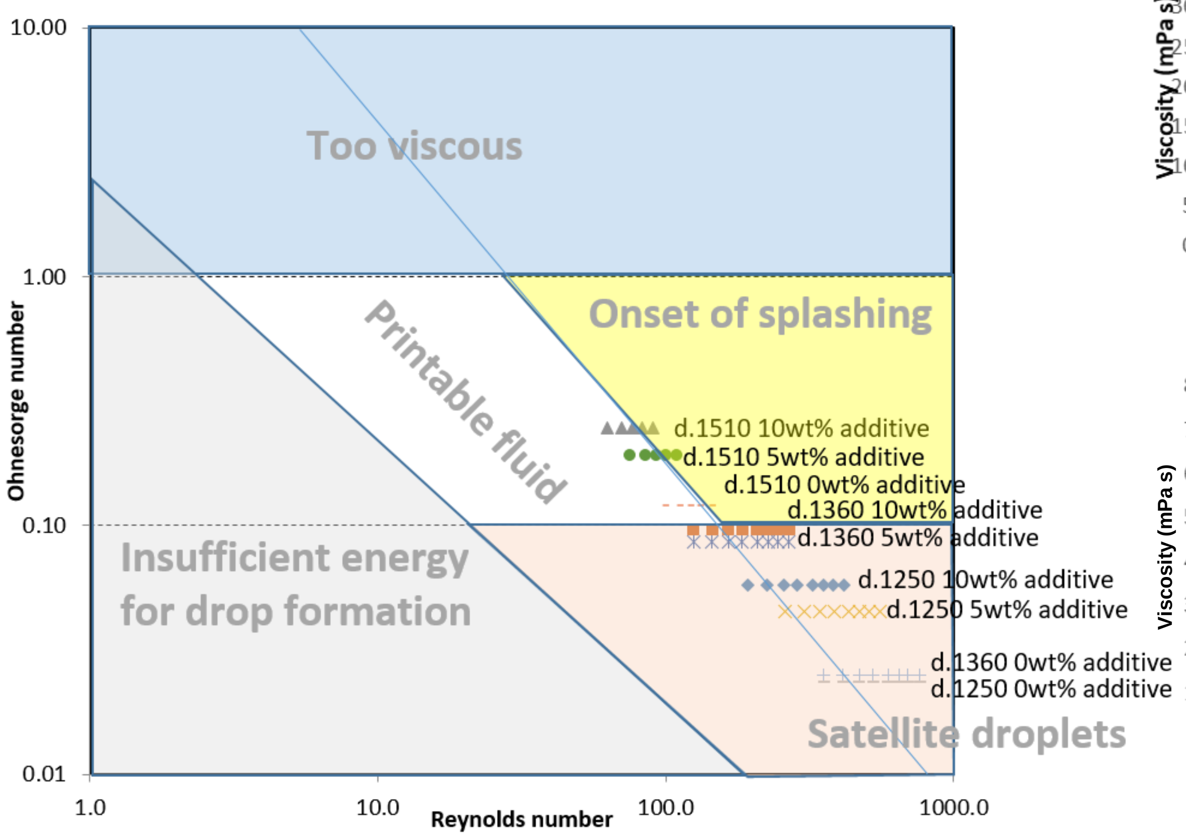


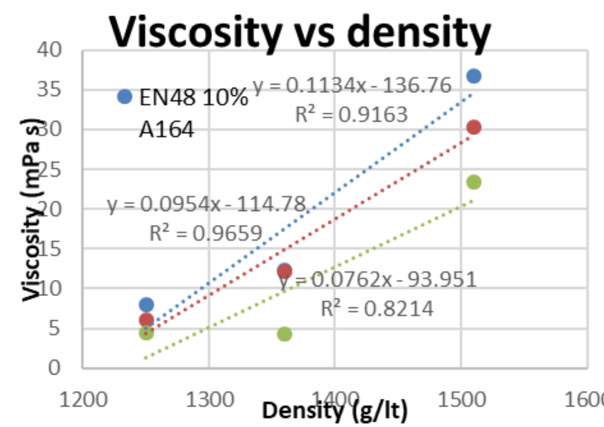
Dyes and Pigments, 2016,127, pp.148-154

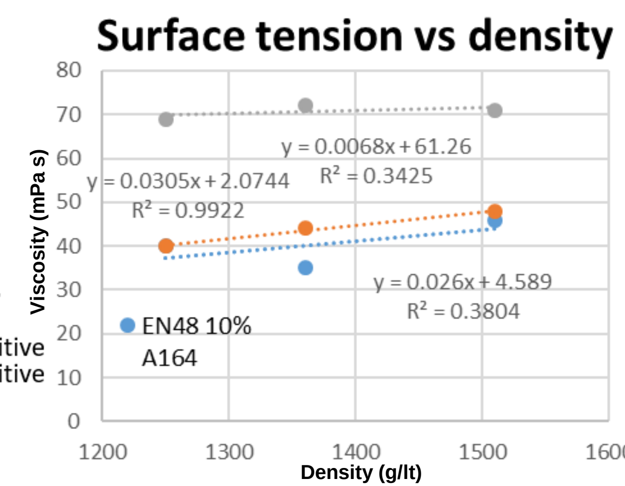


Design of printability fluid region in DOD mode

Semi-empirical model; EN48 at different concentration of additive and different density







15 de junio 2018 – Cooperazione Universitaria Argentina - Italia

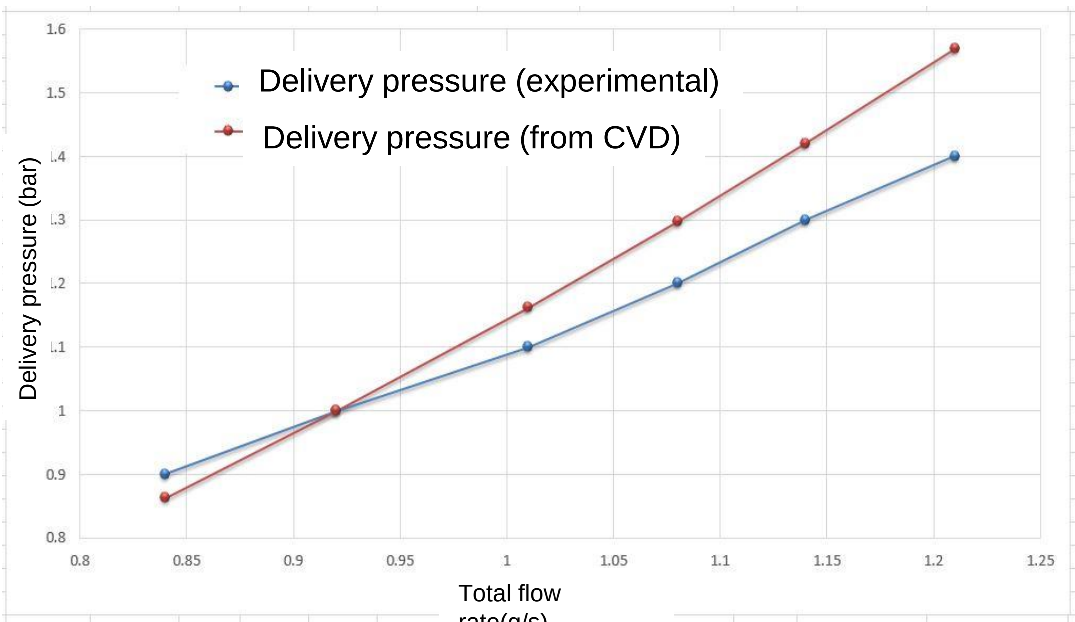
RCAI www.rca...t - Red de Científicos Argentinos en Italia

UNIMORE

Computational Fluid Dynamics (CFD) Simulation
(Open Foam)

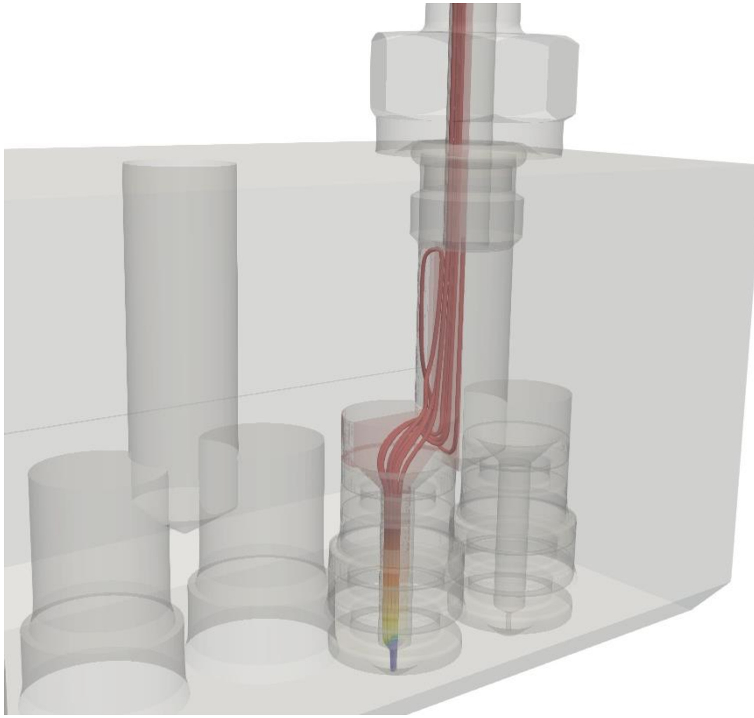
Experimental vs. predicted values of flow rate as function of working pressure

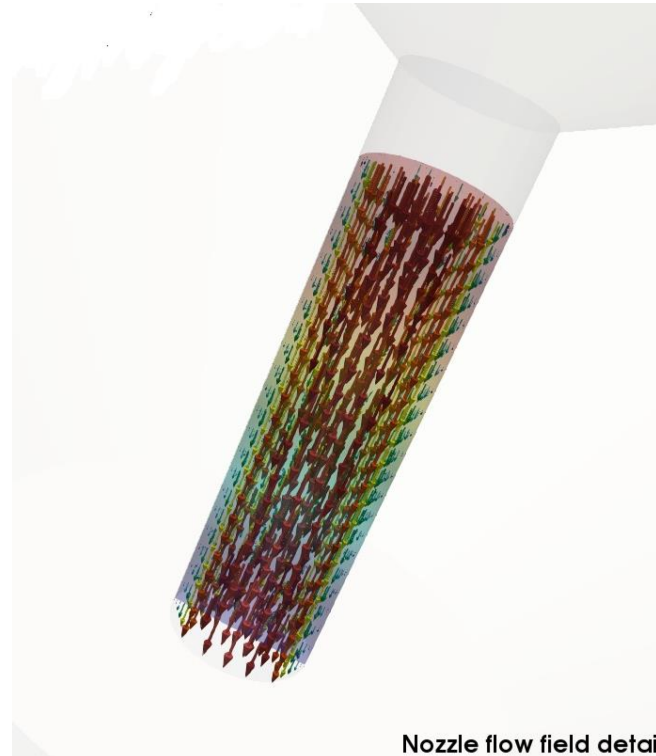
Inputs of the model: geometry, pressure and viscosity for EN48



The rest of the flow rates were determined by CFD simulation with the inputs of geometry, pressure and viscosity of the glazes for the same applied pressures case than the EN48

Computational Fluid Dynamics (CFD) Simulation

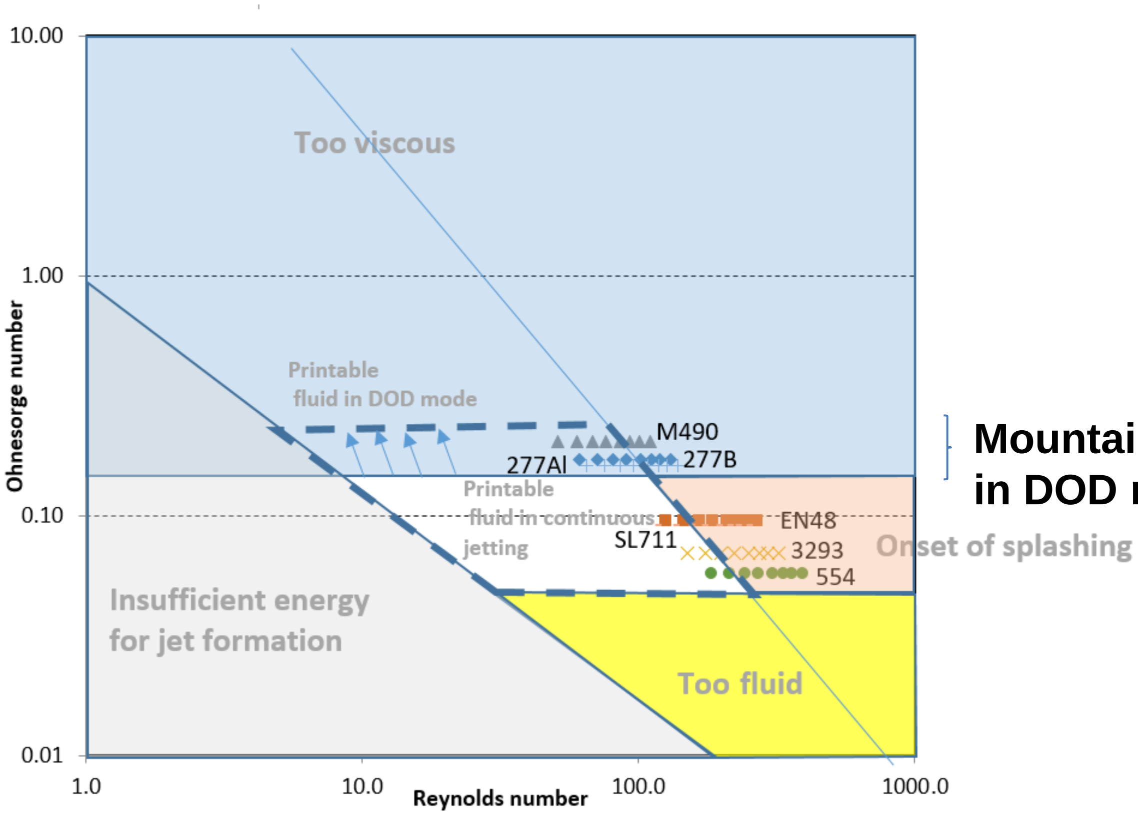




Studies of flow rates, shear rate through the resolution of Navier Stokes equations for incompressible isothermal flow → Optimization of nozzle geometry and study of pressure loss in the circuit

Design of printability fluid region

comparison DOD vs continuous jetting mode



Mountain wave defect disappears in DOD mode

Conclusion

- Physical chemical properties of glazes influence the printability in continuous mode system;
  EN48, 554 and 3293 -> best behaviour: viscosity in the range 5-12 mPas; surface tension in the range 44-50mN/m

- All the investigated glazes show a good performance when used in drop on demand mode

- Semi empirical model design of printability fluid region: EN48 at different concentration of additive; different density

- Studies of flow rates, shear rate and stress tensor of viscosity, study of pressure loss in the circuit to optimize the nozzle geometry

Digital printing is a reliable and cost effective technique in ceramic tile processing with potential for expanding to other industrial fields

THANK YOU VERY MUCH!

Digital printing of glass-ceramic glazes