

Combustion reactivity of unburned carbon in coal combustion fly ashes

Federico Cangialosi¹, Francesco Di Canio¹, Michele Notarnicola¹, Lorenzo Liberti¹, Pompilio Caramuscio² and Giulio Belz²

¹Department of Environmental Engineering and Sustainable Development, Technical University of Bari, v.le del Turismo 8, 74100, Taranto, Italy

²ENEL Produzione Ricerca, Litoranea Brindisi Casalabate, 72020 Tuturano (Brindisi) Italy

Corresponding author:

Federico Cangialosi: f.cangialosi@poliba.it

Fly ash reutilization

Coal combustion in Italian utility boilers produces 900.000 tons/year of fly ashes. These ashes can be re-used in cement and concrete markets, provided that fly ash meets specifications for carbon content (**UNI-EN 450**):

LOI (loss on ignition) $\leq 5\%$

Fly ash beneficiation

Separation techniques:

Wet separation:
froth flotation

Dry separation:
triboelectrostatic separation

Thermal treatments:

Carbon Burn-Out (fluidized bed)
Microwaves

Goals

1. Investigation of reactivity in thermogravimetric (TG) analyses of unburned carbon, derived from two large utilities
2. Investigation of motion and axial mixing of ash in a pilot scale rotary kiln, described with an advective-dispersive model
3. Use of kinetic parameters derived from TG measurements and residence time distributions to predict combustion efficiencies within the kiln

Materials

Fly ashes of two different low-NOx utility boilers (UB1, UB2), were used.

UB1 Samples

The as-received sample (AR) from UB1 was dry-sieved, obtaining three samples labeled as:

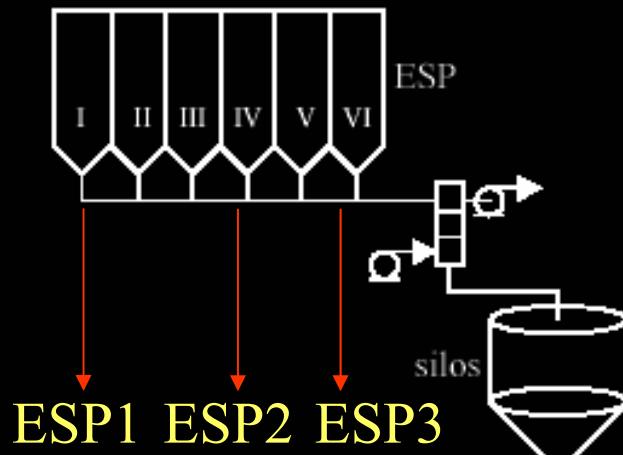
- SF1 ($>150 \mu\text{m}$)
- SF2 ($75 \div 150 \mu\text{m}$)
- SF3 ($<75 \mu\text{m}$)

Materials

UB2 Samples

Three UB2 fly ashes, derived from a 60/40 blend of Venezuelan/Russian coals, were collected at different lines of an electrostatic precipitator:

- ESP1
(LOI=9%)
- ESP2
(LOI=21%)
- ESP3
(LOI=40%)



A **char** was originated by TG pyrolysis at 950°C of UB2 coals blend and was labeled as VE/RU Char

Adsorption isotherms

Surface areas were measured for carbon concentrates obtained from samples AR, SF1-3.

All the samples were obtained by means of density gradient centrifugation (DGC) separation, using a high-density media.



The porosity of all samples was determined via N_2 -adsorption isotherms at 77 K using an Autosorb-1 adsorption apparatus (Quantachrome Instruments, USA).

Thermal Analyses

Netzsch STA 409 was used for char pyrolysis and also for reactivity measurements during two series of analyses:

- **non-isothermal oxidation** with a heating rate of 10 K/min for UB1 samples (AR, SF1-3), UB2 samples (ESP1-3) and VE/RU Char
- **isothermal oxidation** for UB1 samples (AR, SF1-3) at temperatures of 550, 600, 700 e 1000 °C

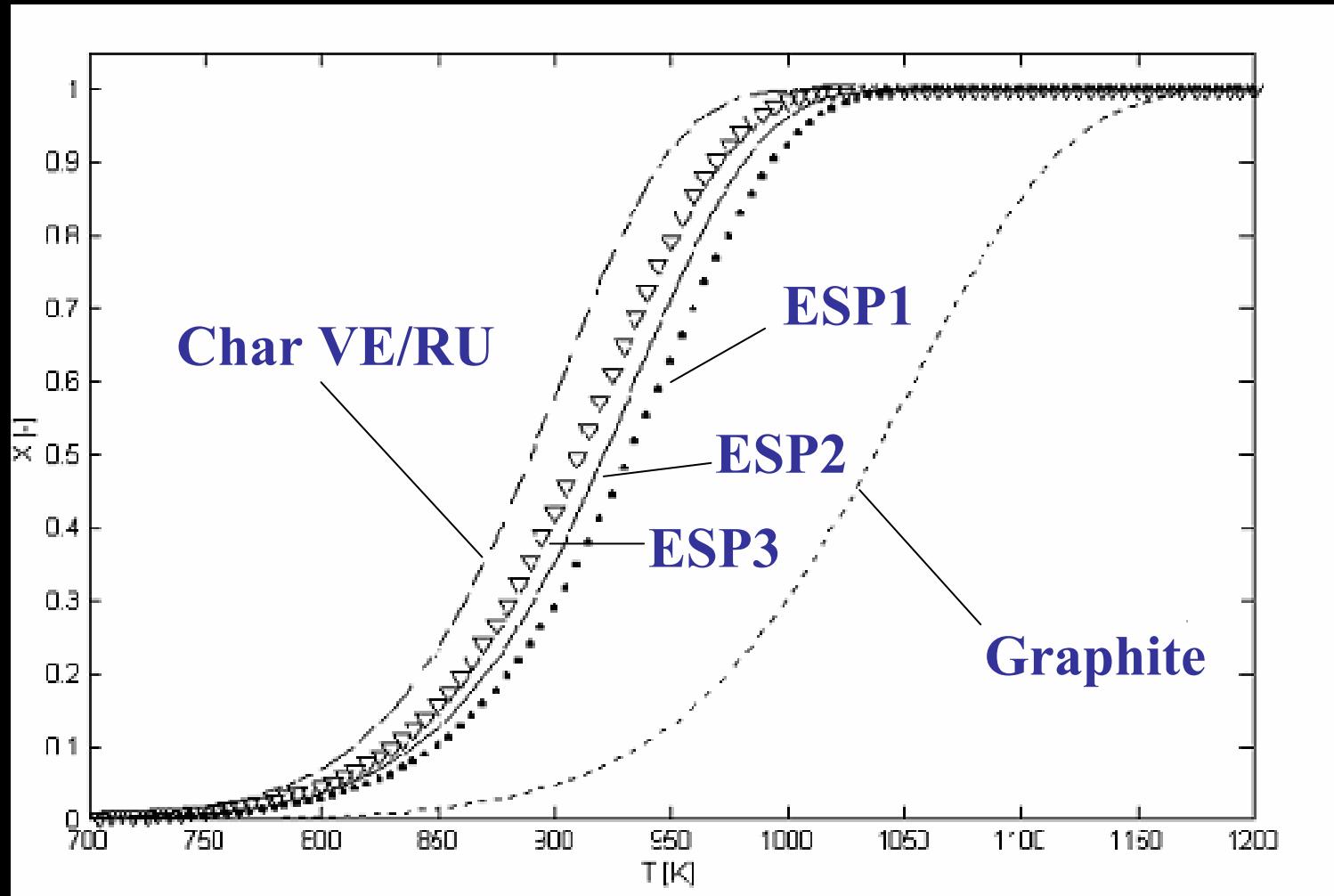
Rotary kiln

Electrically heated rotary kiln
(Lenton furnaces, U.K.)



- Experiments with a *tracer* to obtain residence time distributions for three parameters settings
- Combustion experiments with AR and SF3 samples in the temperature range 525÷600°C

Results and discussion: TG analyses



TG oxidation profiles of ESP1-3, VE/RU Char and graphite

Experimental data, fitted with VRM, show that ash samples reactivity is intermediate between char and graphite

Thermal annealing

- Carbon particles exposition to heat treatment before oxidation causes structural changes which result in **annealing of active sites for reaction** [Davis et al., 1995]
- Transformation of carbonaceous matrix, associated with annealing, is referred to as pre-graphitization [Hurt et al., 1998]: the change of micro-texture leads to the **growth of graphite-like crystallites**

A *shifted Γ function* [Zolin et al., 2002] was employed to describe the initial distribution for annealing activation energy

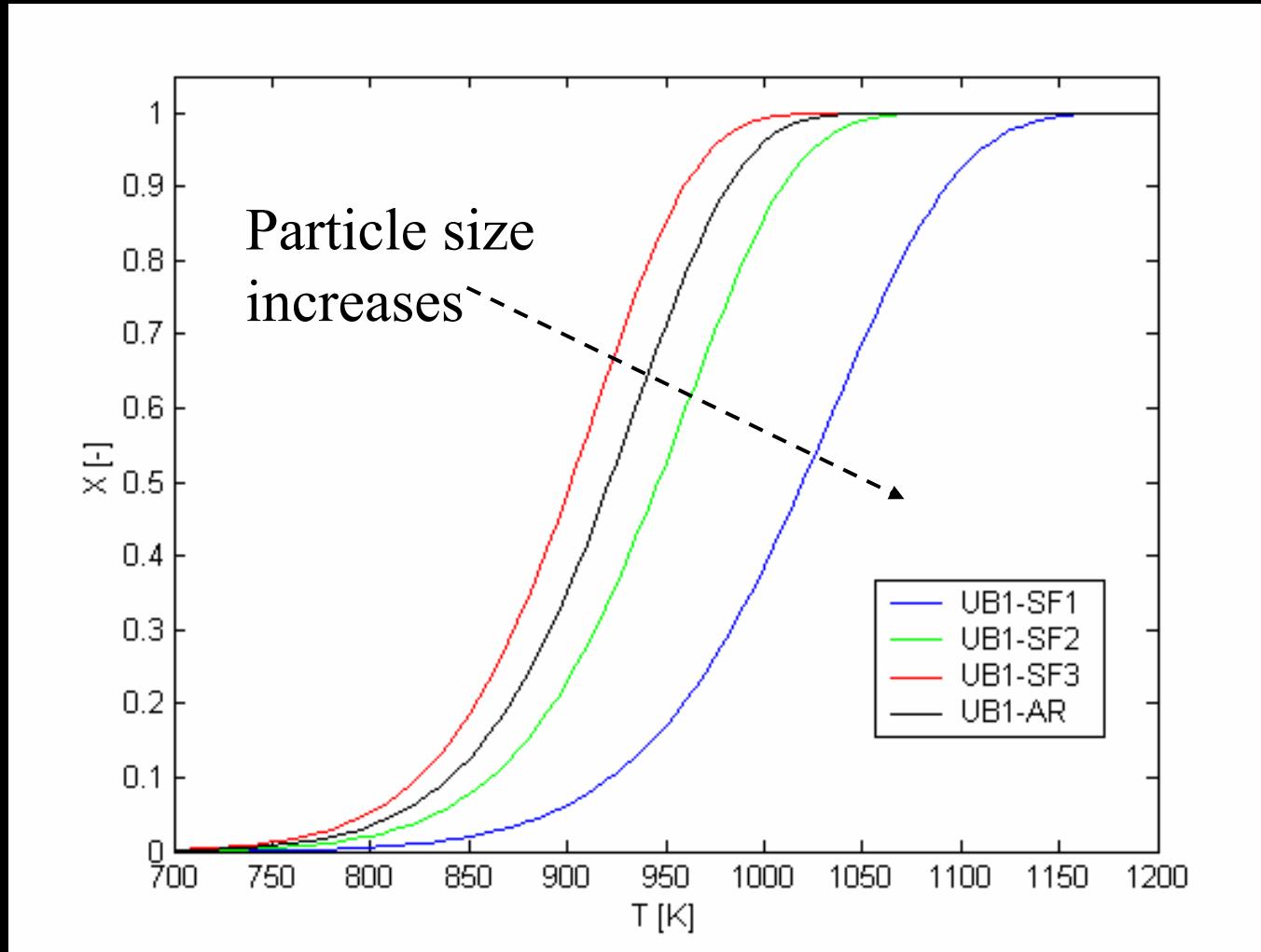
Thermal histories of particles were obtained from *CFD simulation* of the boiler

| Char | UB2 samples |
|------|-------------|
|------|-------------|

| | |
|-------|-------|
| 0.095 | 0.048 |
|-------|-------|

Annealing ratios:

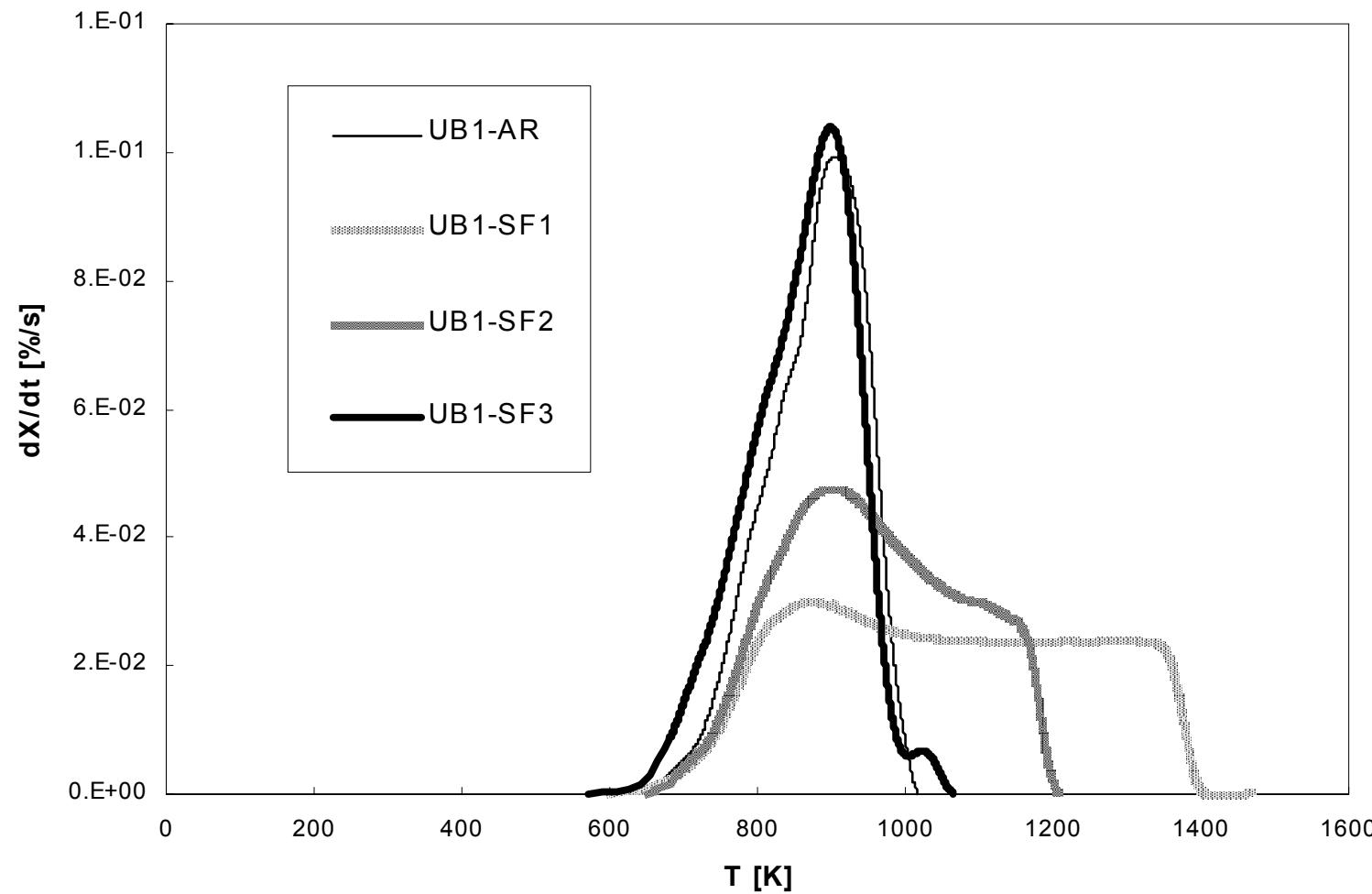
Oxidation reactivities of different size fractions/1



TG oxidation profiles of UB1 samples (AR, SF1-3) obtained during non-isothermal analyses

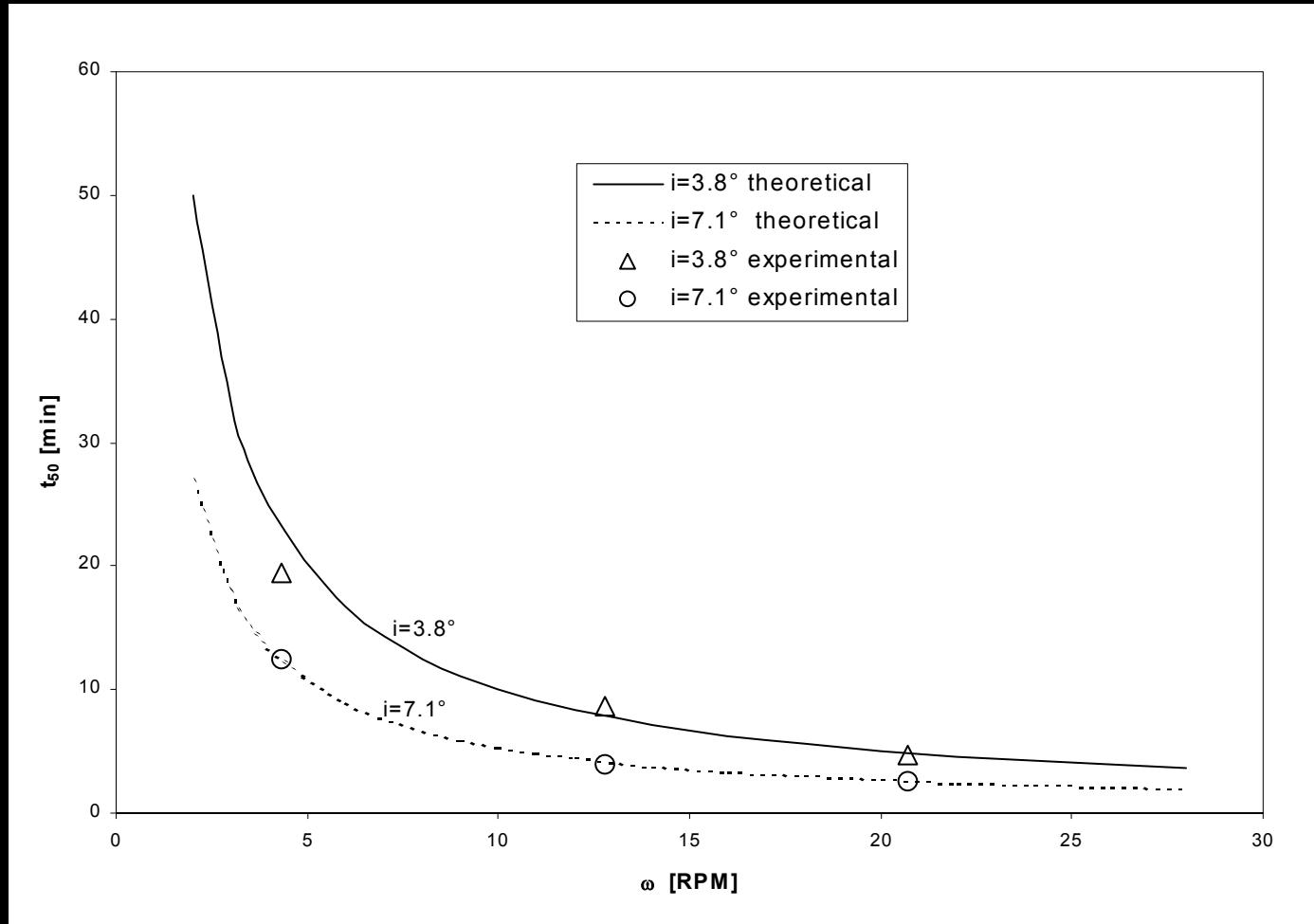
Oxidation reactivities of different size fractions/2

DTG of
UB1
samples



Two or more phases of carbon with different reactivity in larger particles

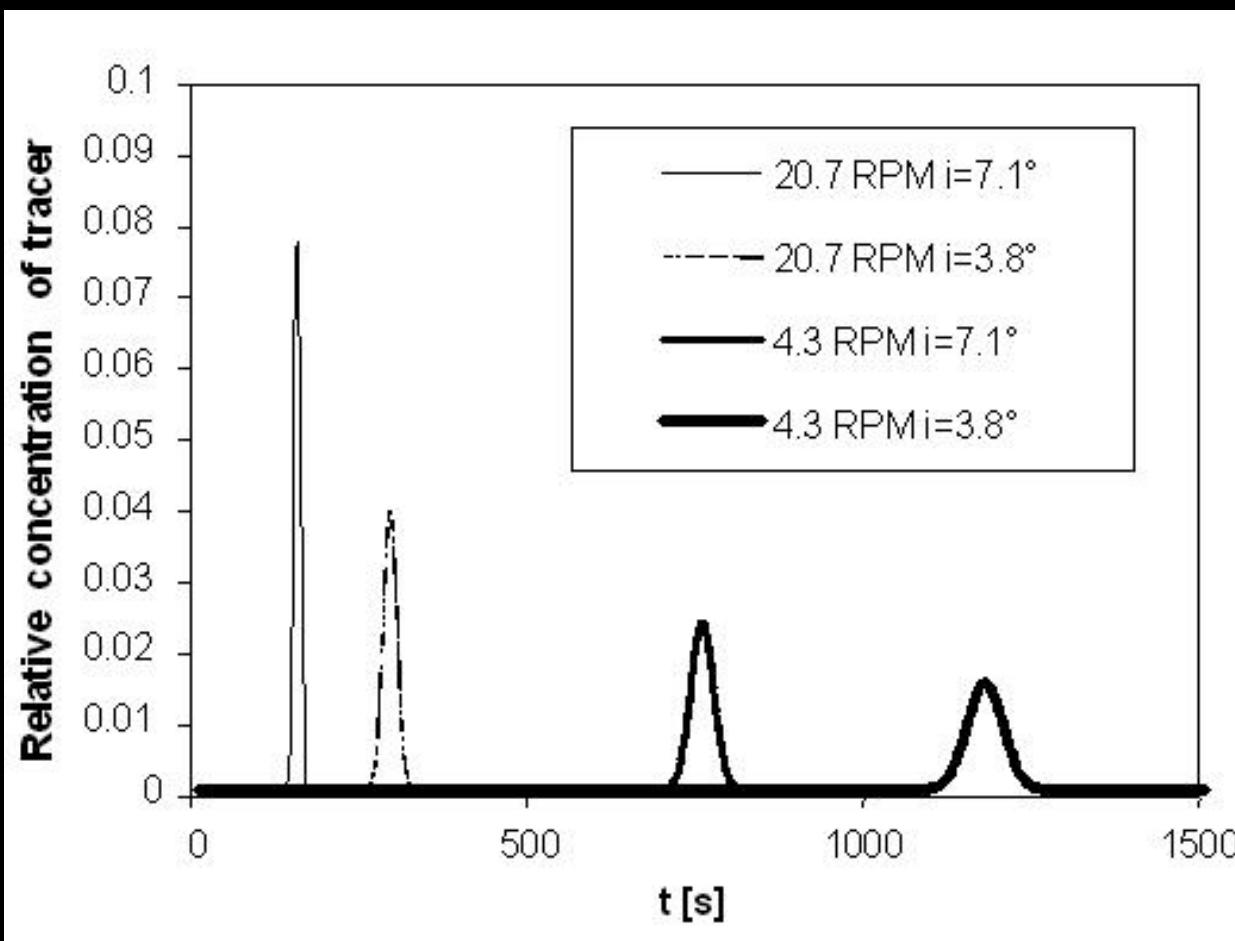
Advective component of fly ash motion in the kiln



Validation of cinematic model of ash motion in the rotary kiln

For both inclination angles there is good agreement

Dispersive component of fly ash motion in the kiln



Residence time distributions of various settings of the kiln

$$\frac{\partial c}{\partial t} = D_z \frac{\partial^2 c}{\partial z^2} - u_z \frac{\partial c}{\partial z}$$

Standard deviation increases as rotational speed and kiln inclination decreases: **(axial backmixing)**

Segregated flow modeling of carbon burn-out

Unburned
carbon
conversion

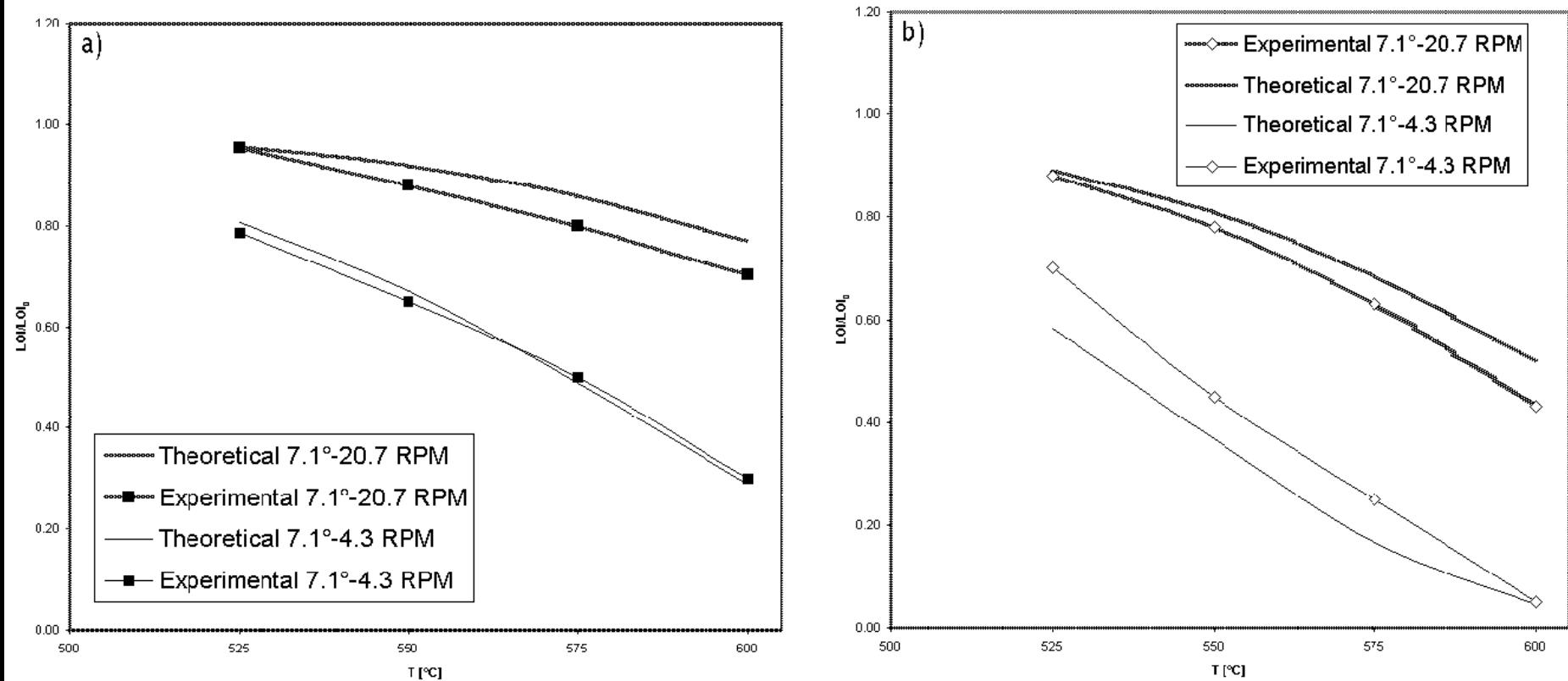
$$\frac{C}{C_0} = \int_0^{\infty} E(t) C_k(t) dt$$

Residence time
distribution of carbon
particles in the kiln

Carbon residual
concentration
after a time t

Convolution integral was numerically evaluated for different reactor configuration (wall temperature, kiln inclination, feed rate..)

Carbon removal efficiencies in the kiln



Experimental and theoretical curves of AR and SF3 samples

The simple theoretical model can predict to some extent the trends of LOI removal efficiency

Conclusions

- Thermal analyses were used to obtain kinetic parameters of unburned carbon and char, originated from the same parent coal.
- By means of an annealing model, thermal deactivation experienced by coal during boiler combustion was quantified
- Different degrees of thermal deactivation occurred for coarser particle fractions: presence of at least two phases with different thermal reactivity for particles larger than 75 micrometers.

Conclusions

- Tracer tests were carried out to measure ash motion in the kiln:
 - 1) mean residence times agree with theoretical predictions
 - 2) the dispersive component of ash motion is well-characterized (theoretical predictions proposed by other authors adequately fit the data)
- Conversion rates were coupled with residence time distributions by means of a convolution integral in order to predict carbon removal efficiency.
- Theoretical and experimental curves have similar trends under different experimental conditions

Acknowledgments

The financial support for the present study by MIUR under grant 12941/01 "Sviluppo di un sistema innovativo per la produzione di ceneri di qualità - Ceneri DOC" is gratefully acknowledged.

Thank You !