Behavior of limestone in a large-scale pressurized fluidized bed combustor

- attrition, fragmentation and SO_2 capture -

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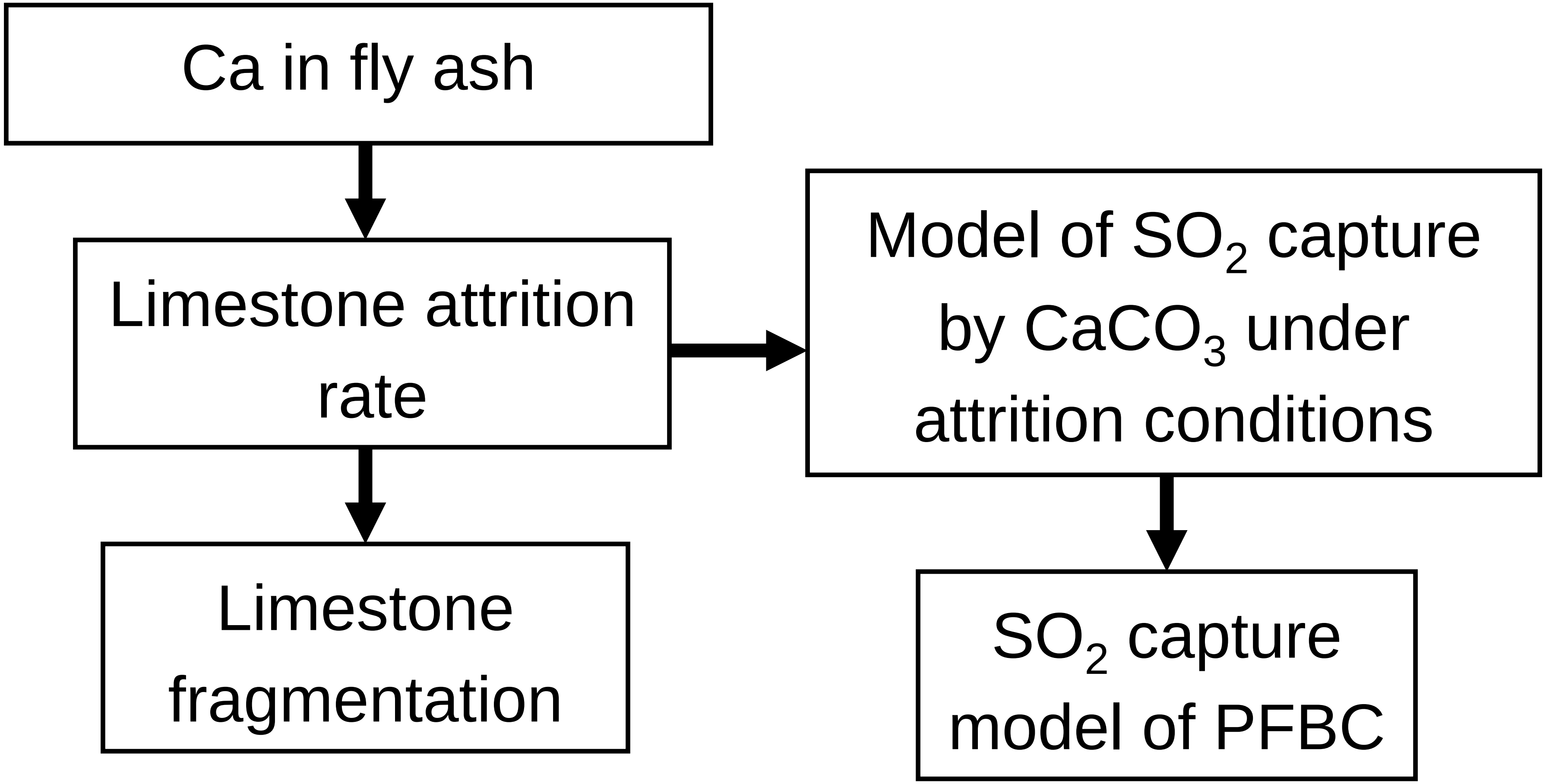
ABSTRACT

Cooperative research work between EPDC and Niigata Univ. on behavior of limestone in a 71MWe PFBC

- Limestone attrition rate
- Fragmentation of limestone
- Model of SO_2 capture by single limestone particle under attrition condition
- SO_2 capture model in PFBC

Structure of this work



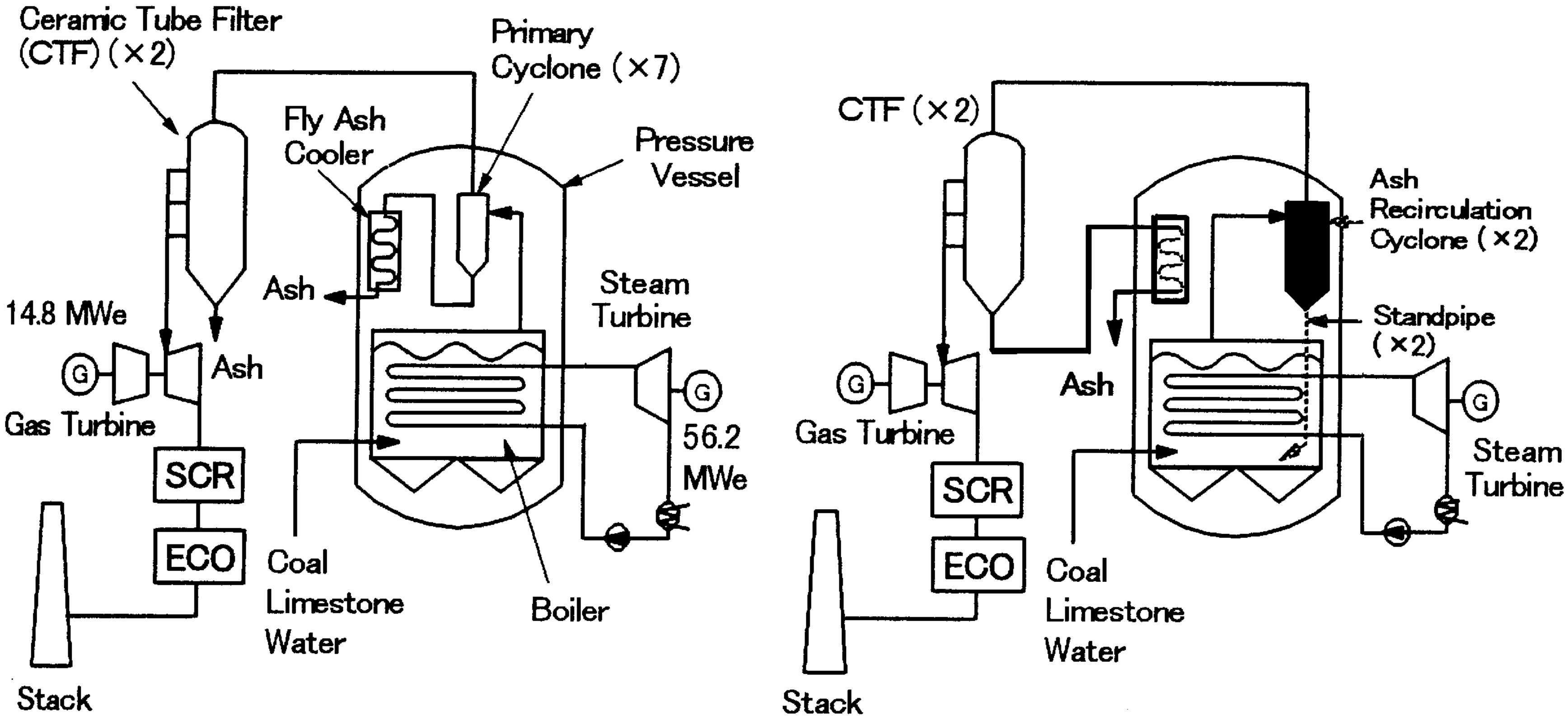
This report summarizes the investigations on limestone behavior in 71MWe PFBC listed below:

1. S. Sakuno et al., *Nihon-Energy-Gakkai-Shi (J. Jpn. Inst. Energy)*, 80, 747(2001)
2. Ueda, H. et al., "Fluidization characteristics of PFBC, attrition and fragmentation of limestone" *Proc. 7th SCEJ Symp. on Fluidization* (Awaji, Japan), 524 (2001)
3. T. Shimizu, et al., *Chemical Engineering Science*, 56, 6719 (2001)
4. T. Shimizu et al., "A mathematical model of SO_2 capture in PFBC", *Proc. 7th SCEJ Symp. on Fluidization* (Awaji, Japan), 235 (2001)
5. T. Shimizu et al., To be presented at ISCRE 17 (Hong Kong, 2002)

EPDC's Wakamatsu 71MWe PFBC

Phase-1 test series: Without cyclone ash recirculation

Phase-2 test series: With cyclone ash recirculation



(a) Phase-1 configuration (without ash recirculation)

(b) Phase-2 configuration (with cyclone ash recirculation)

Measurement

Coal feed rate

Limestone feed rate

Limestone size distribution

Amount of bed material (limestone)

Size distribution of bed material

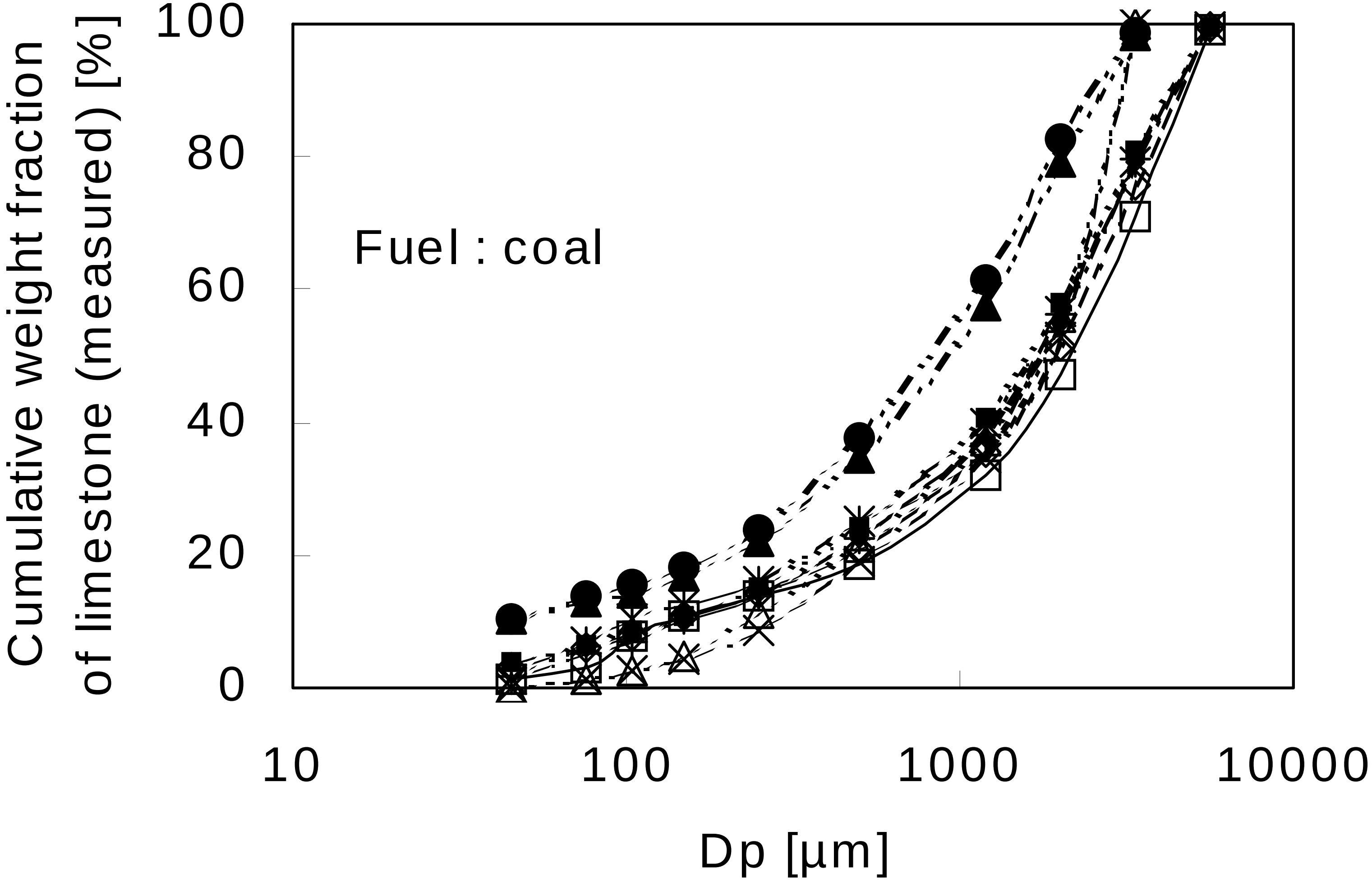
Fly ash drain rate

Ca content in fly ash

SO_2 emission

Size of fed limestone

Size<5mm



Part.1

Evaluation of solid attrition rate

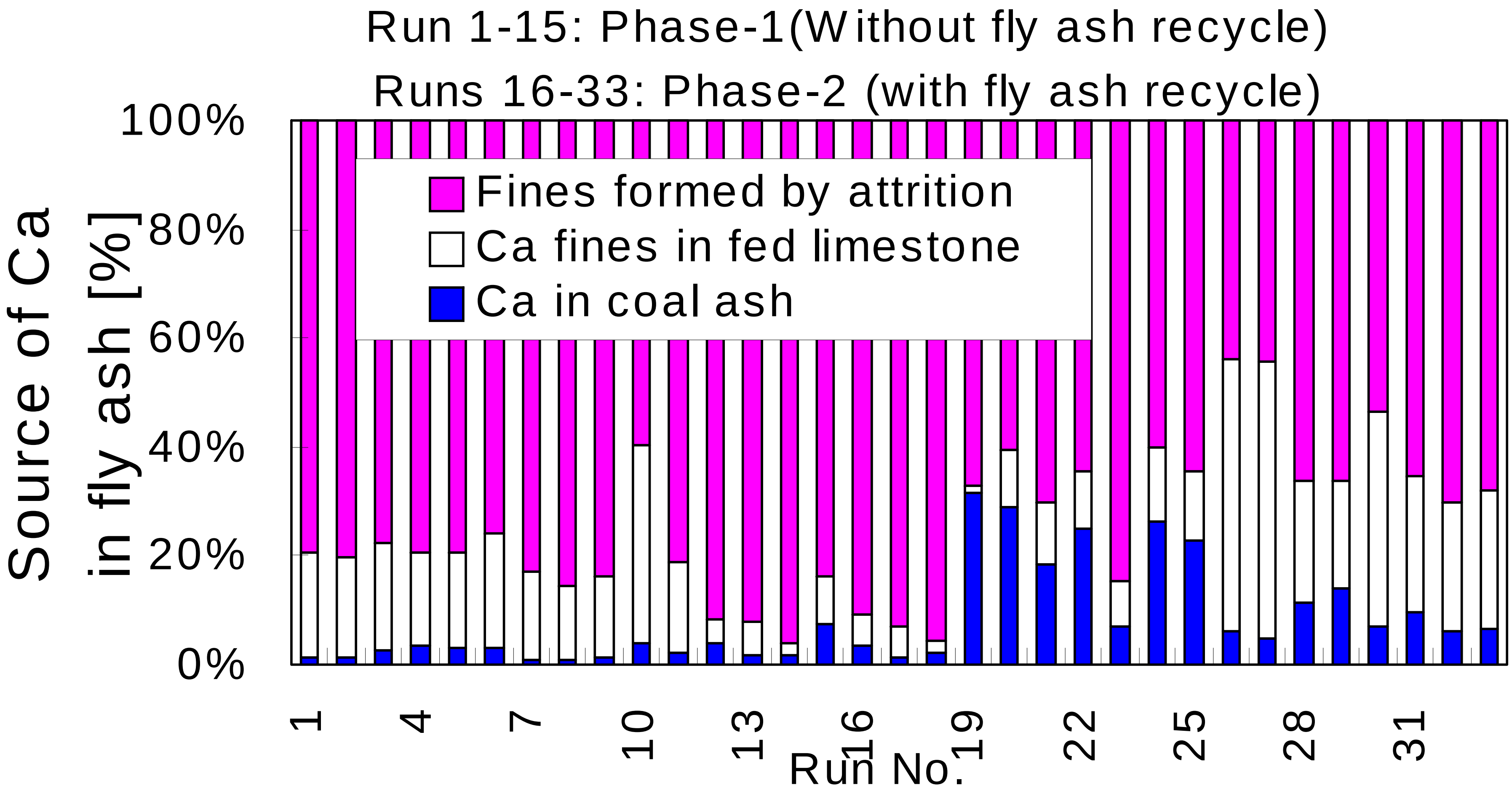
and

fragmentation of limestone[1)2)]

Source of Ca in fly ash[1)]

(Ca in fly ash)>(fine limestone in feed)+(Ca in coal ash)

→ fine formation by attrition



Evaluation of limestone attrition rate

(fine formation by attrition)

=(Drain rate of Ca in fly ash)

- (fine limestone in feed)

- (Ca in coal ash)

Surface area of bed material was calculated from size distribution and mass of bed material

(Fine formation)/(Surface area) = Rate

Attrition rate

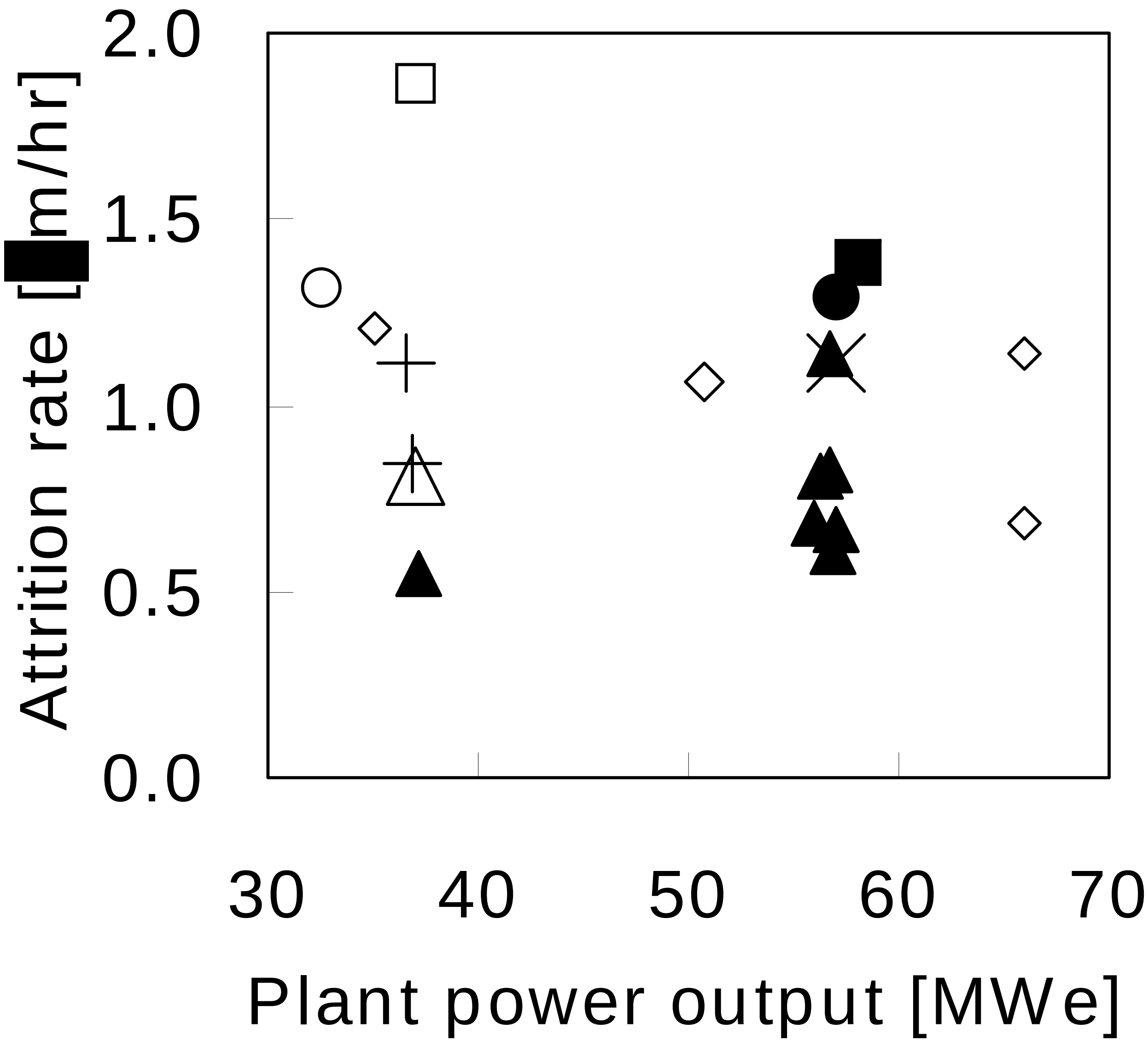
dR/dt =

1 - 2

μm/hr[1)]

No clear effect of coal type and load on rate.

(R: radius)

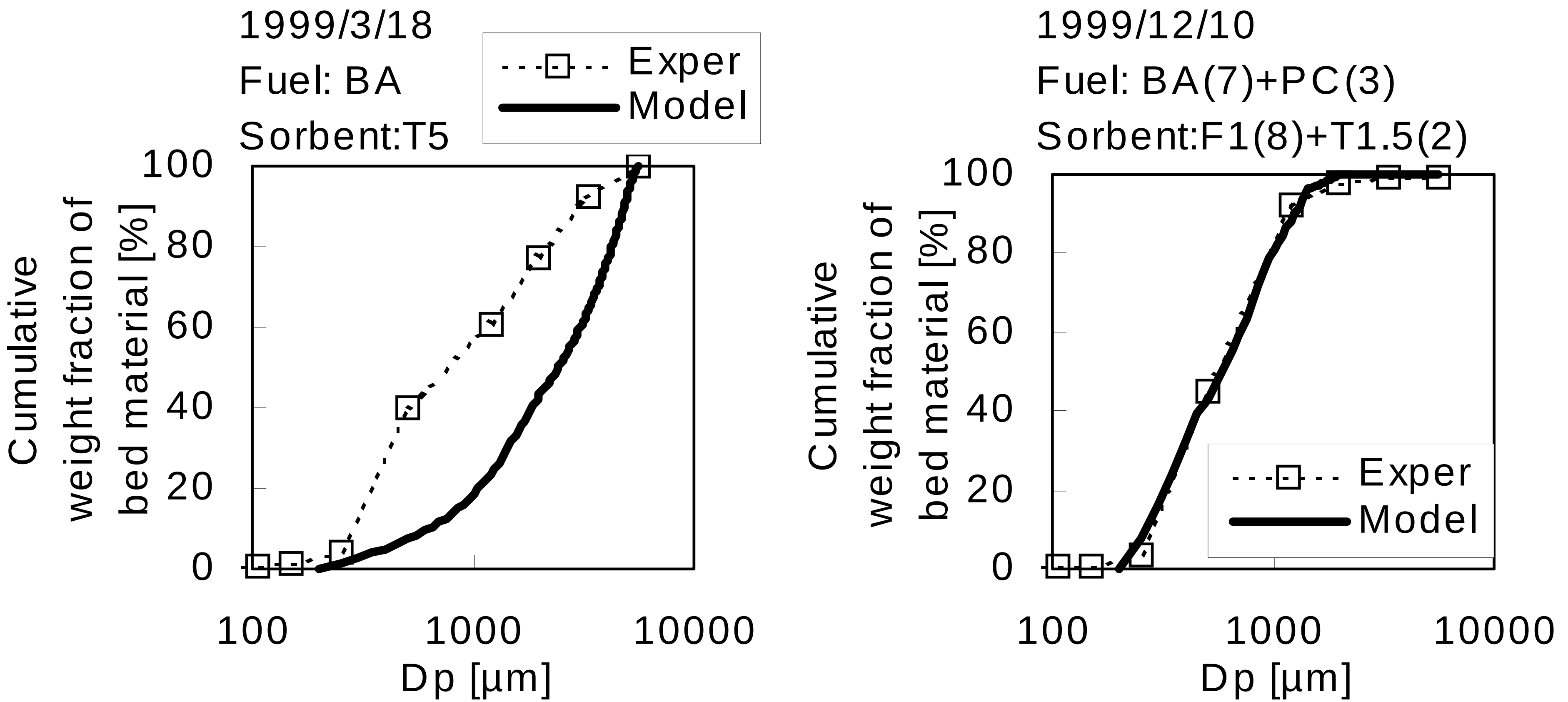


A model of change in limestone particle size by attrition

A model of change in particle size due to attrition assuming constant attrition rate.

Bed material size distribution, comparison between model and experimental results[1)]

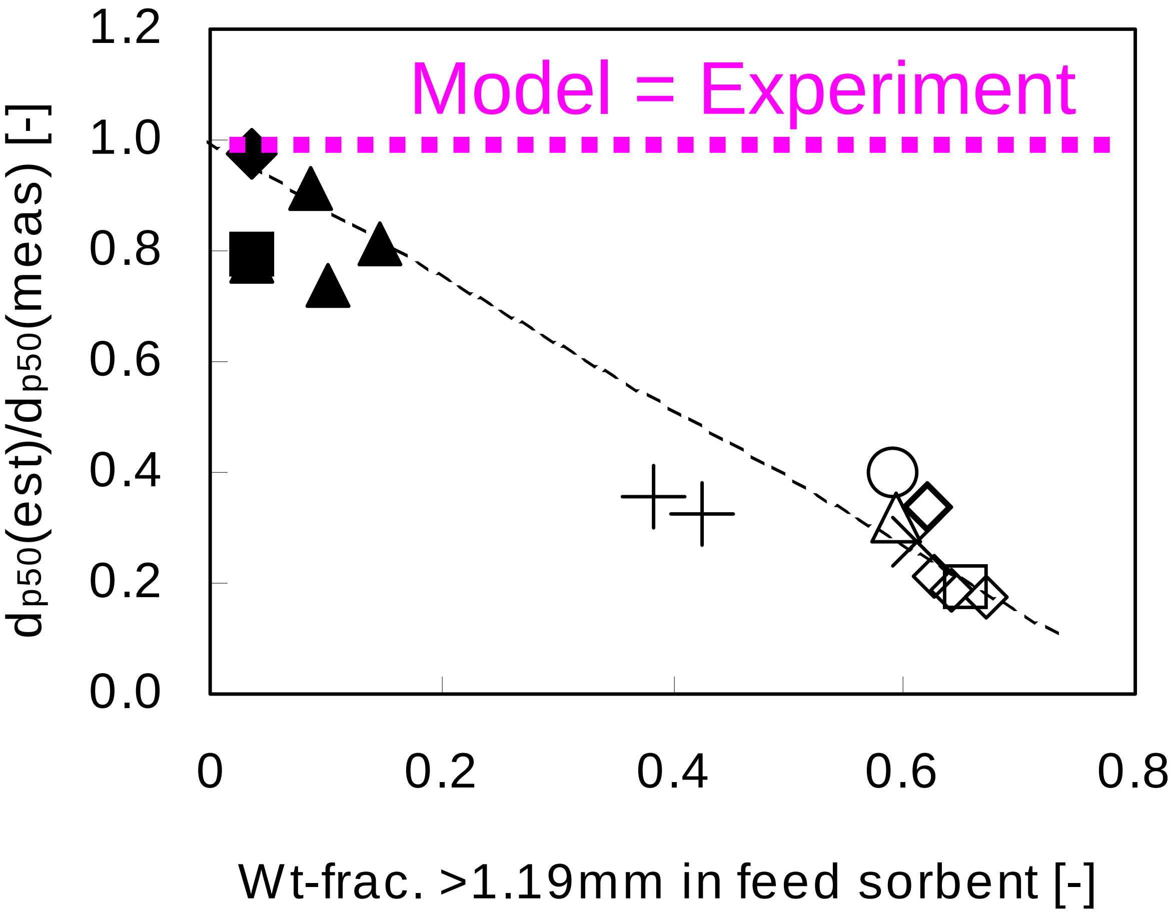
Some agreed but the others not. Why?



Effect of coarse particle content on discrepancy between model and experimental results [1)]

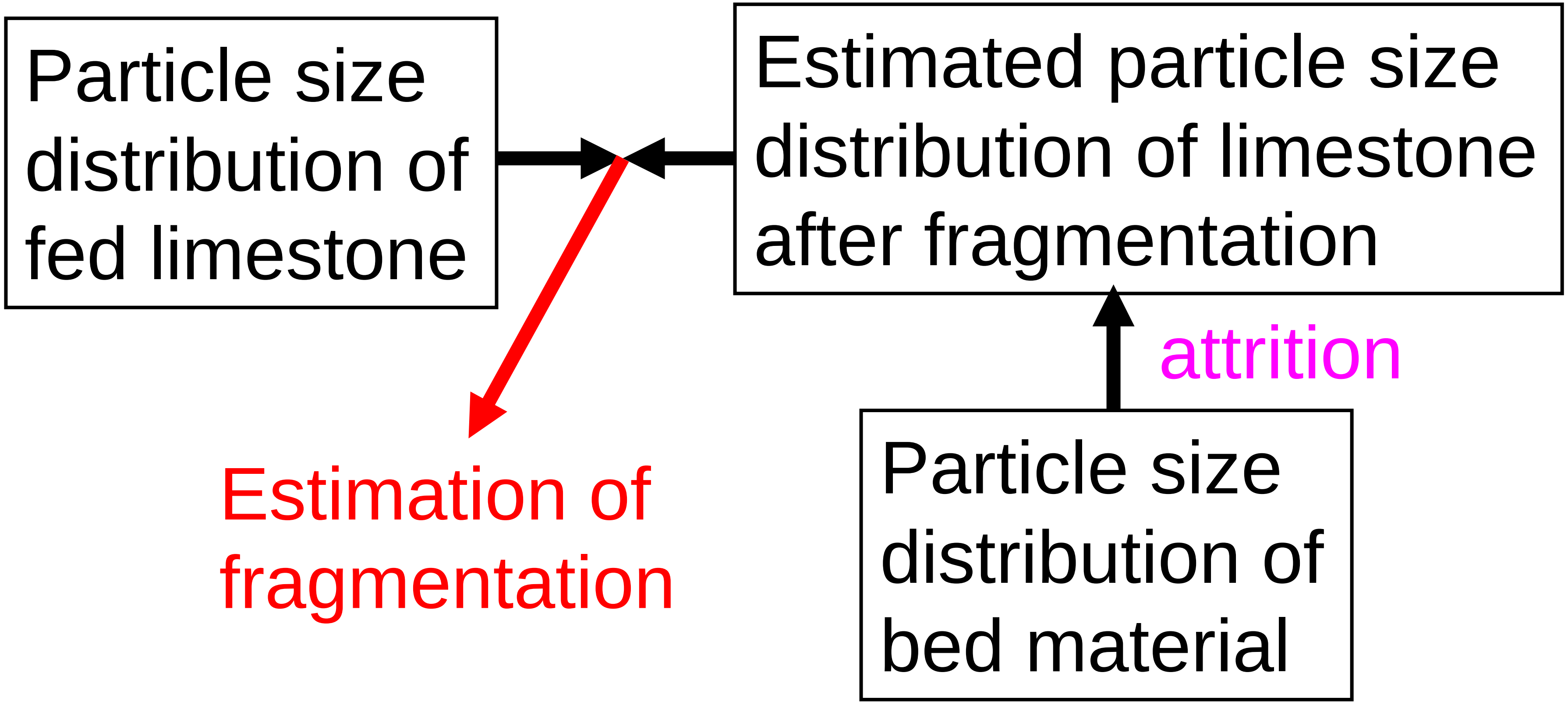
With increasing content of coarse particles, the discrepancy became larger.

→Fragmentation of coarse particles by thermal shock



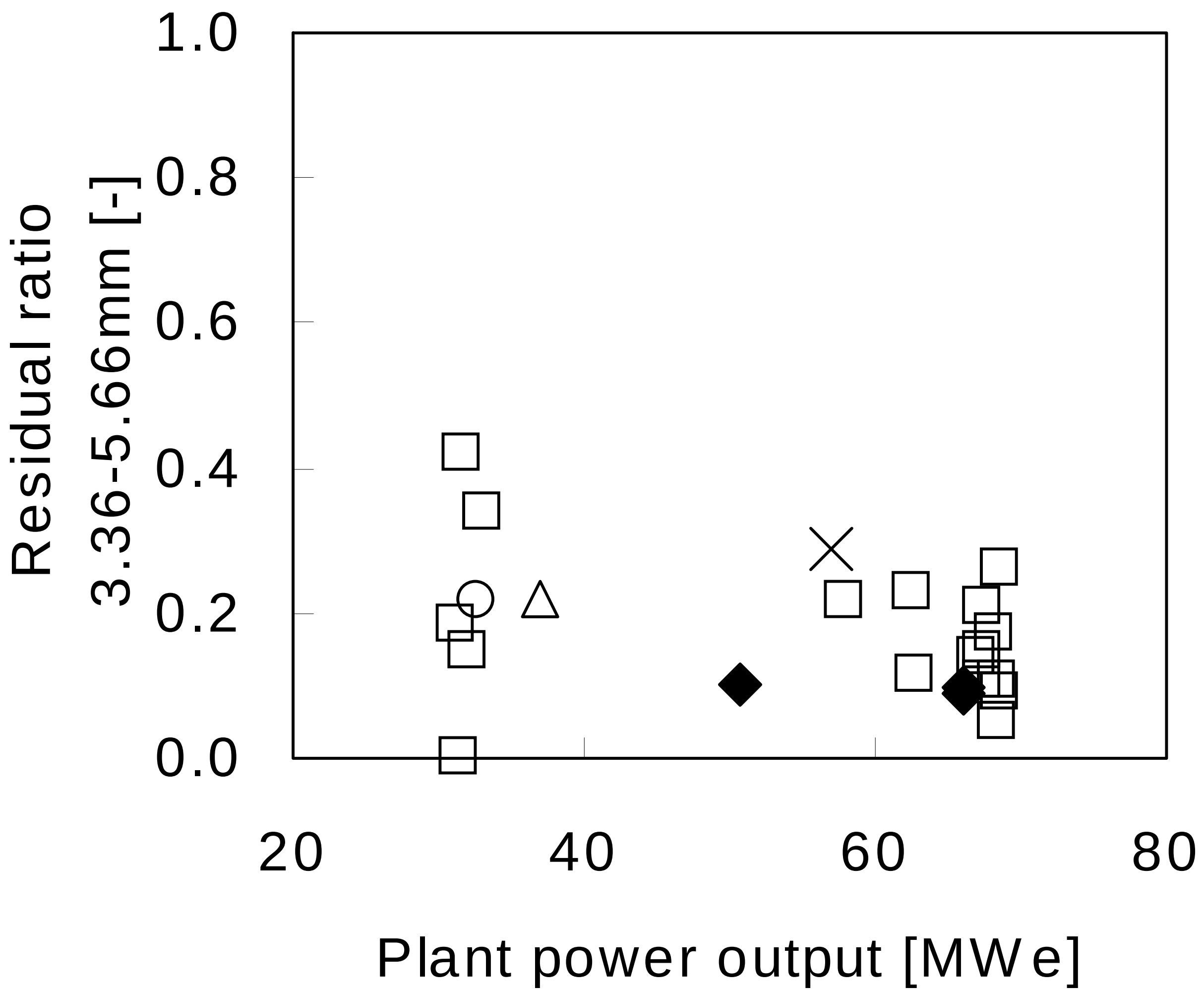
Fragmentation of coarse particles

Fragmentation of coarse particles was estimated by a model.



Fragmentation of coarse particles[2)]

Fragmentation of coarse particles was estimated by the model.
Approx. 80% of coarse (3.4- 5.7 mm) particles was broken into small particles.



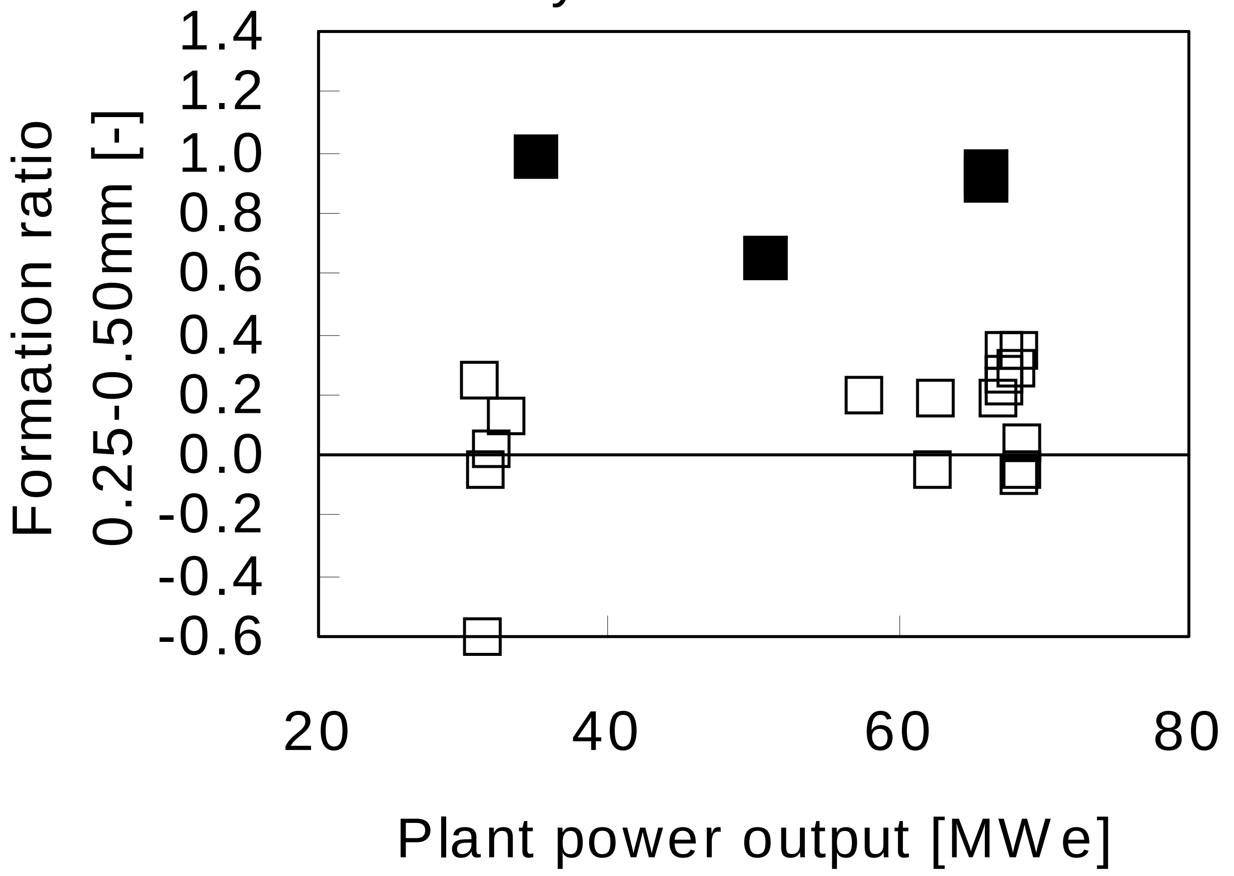
Formation of smaller particles(0.25-0.5mm)

Phase-1: Only little formation of 0.25 – 0.5mm

Phase-2: Nearly all of the fragments → 0.25- 0.5mm

BA coal, Open symbols: Phase-1,

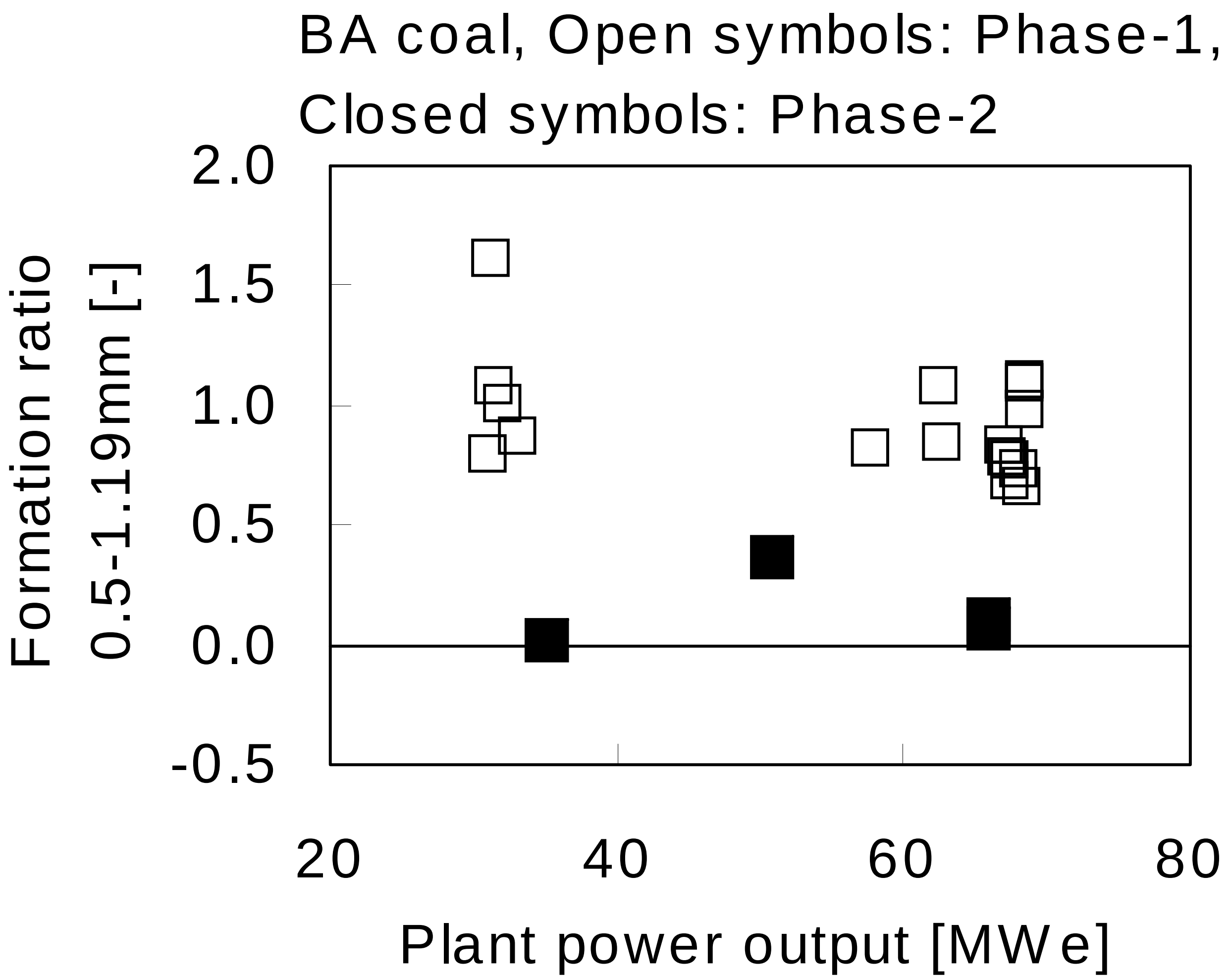
Closed symbols: Phase-2



Formation of smaller particles(0.5-1mm)

Phase-1: Nearly all of the fragments → 0.5- 0.1 mm

Phase-2: Only little formation of 0.5 – 1 mm



Summary of Part 1

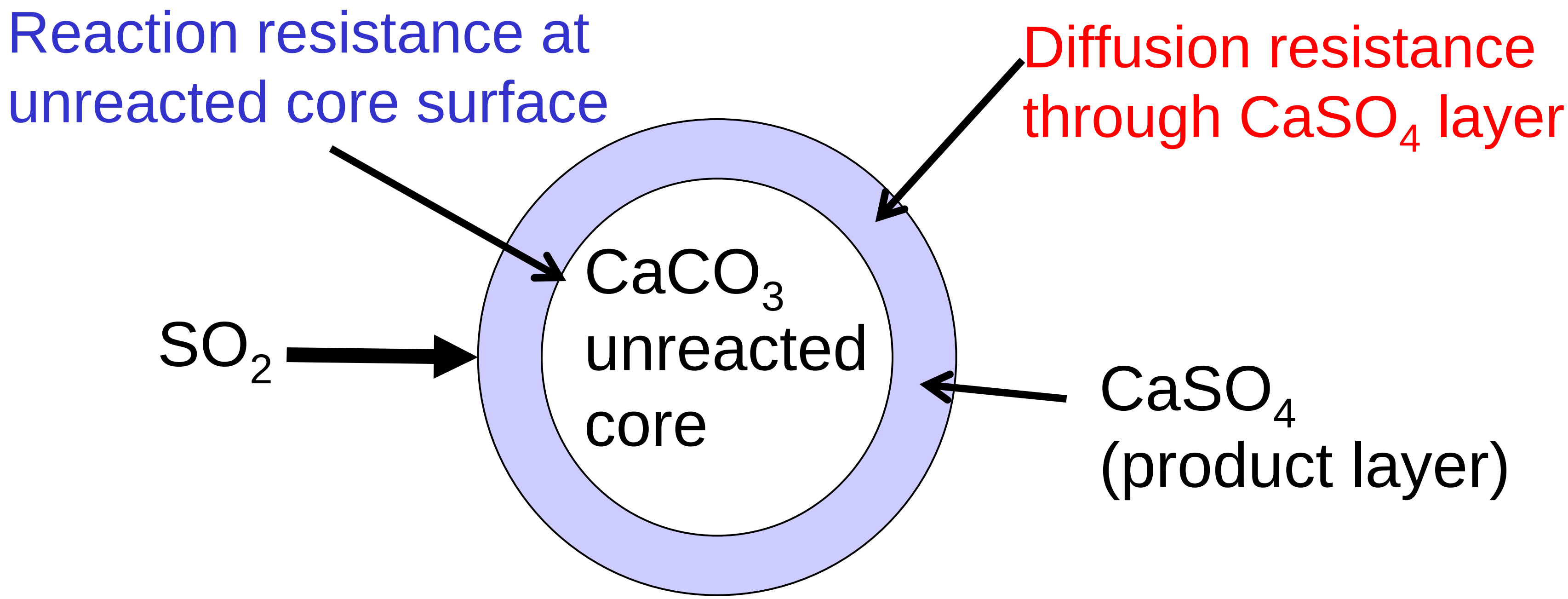
- Considerable attrition of limestone
- Attrition rate = 1 – 2 μm/hr
- Fragmentation of coarse (>1.2mm) limestone
- Size of smaller particles formed by fragmentation was affected by cyclone ash recycle.

Part.2

A model of SO_2 capture by limestone under solid attrition conditions[3)4)5)]

Reaction mechanism (in TGA)

TGA results (in literature): shrinking unreacted core model controlled by both reaction resistance and diffusion resistance through $CaSO_4$ layer.



In actual PFBCs, attrition occurs.

Role of attrition in SO_2 capture by limestone - unknown. Two possible effects of attrition:

- Attrition increases reaction rate by removing $CaSO_4$ layer (diffusion resistance)
- Attrition decreases solid utilization efficiency by removal of unreacted $CaCO_3$

→Modeling work is necessary to evaluate the effect of attrition on SO_2 capture rate and limestone utilization efficiency

Attrition model

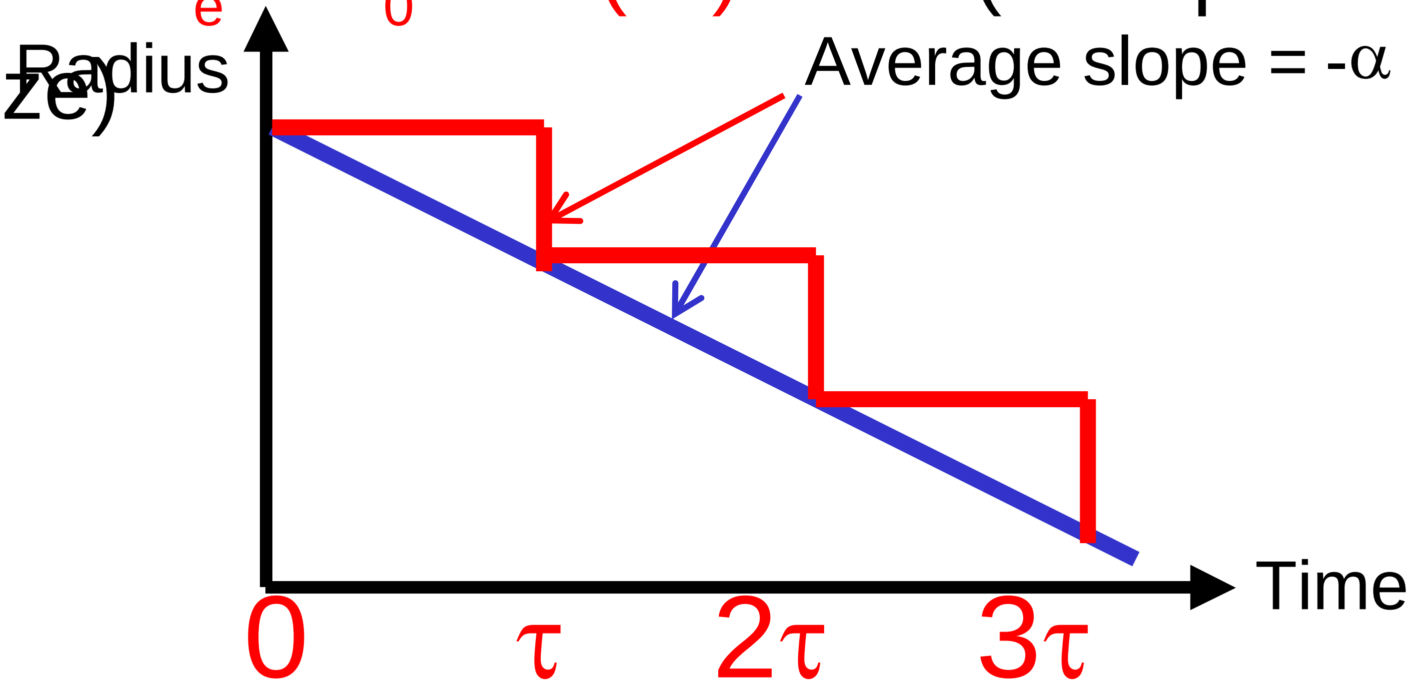
Two different attrition modes:

Continuous attrition: α=average attrition rate

$$R_e = R_0 - \alpha t$$

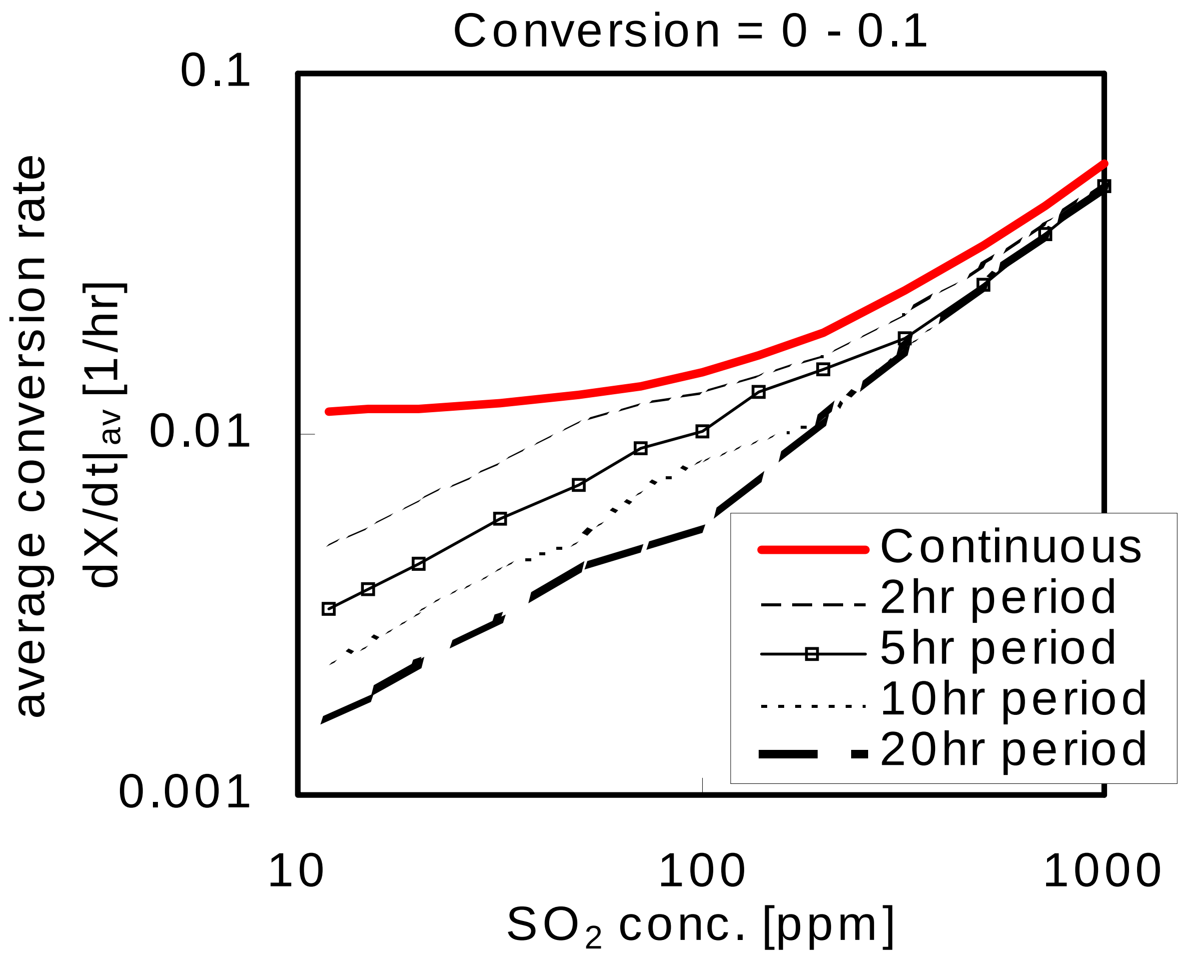
Intermittent (periodical) attrition:

$$R_e = R_0 - \text{int}(t/\tau)\alpha\tau$$ ($\alpha\tau$<<particle size)



Results: Initial reaction rate[5)]

At low SO_2 concentrations (<100ppm), attrition mode affects reaction rate.

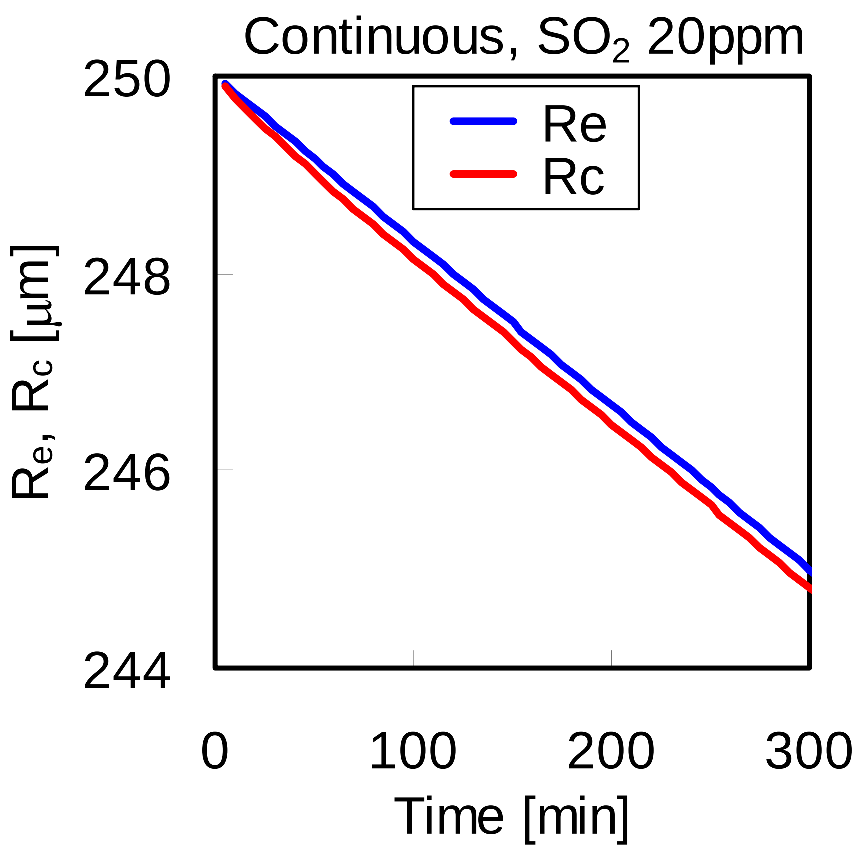


Effect of attrition mode on removal of product layer at low SO_2 concentration [5)]

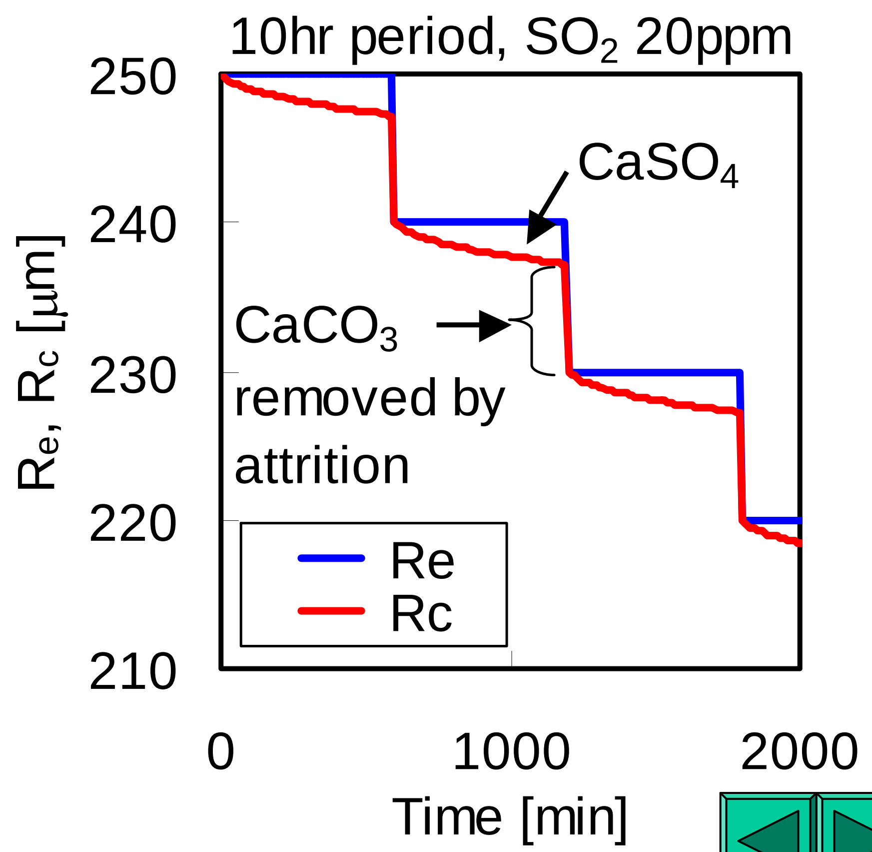
Continuous : Only $CaSO_4$ is removed.

Intermittent: $CaCO_3$ is also removed.

Continuous



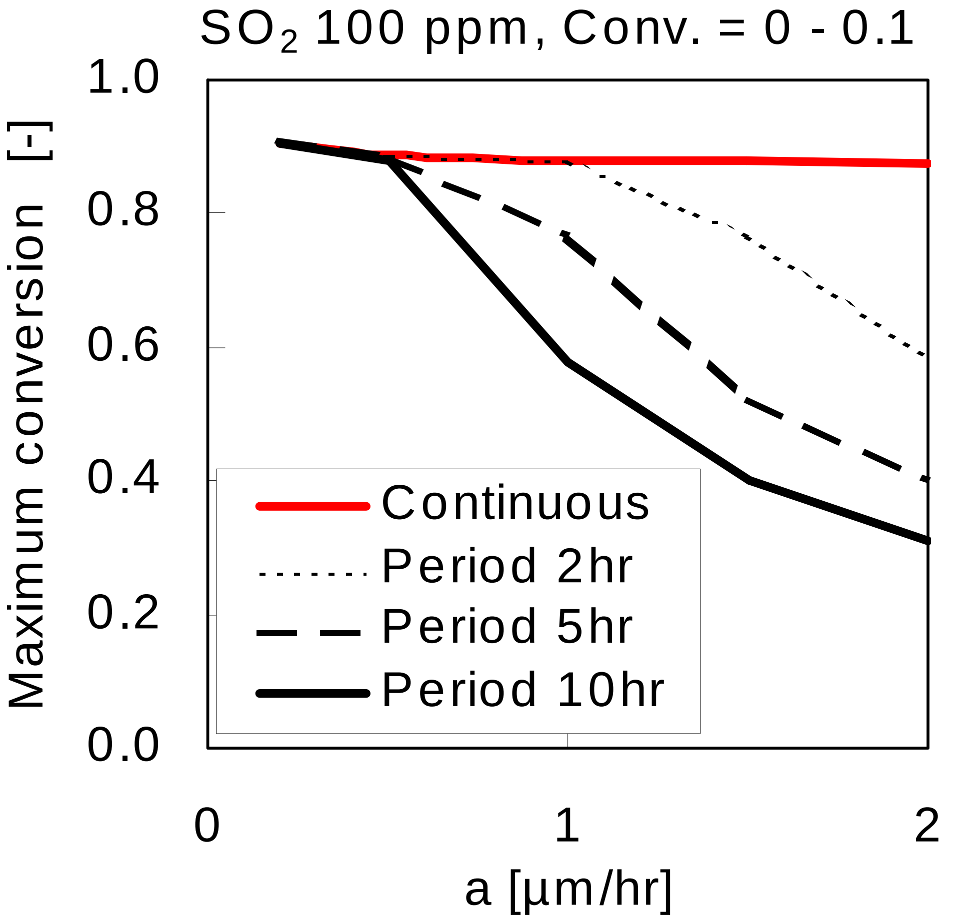
Intermittent



Effect of attrition rate on limestone utilization efficiency [5)]

Continuous: No change

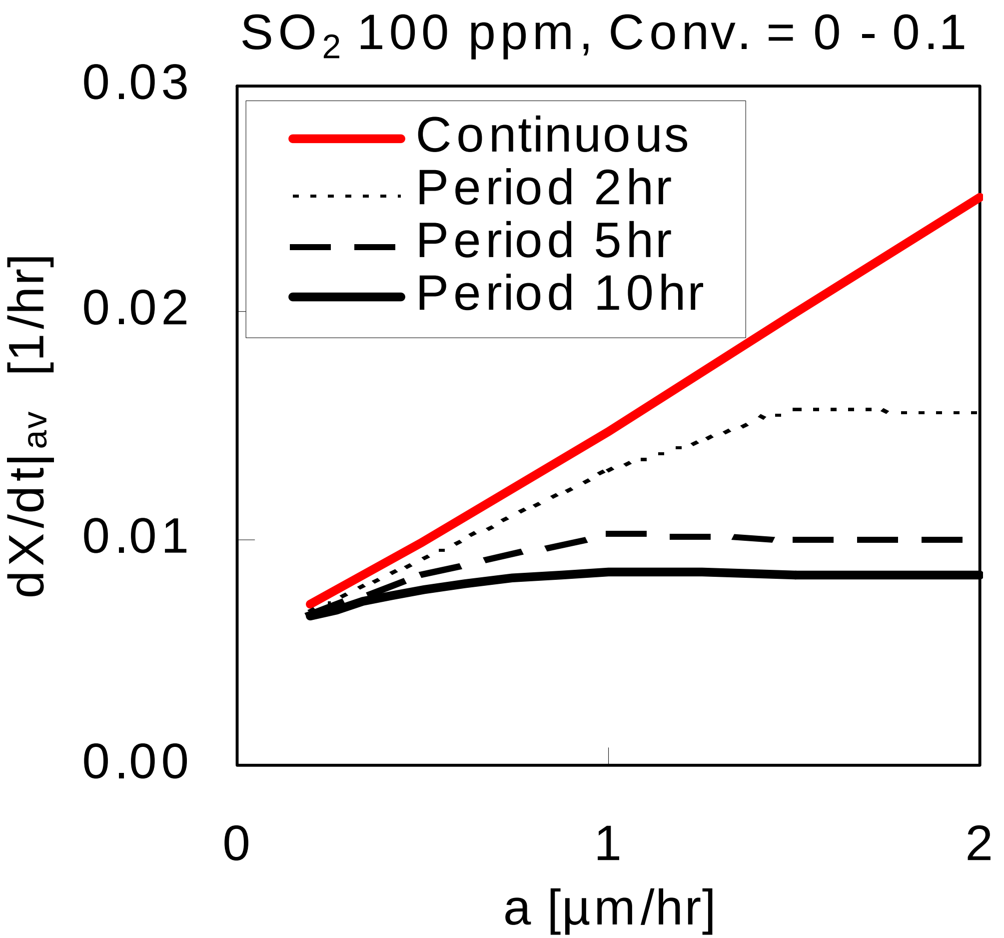
Intermittent: Attrition decreases efficiency.



Effect of attrition rate on apparent reaction rate [5)]

Continuous: Attrition increases rate.

Intermittent: No change in reaction rate.



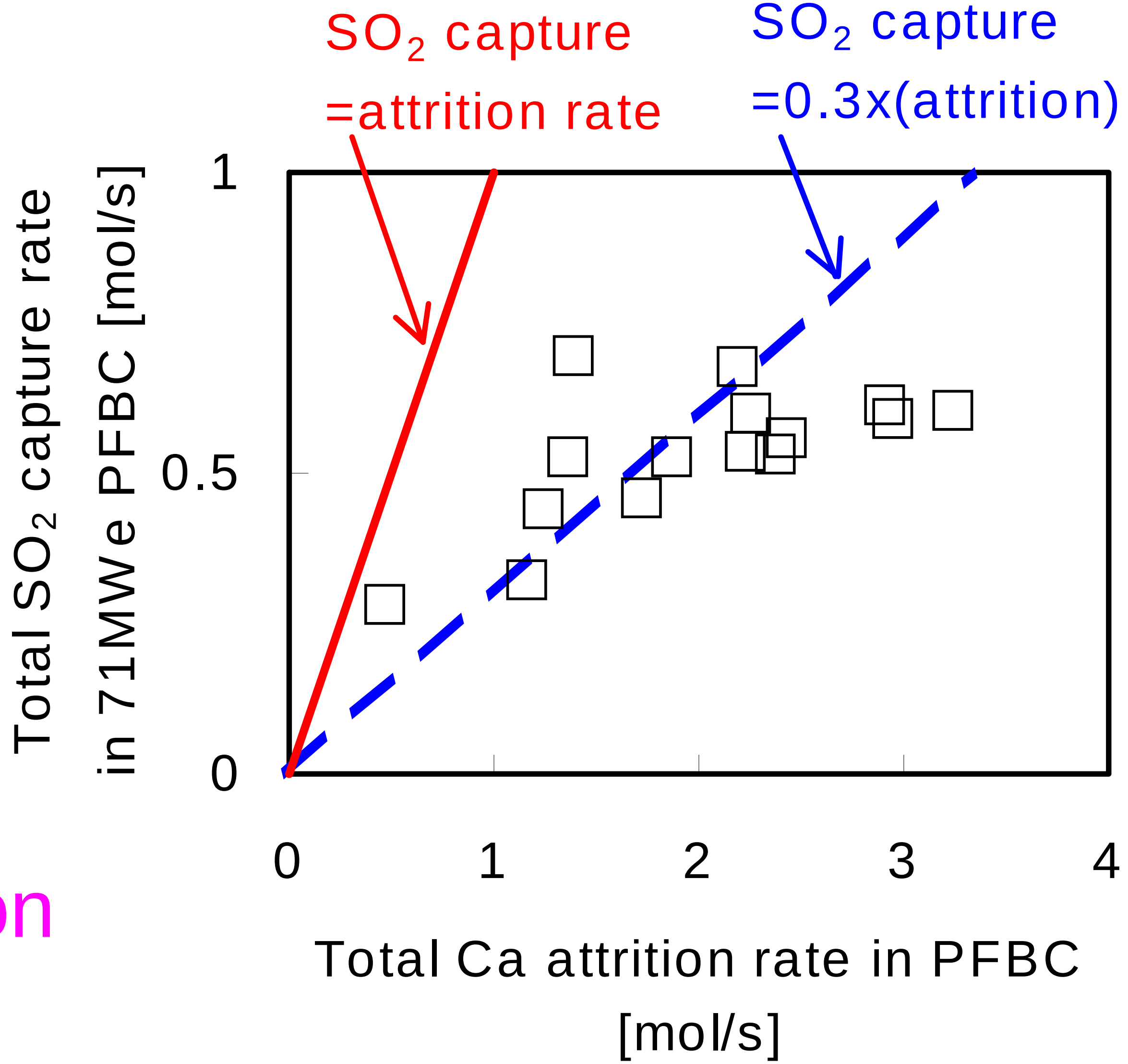
IF continuous attrition occurs in PFBC ...

Attrition rate =

SO_2 capture rate

However, in 71MWe PFBC SO_2 capture rate was only 1/3 of attrition rate [3].

Intermittent attrition model is applied.



Simplified SO_2 capture model for intermittent attrition model [3)]

Assumptions:

Product layer thickness << Particle size

→Flat surface

Diffusion resistance >> Reaction resistance

→Controlled by diffusion through $CaSO_4$

Fresh surface appears when attrition occurs

→Product layer thickness = 0 when attrition occurs

Simplified rate expression of SO_2 capture for intermittent attrition model [4)]

SO_2 capture rate per unit external surface area of limestone:

$$r_S = (2D_e\rho/M\tau)^{1/2}\, C^{1/2}$$

D_e: Effective diffusivity

τ: Period of attrition

C: Concentration of SO_2

ρ/M: Molar density of $CaCO_3$ in limestone

Simplified SO_2 capture model in PFBC [4)]

Assumptions:

VM-S forms SO_2 at the bottom

→SO_2 concentration at the bottom

Char-S forms SO_2 uniformly in bed

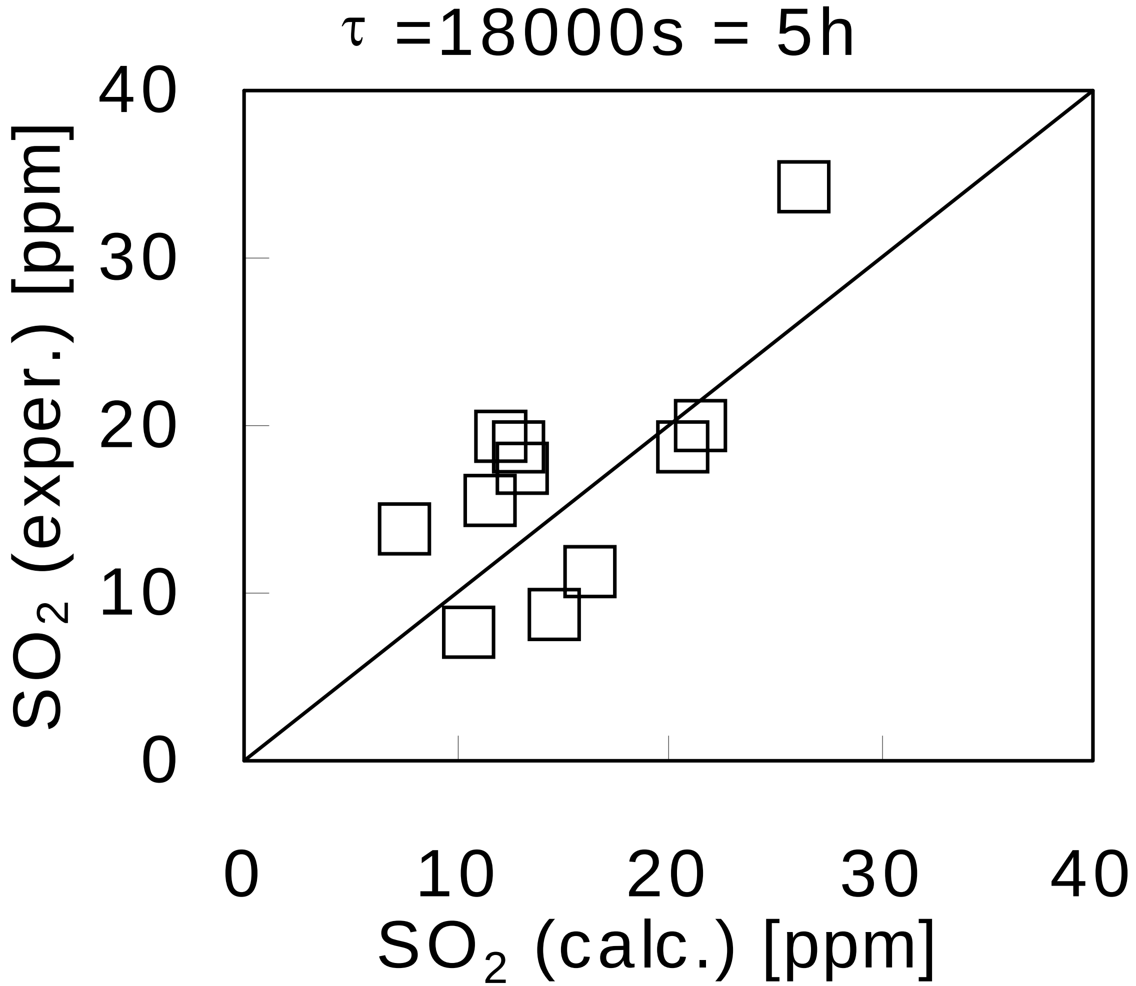
→SO_2 formation rate per unit volume of bed

Bed consists of Geldart's "D" particle

→mass transfer resistance from bubble to emulsion is sufficiently small→ plug flow model

Comparison between model and experimental results [4)]

Attrition interval was given as a fitting parameter. By giving τ=5 hr, model agreed well with experimental results.



Is τ=5 hr appropriate?

Best fit between model and experiments was obtained at τ=5 hr.

$\alpha\tau$ = (1- 2 μm/hr)x(5 hr) = 5 - 10 μm

<< Particle size (>250 μm)

For further analysis, measurement of size distribution of Ca-rich fines in fly ash by CC-SEM is necessary.

CONCLUSION

Behavior of limestone in 71 MWe PFBC was analyzed.

- Attrition rate of limestone was 1-2 μm/hr.
- Limestone particles greater than 1.2 mm was broken when they are fed into PFBC.
- Limestone attrition mode (continuous or intermittent) plays significant role in SO_2 capture. Continuous attrition model over-estimates SO_2 capture in PFBC.

CONCLUSION (continued)

- Intermittent attrition model agreed PFBC results when period of attrition was given as τ=5hr.
- To establish complete model, period of attrition should be experimentally determined. Size distribution of Ca-rich particles in the fly ash is necessary for further study.

Acknowledgement

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