Japan-Korea powder technology symposium 2015
Sept.14,2015　Hold on Soul National University

Studies of milling technology's approaches for establishing the chemical recycles on some wasted glasses.

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1. The Objects and Targets of This study.

Objects of this study

- To explore the possibilities of **chemical recycle** technology
- Material science approaches for environmental cleanup

Targets of development

- With **wasted glass materials**
- *Silicate devices for environment cleanup*
- In-line measurement system development

2． Some directions for wasted glass chemical recycle applications

①Silicate resources for minerals and ceramics synthesis

Abstracts of Spring Meeting of Japan Society of Powder and Powder Metallurgy,2013
IREP the first Meeting in Imabari,2013
M.kamitani,A,Nakahira,T.Wakihara、et.al　ISAC-5,Wuhan,Chaina 2014
Fabrication and evaluation of hybrid materials from A-zeolite and ground glass powders for vitrified radioactive, j. ceram. soc, japan 122 (2) 151-155,2014

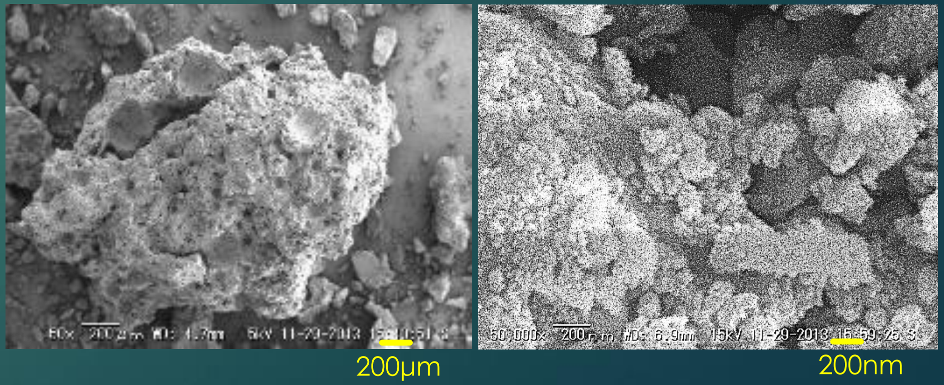
Synthesized LTA in Bamboo inside pore

②Ion exchanging devices for environmental cleanup

2nd meeting on Environmental radioactive decontamination technology, Tokyo 2013
Abstracts of Autumn Meeting of Japan Society of Powder and Powder Metallurgy,2013
M.kamitani,A,Nakahira,T.Wakihara、et.al　ISAC-5,Wuhan,Chaina 2014

③The dehydration condensation for like cement

Materials Science Forum Vols,22-227 (1996) pp.587-592
Kinzoku,Vol.68 (1998) No.9
Abstracts of Autum Meeting of Japan Society of Powder and Powder Metallurgy,2014
M.Kamitani,M.Kondo.A.Nakahira, J. Jpn. Soc. Powder Powder Metallurgy Vol. 62, No. 6 ,2015



Condensed mass from LCDG

3. Fundamental procedure of chemically activation for wasted glass by Ball milling

Energy consumption of milling with ball media

Fracture mode of glass grain by impact

ref. Rumpf, H, Struktur der Zerkleinerungswissenschaft
Aufbereitungs-Technik No. 8/1966 421-435

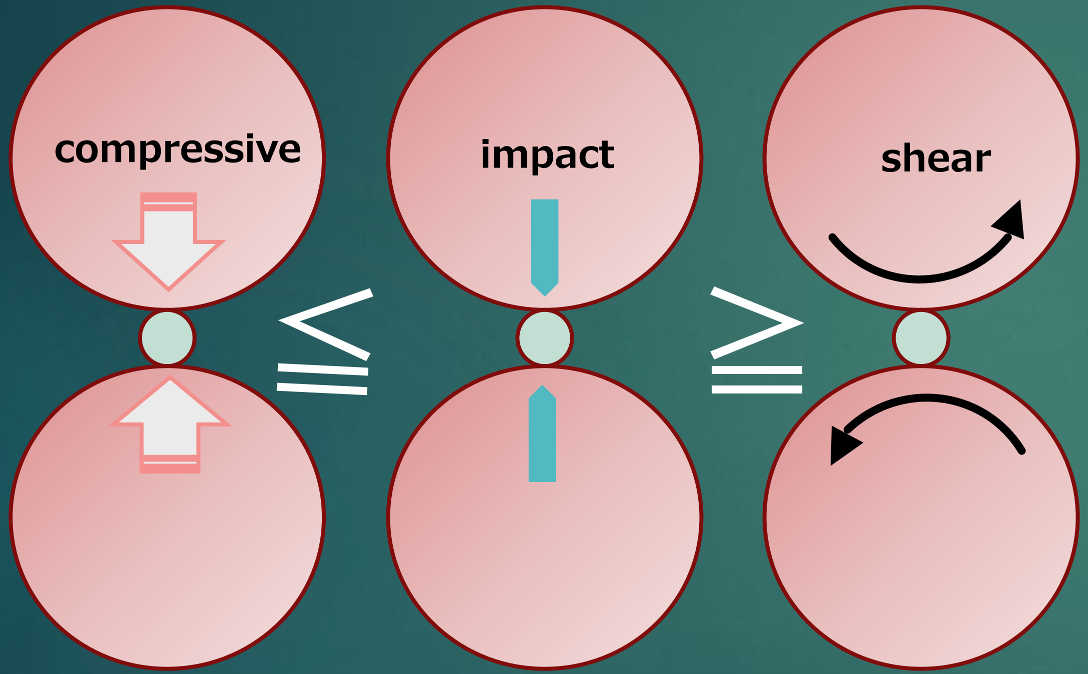


Fig.1 model of generating forces in ball mill

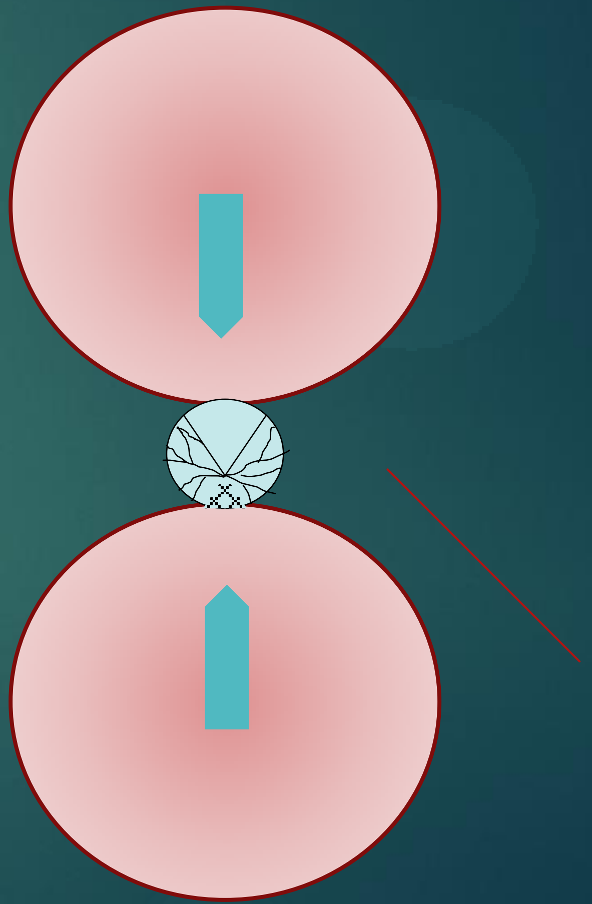


Fig.2 fracture model from reference

Optimization of ball milling condition by DEM simulation

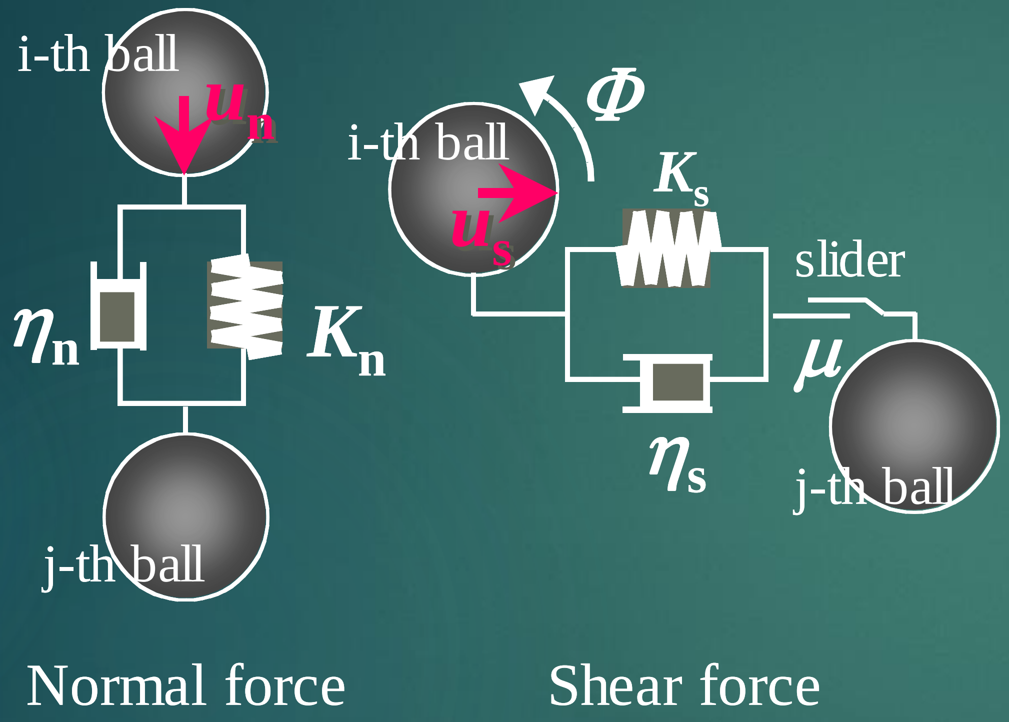
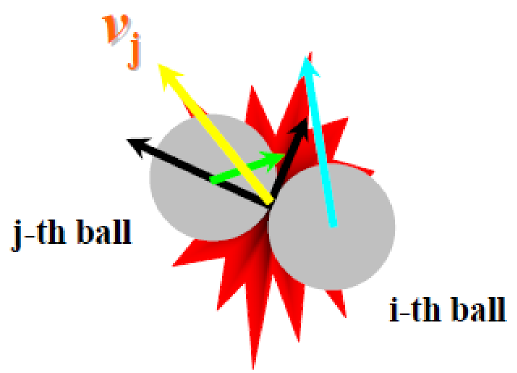


Fig.3 DEM simulation based on Voigt model

$$E_W = \sum_{j=1}^{n} \frac{1}{2W} m v_j^2$$



m: Ball weight

v: Impact speed

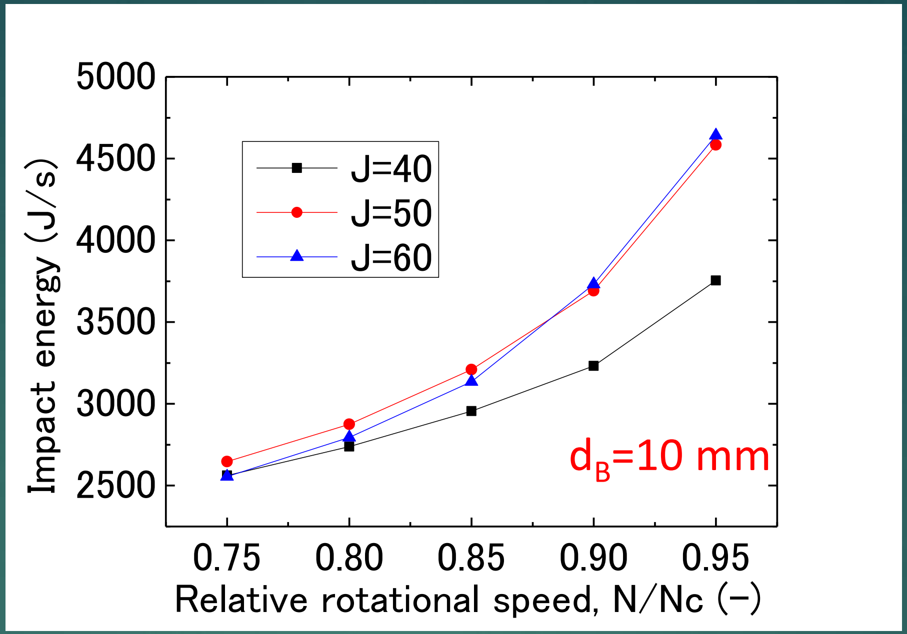
W: Specimen weight

n: Number of impact

Energy consumption

Ball: φ＝10-30mm steal
Mill dimension

L=725mm
diameter=725mm



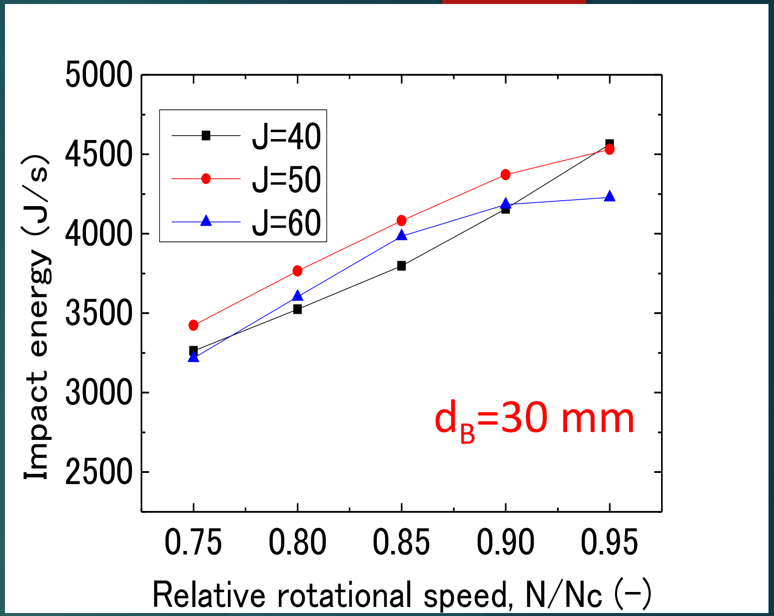
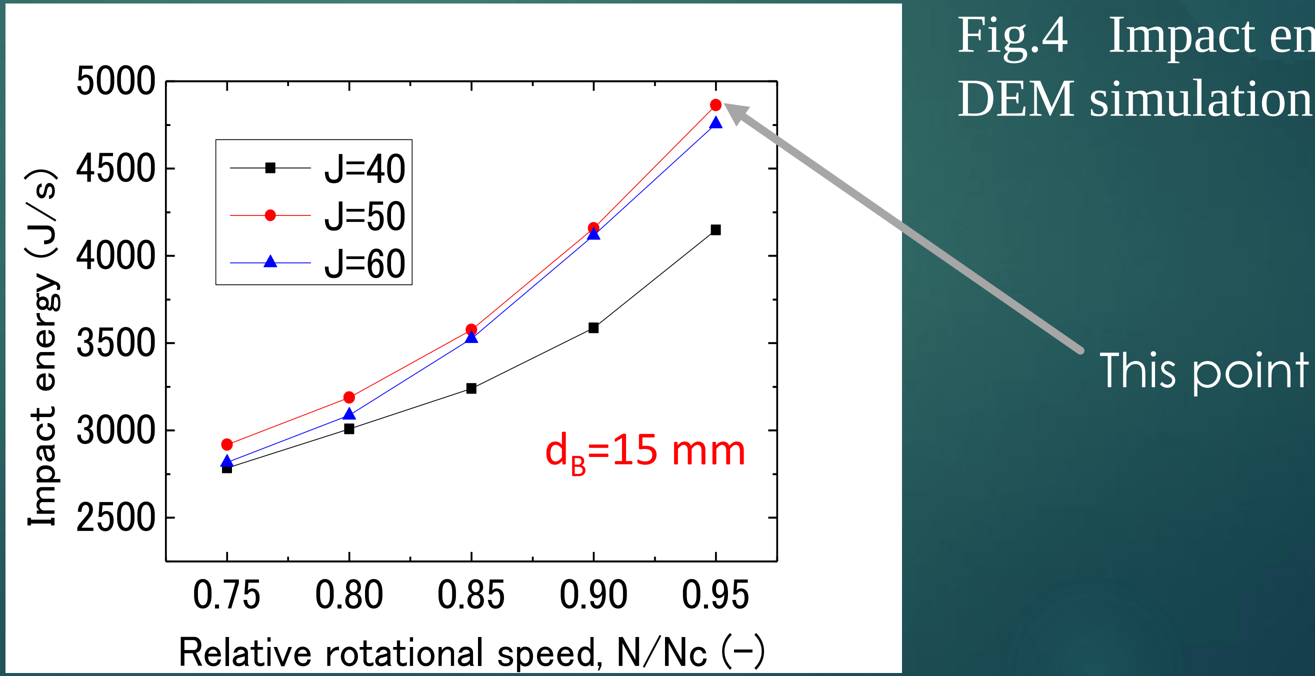


Fig.4 Impact energy estimation by DEM simulation.



4.Experiment and Results

①Milling test plan

Ball: φ＝15mm steal

Mill dimension

L=725mm
diameter=725mm

Ball filling ratio=0.5
Raw material:24-32Kg

Table.1 Test plan

No.	Glass species	Glass weight (kg)	Ball milling condition: rotation (N/Nc)	Ball milling condition: Ball radius (mm)	Ball milling condition: occupy (%)	sampling(hr): 0.5	sampling(hr): 1	sampling(hr): 2	sampling(hr): 3	sampling(hr): 6	sampling(hr): 8
①	LCDG[1]	32	0.95	15	50	○	○	○	○	○	—
②	LCDG[1]	24	0.95	15	50	—	—	○	○	○	—
③	LCDG[1]	32	0.85	15	50	—	—	○	○	○	—
⑥[3]	LCDG[1]	12	0.75	15 Al_2O_3	50	—	○	○	○	○	○
④	SLG[2]	30	0.95	20	50	○	○	○	○	○	○
⑤	SLG[2]	30	0.95	15	50	○	○	○	○	○	○

1)①②③:LCDG alumino-silicate glass:$SiO_2/Al_2O_3/CaO/Na_2O$=58.8/17.1/9.5/0.3(wt%ratio)

2)④⑤:Soda-Lime Glass:$SiO_2/CaO/Na_2O$=73/5/17(wt%ratio)

3) Test ⑥ is another experiment for in-line measuring system development.
Milling by small 50L mill on another glass:$SiO_2/Al_2O_3/MgO/Na_2O$=60.2/15.2/7.2/16.8(wt%)

②Grain size distribution change

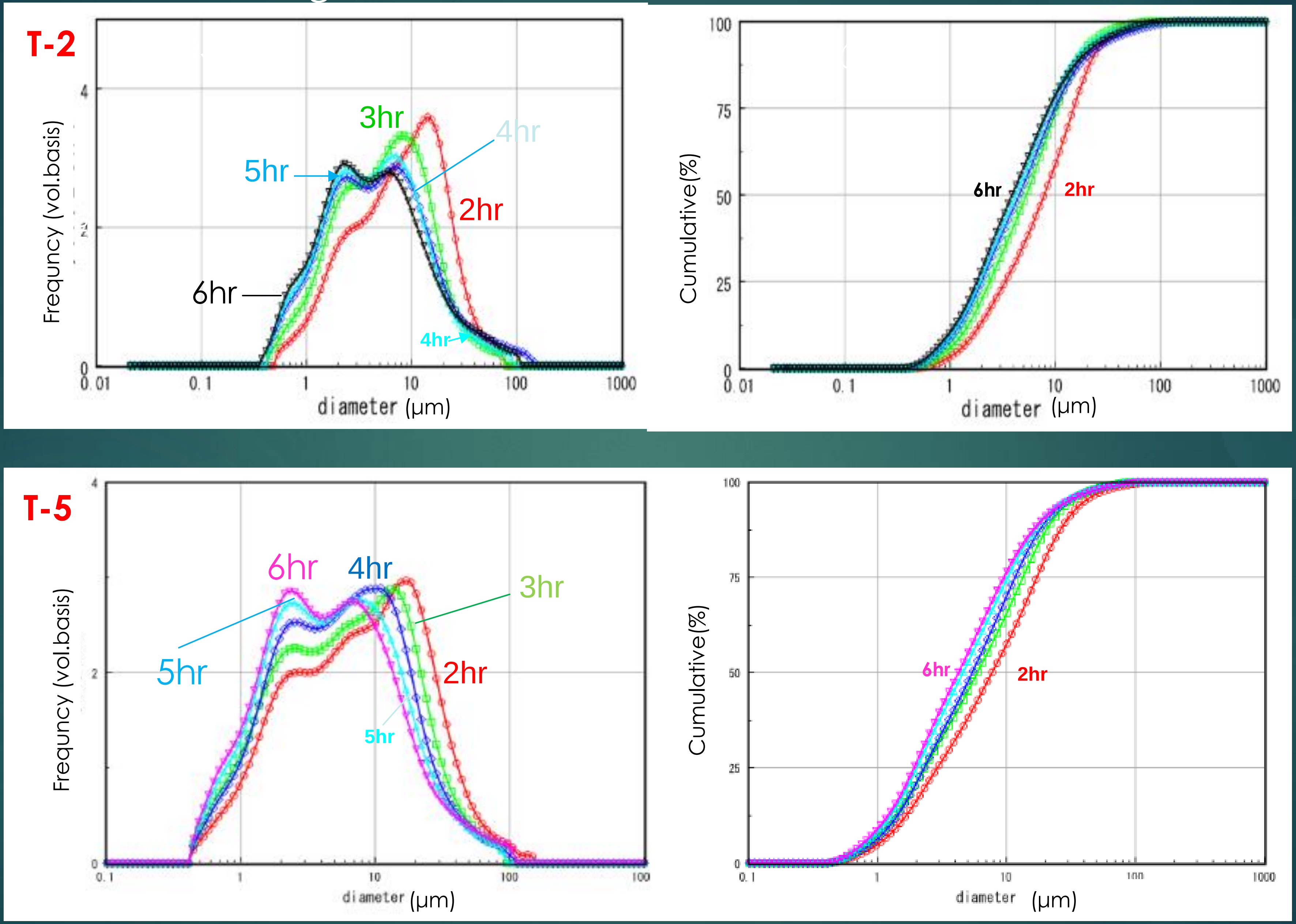


Fig. 5 Grain size distribution of test2 and test5 by Laser diffraction MT-3000 II

③Morphology on SEM's images

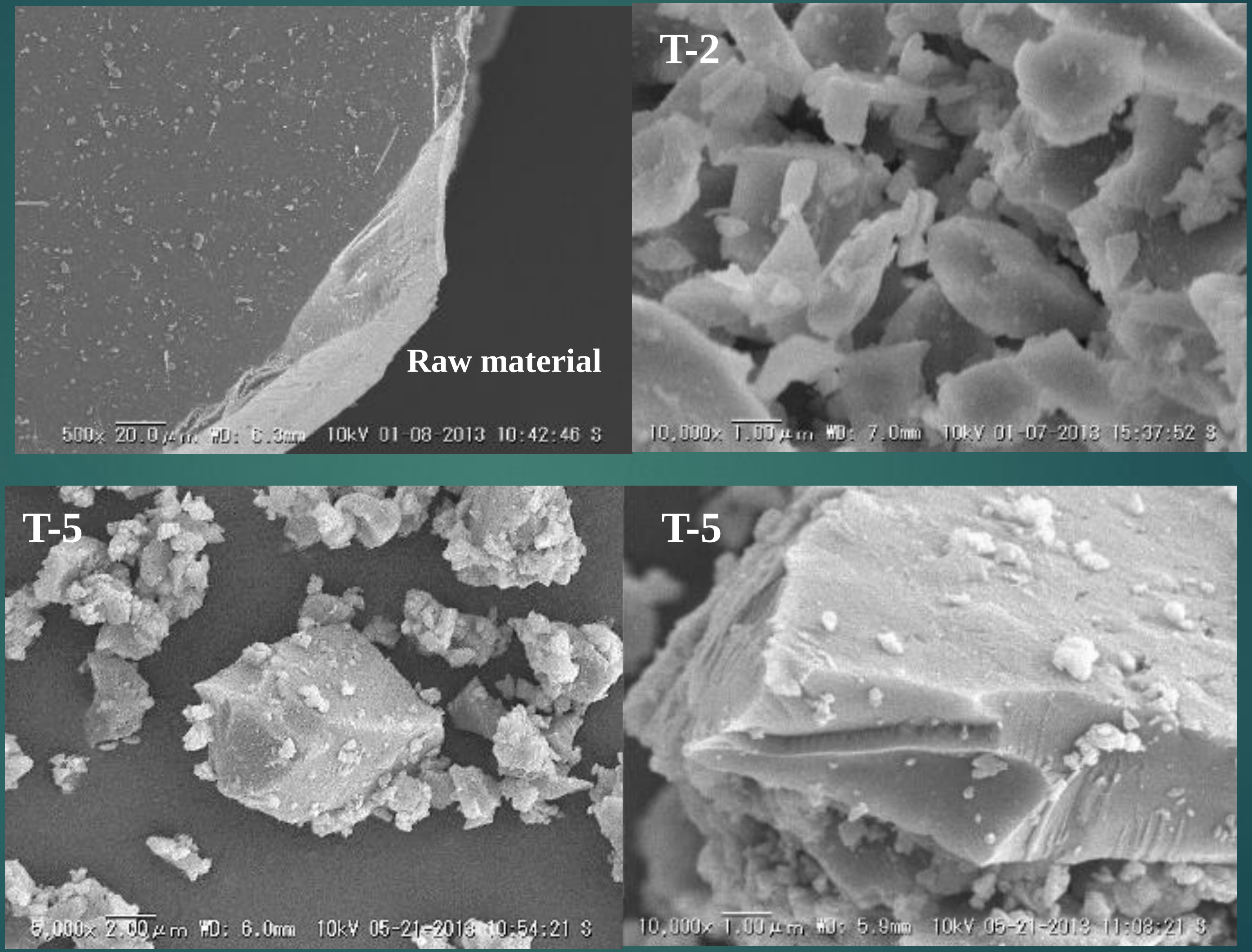


Fig.8 SEM's images of T-2 and T-5 samples that 6hr milled.

④Specific surface area

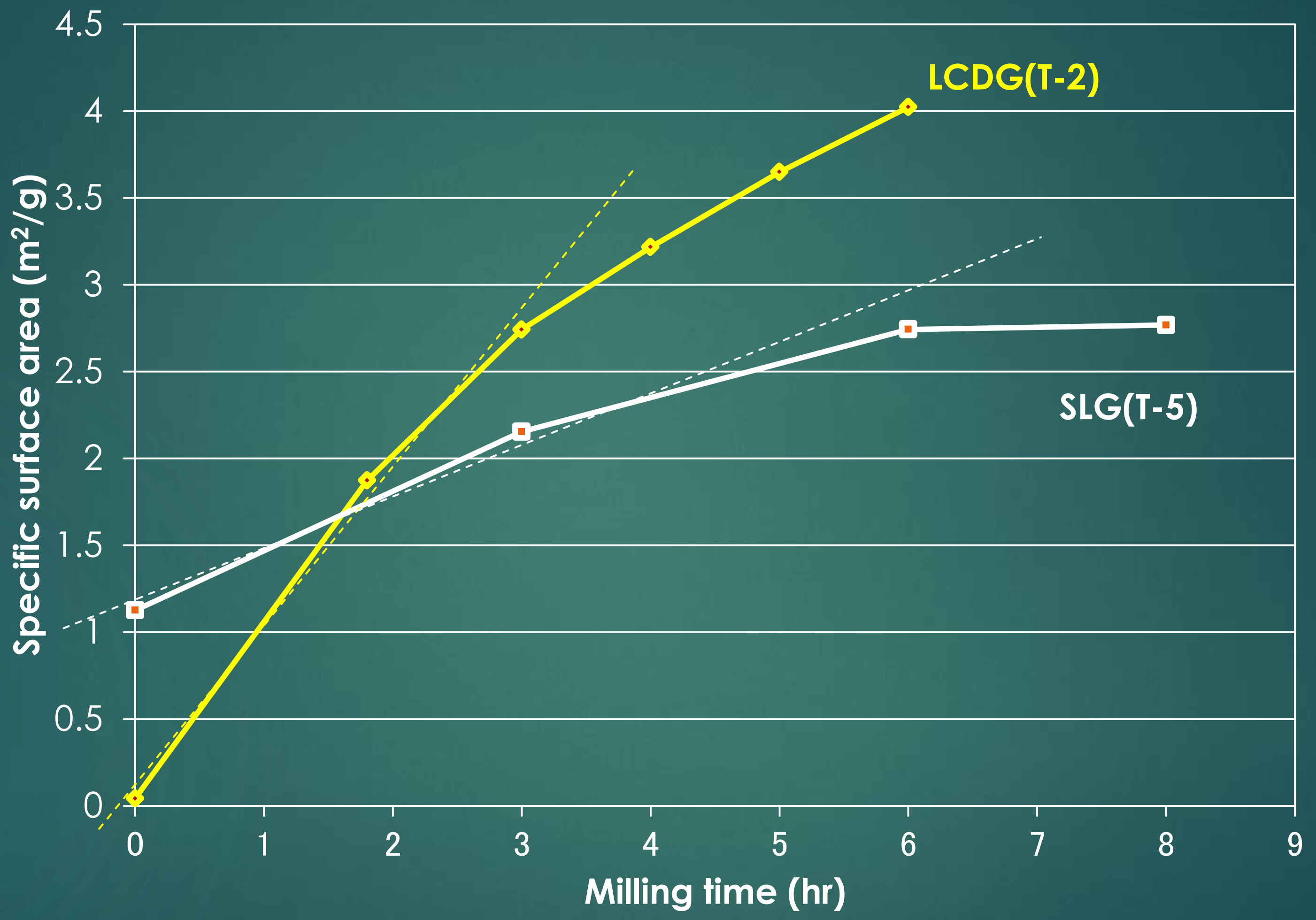


Fig.9 BET specific surface area of T-2 and T-5

measured by Bellsorp mini Ⅱ.

Soft X-Ray Beamline for Photoabsorption Spectroscop

⑤XAFS analysis Si-K

The monochromator serves soft X-rays in the energy region from 585 to 4000 eV

KTP (KTiOPO4)

Thanks UVSOR

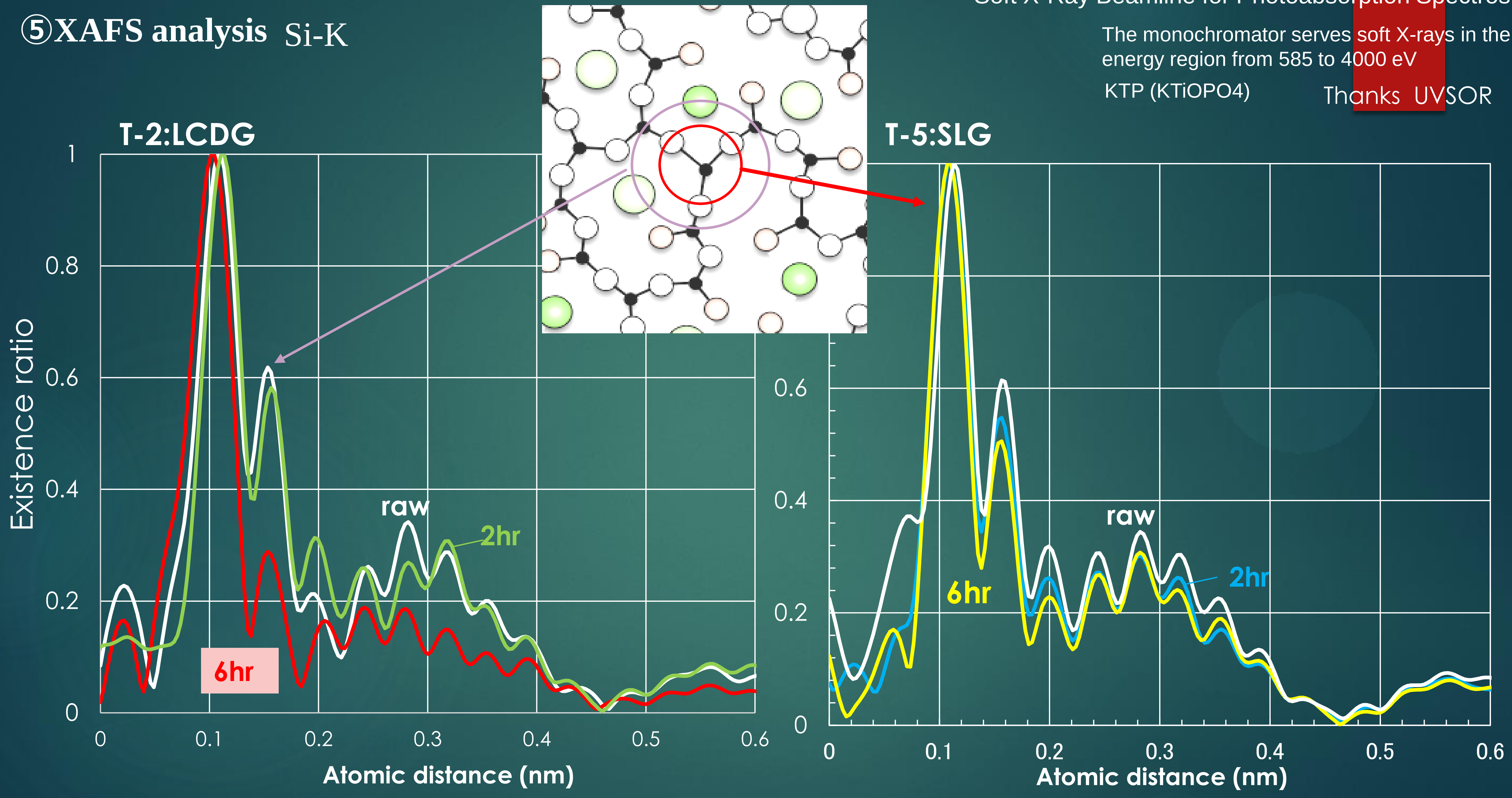


Fig.10 XAFS profiles of T-2 and T-5

⑥Titration for surface analysis

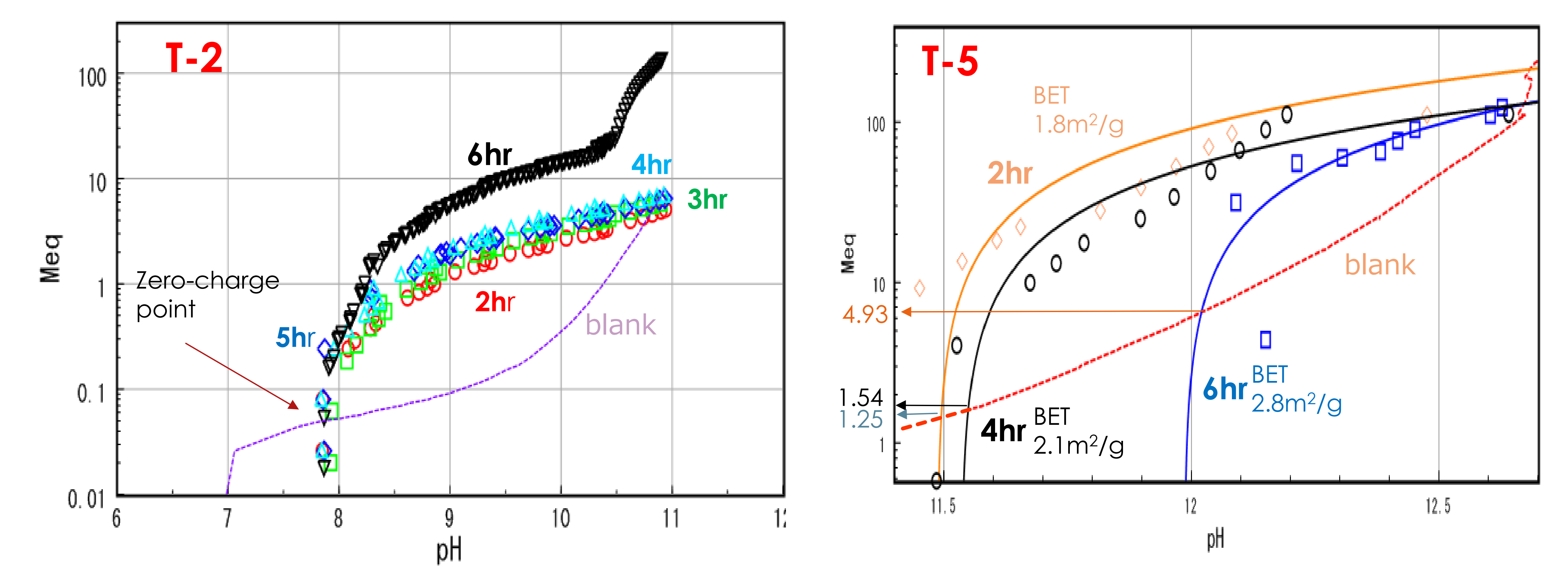


Fig.11 Titration curves of T-2 and T-5 samples.

Solid concentration is 10% 1 N-NaOH used

Measured by DT-1200

5. For Silica resource

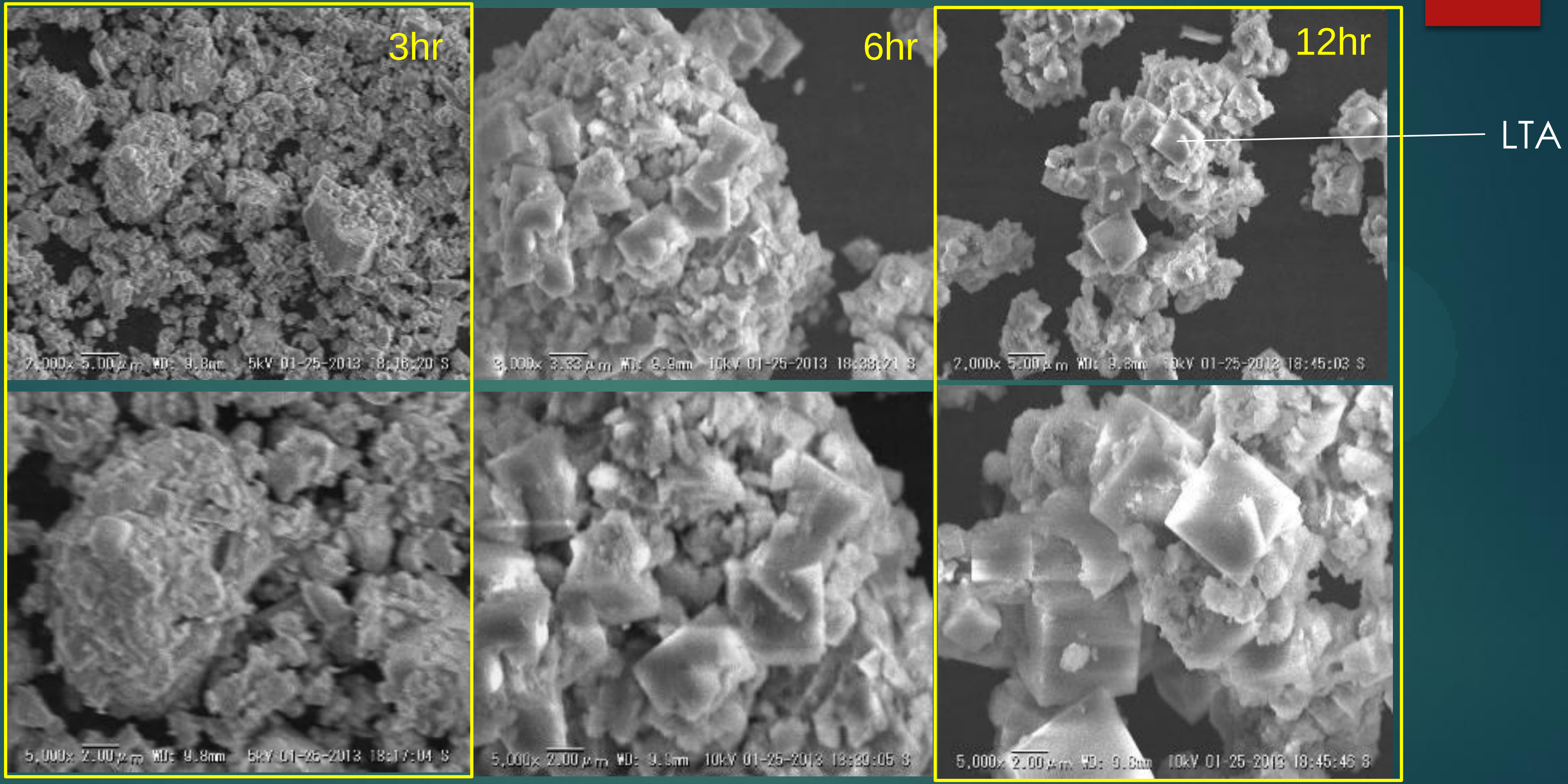


Fig.12　SEM's images of autoclaved grains

Test2-6hrmilling　reacted in S-solution for 3-12hr at 95℃

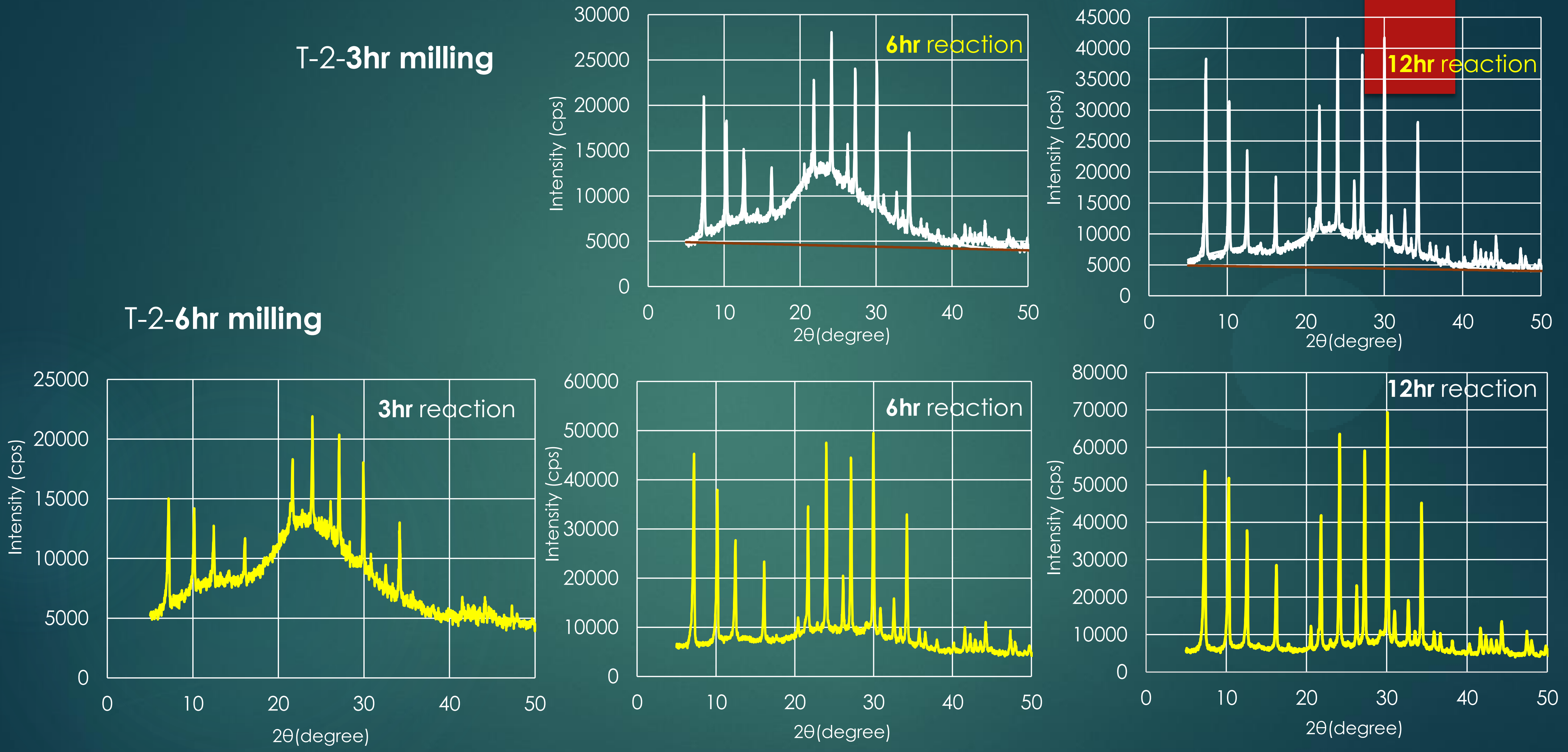


Fig.13 XRD profiles of autoclaved sample

6. For Ion exchange device

①aqueous washing treatment

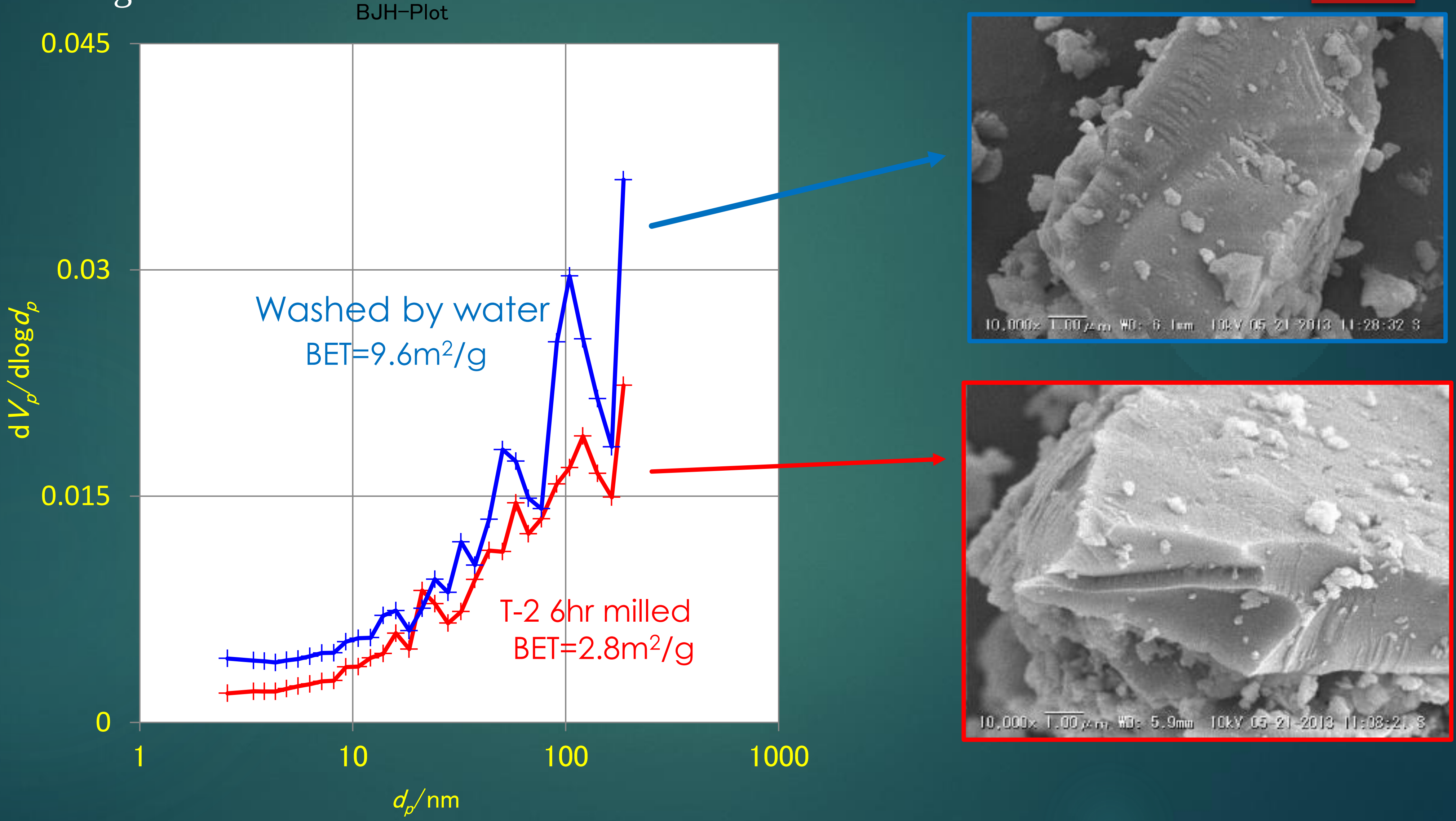


Fig.14　BJH profiles of T-5-6hr milling samples that washed by pure water.

②Decomtanimation of radio active material;^{137}Cs

- Testing solution

Wash out solution from sewage ashes in Fukushima pref.

^{134}Cs: 213±7.5 (Bq/kg)
^{137}Cs: 383±14 (Bq/kg)

Ge detector model GC-3020,canberra

→ Concentrate to around ^{137}Cs:1200Bq/kg

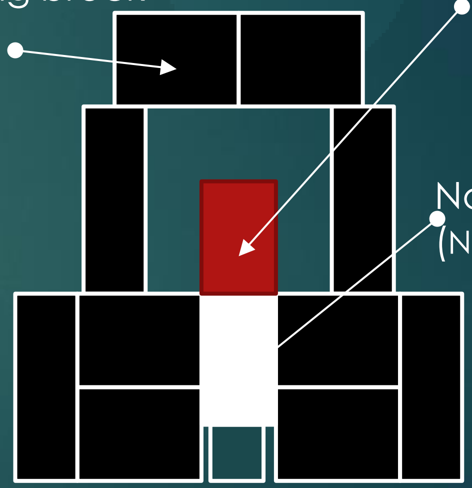


Fig.15 photos and schematic view of radioactive Cs removing test.

Table.3 Test result of removing ^{137}Cs

material	w/s	shaking time(min)	^{137}Cs initial (Bq/kg)	^{137}Cs remain (Bq/Kg)	removing(%)
washed milling Glass powder T-2-6hr&washed	10	10	1262	902	**18.9**
fine Mordenite		10		382.9	69.6
coarse Mordenite	10	10	1262	786	37.7
A-type Zeolite		10		1219	3.3

7. For Dehydration Condensation

① Hardening procedure

6hr milled LCD glass(30g)

← 10N NaOH 30ml

Mixing

Casting

RT one night

↓

Hardened sample

②Morphology

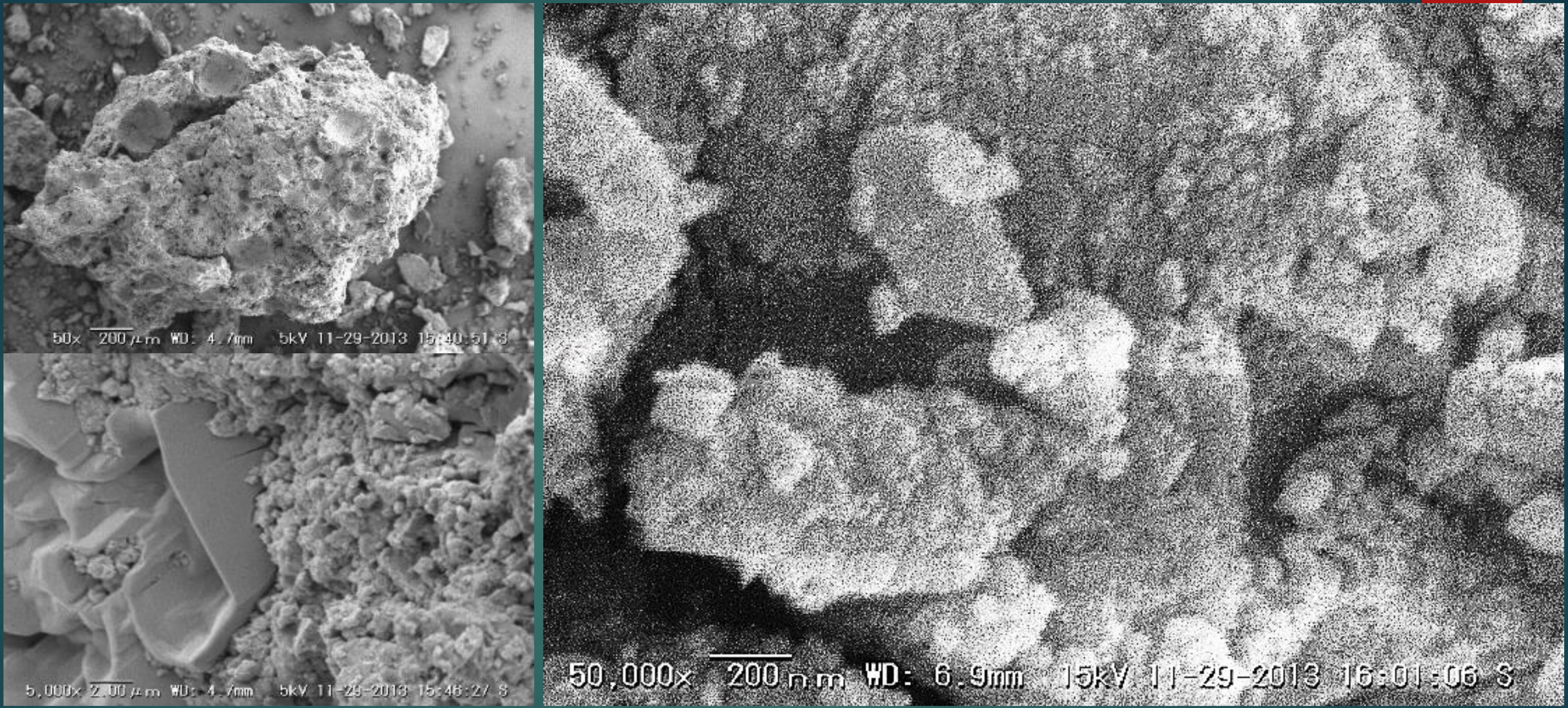


Fig.16 SEM's images of hardens samples

④ Chemical bonding

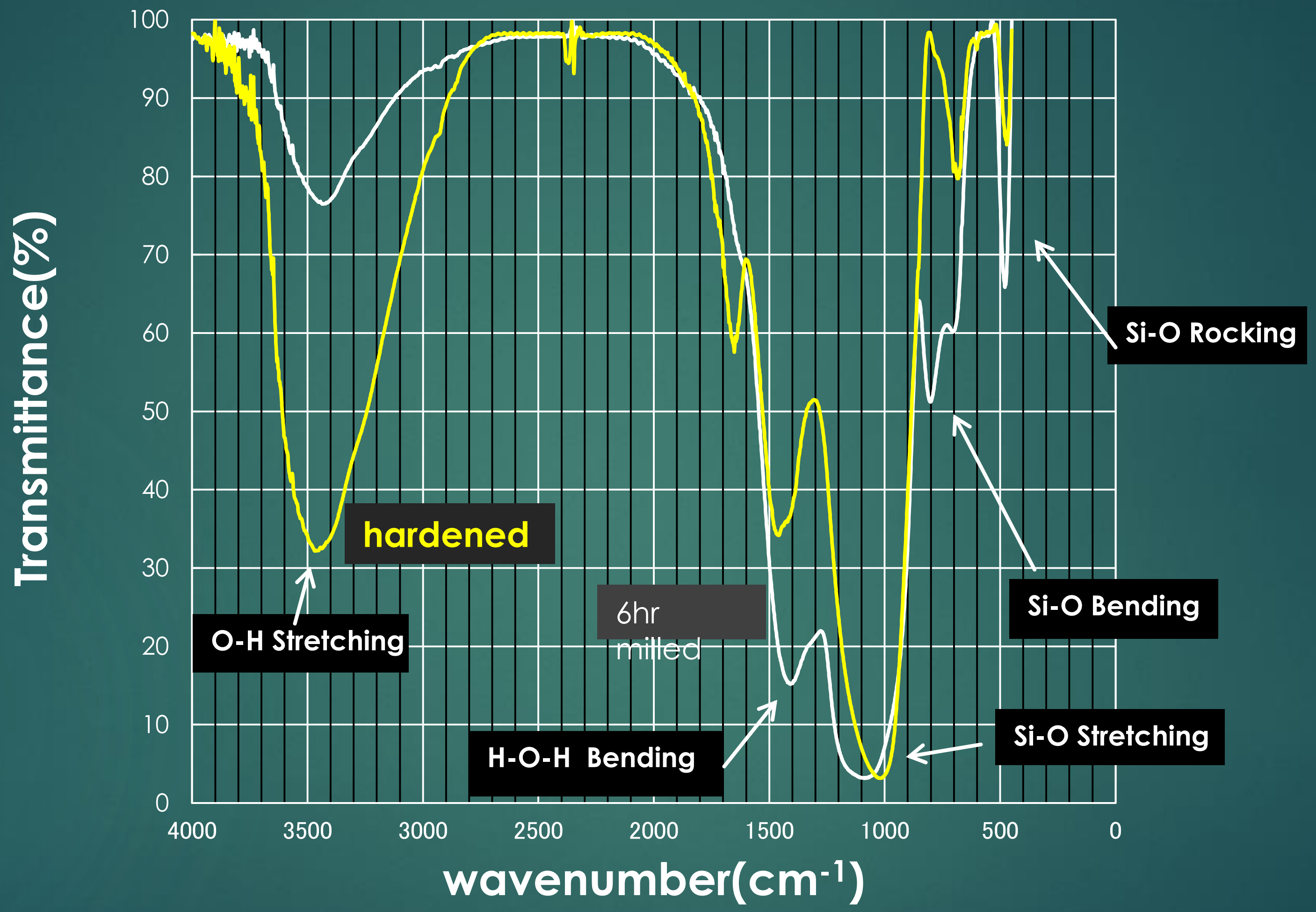


Fig.18 FT-IR spectrums of samples

8. Inline measuring for ball milling

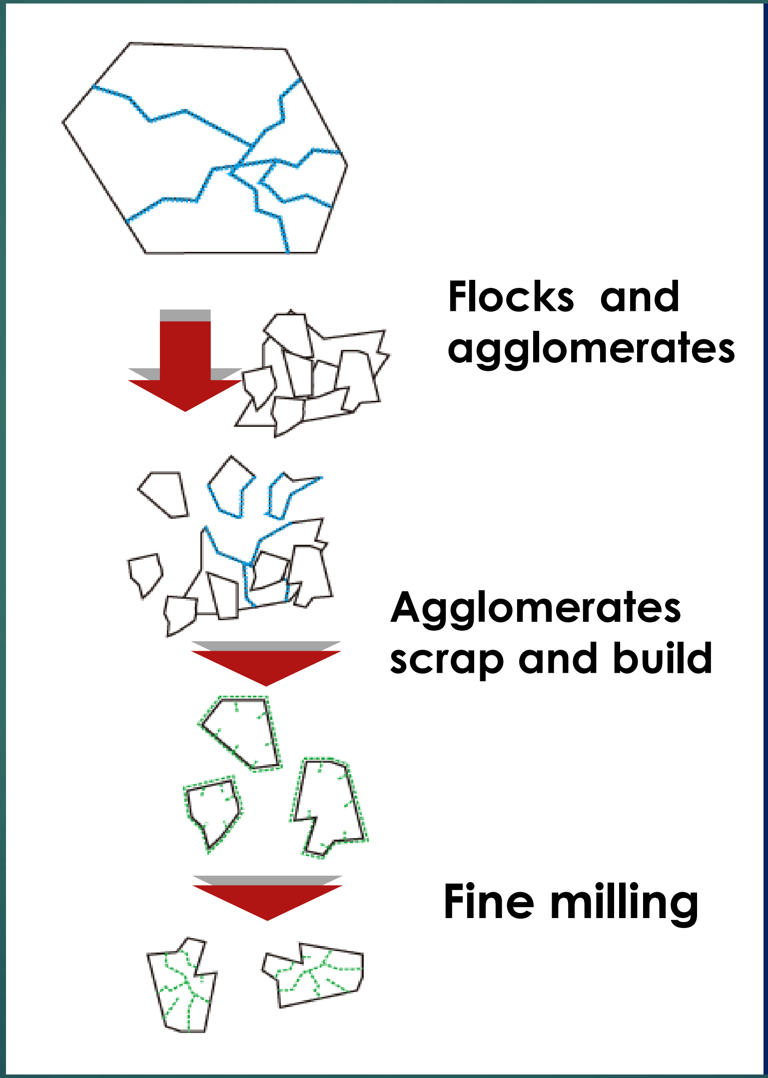
①The model of glass milling from T-⑥

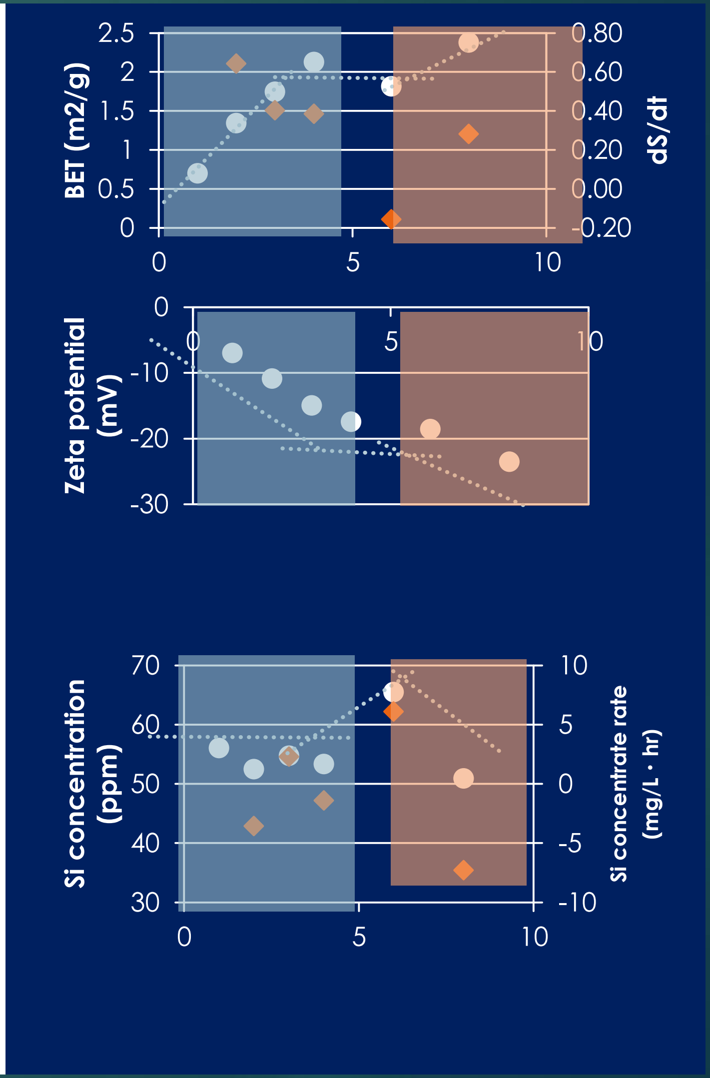
1st St. (Start～4hr)

Particles down sizing and agglomerates formation

2nd St.(4～8hr)

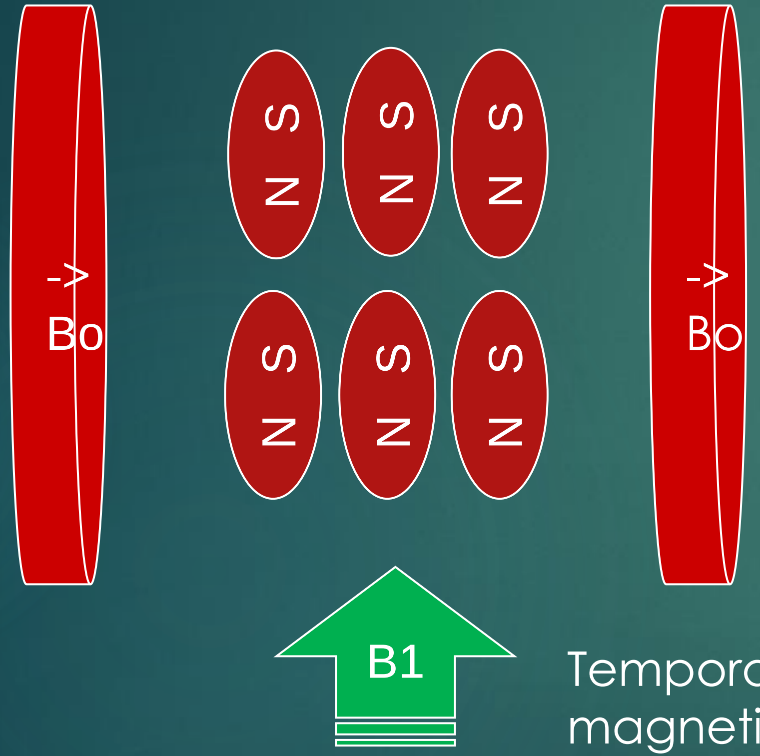
Agglomerates crush and formed





②Specific surface area measurement by NMR

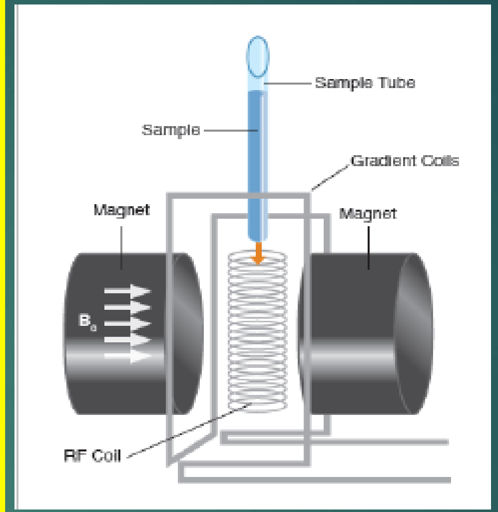
- A short RF Pulse B1 Rotates H atoms

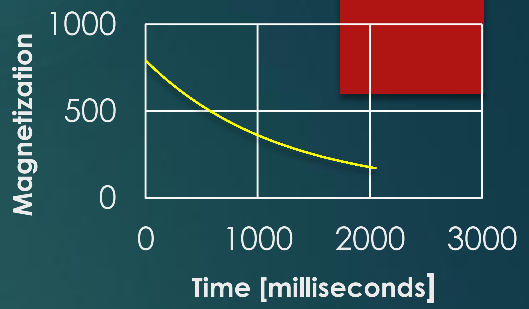


Temporary magnetic field

- When B1 disappears, H atoms realign with Bo producing a signal

Pulse NMR





$$R_{av} = \psi_p S L \rho_p (R_s - Rb) + R_b$$
$$= K_A S \psi_p + R_b$$

R_{av}:reciprocal of sample relaxation time

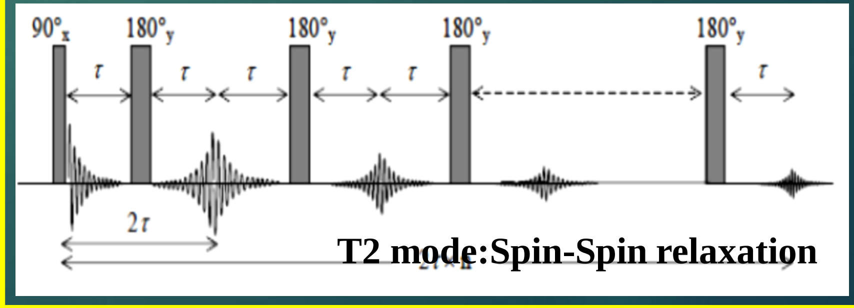
Ψ_p : volume fraction of particles

S : surface area

R_s:reciprocal of adsorption relax.time

R_b:reciprocal of solvent

K_A: coefficient of wettability



$$R_{sp} = \frac{R_{av} - R_b}{R_b}$$

③Comparison with BET and R_{2sp}

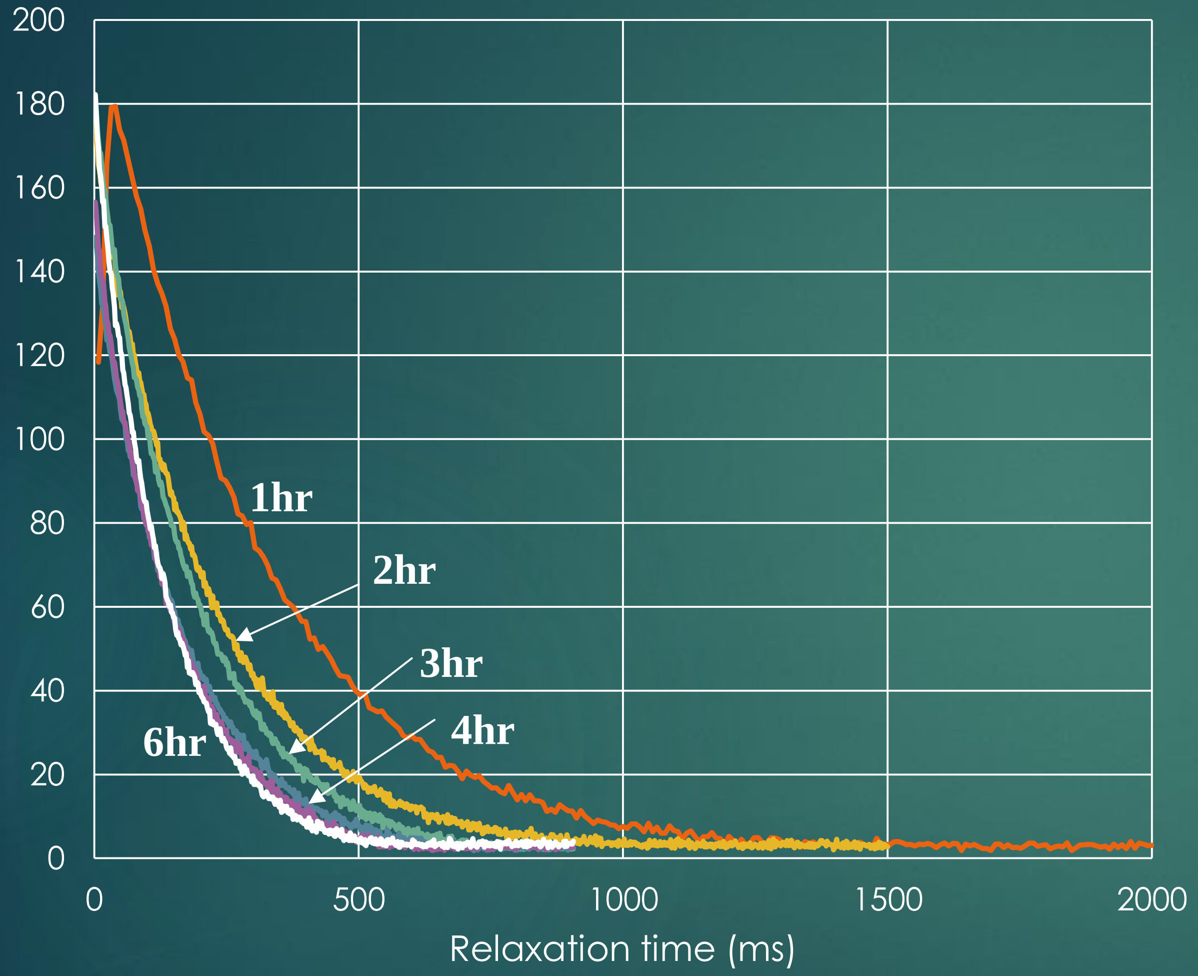
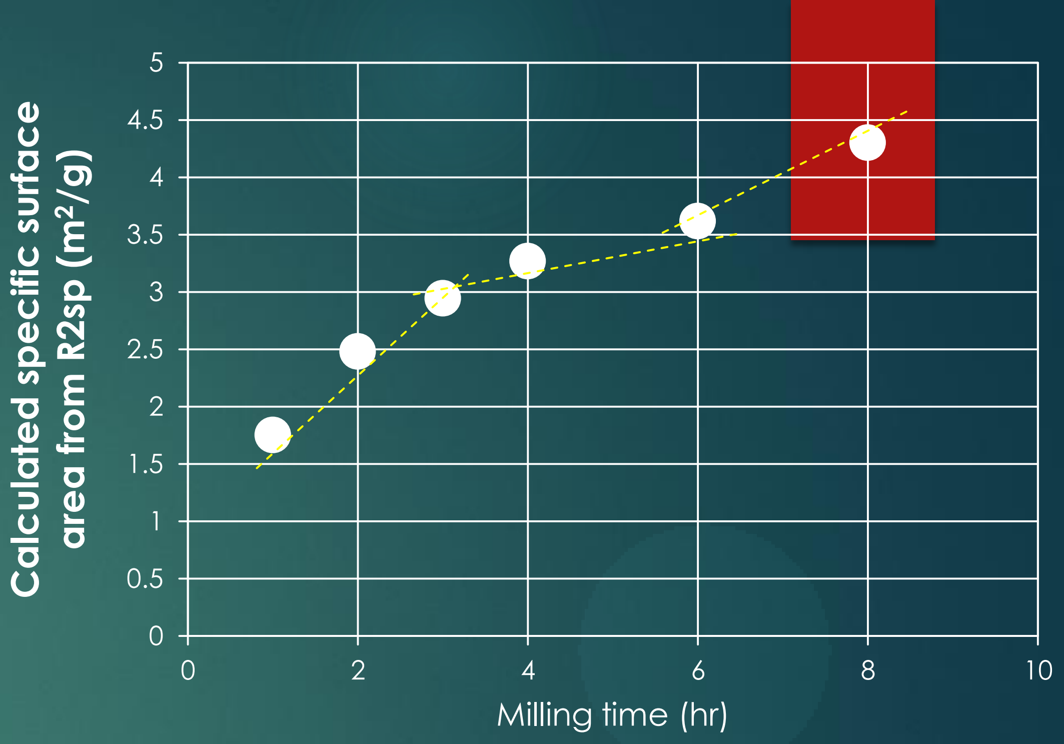


Fig.20 The relaxation time curves on T-⑥



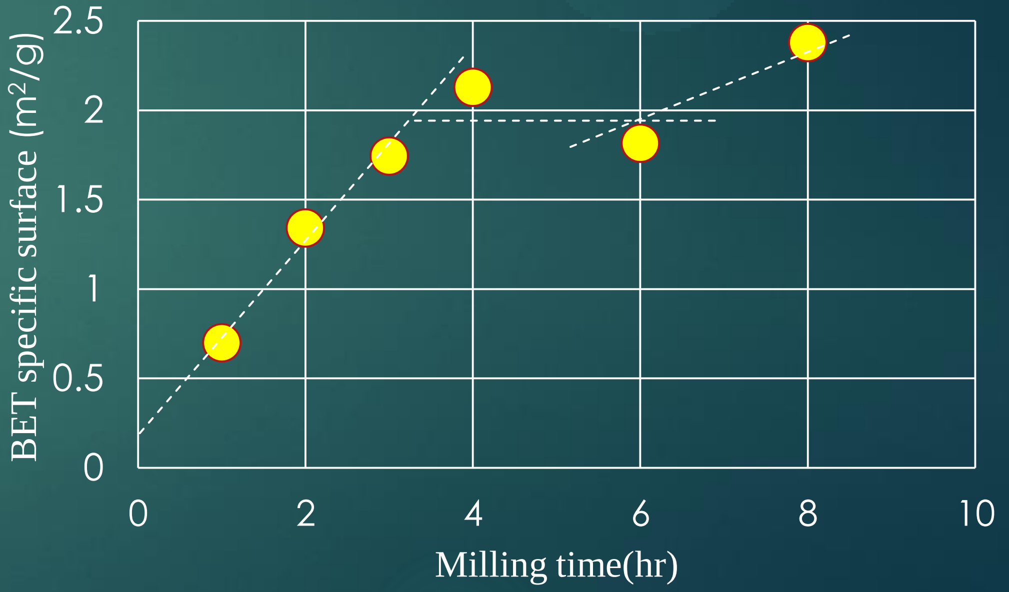


Fig.21 Comparison with cal.surface area and BET

9. Summery of this presentation

1） We've confirmed structural changes of **wasted glass materials** by ball milling.

2） By ball milling , the higher impact energy makes disorder on grain surface or inner structure, We consider they play as dissolving points, and/or to be meso scale cavities on grain surface.
It is very important knowledge for **the chemical recycling technology.**

3) We've recognized these phenomenon induced by **"Mechanochemical effect"**

4） We would develop the operating methods for environmental cleanup with these devices

5) We've already developed the optimized milling systems on inline surface area measuring that mainly consists with P-NMR.