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NH_3 Energy+
549g

Evaluation of the cement clinker fired in the combustion furnace of heavy-oil and NH_3

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Outline

- Business Overview on UBE Industries, LTD
- Background
- Toward Applying NH_3 energy for Cement process
  - ✓ Burning cement clinker in exhaust-gas atmosphere (Ex.1)
  - ✓ Evaluation of clinker fired by NH_3 and heavy-oil (Ex.2)
- Conclusion

Business Overview on UBE Industries, LTD.

UBE INDUSTRIES,LTD.

- FY2017 Consolidated Net Sales: ¥695.5 billion

Chemicals 44% of net sales ¥ 305.4 billion ※	 	• Nylon raw materials and resin • Synthetic rubber • Industrial chemicals • Specialty products • Battery materials • Fine chemicals
Pharmaceuticals 1% of net sales ¥10.2billion	 	• Drug discovery and co-development • Contract manufacturing
Cement & Construction Materials 34% of net sales,¥238.8billion	 	• Cement, ready-mixed concrete • Building materials • Calcia, magnesia
Machinery 13% of net sales ¥90.1 billion	 	• Molding machines (Injection molding machines, die-casting machines) • Industrial machinery • Bridge
Energy & Environment 10% of net sales ¥71.3 billion	 	• Coal storage/sales • IPP/Power business

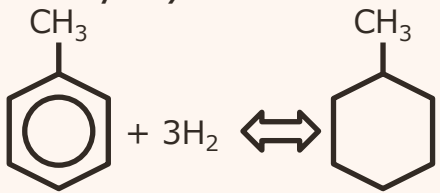
※:Inter-segment internal sales are included (percentages add up to above 100%).

- We have ammonia (NH_3) and cement manufacturing process

【Background】 SIP “Energy Career” (NH_3 energy)

SIP “Energy Career”

Metal Hydride

Liquefied H_2	Ammonia (NH_3)	Methyl *cyclo*-hexane
-253 °C	**Direct combustion**	

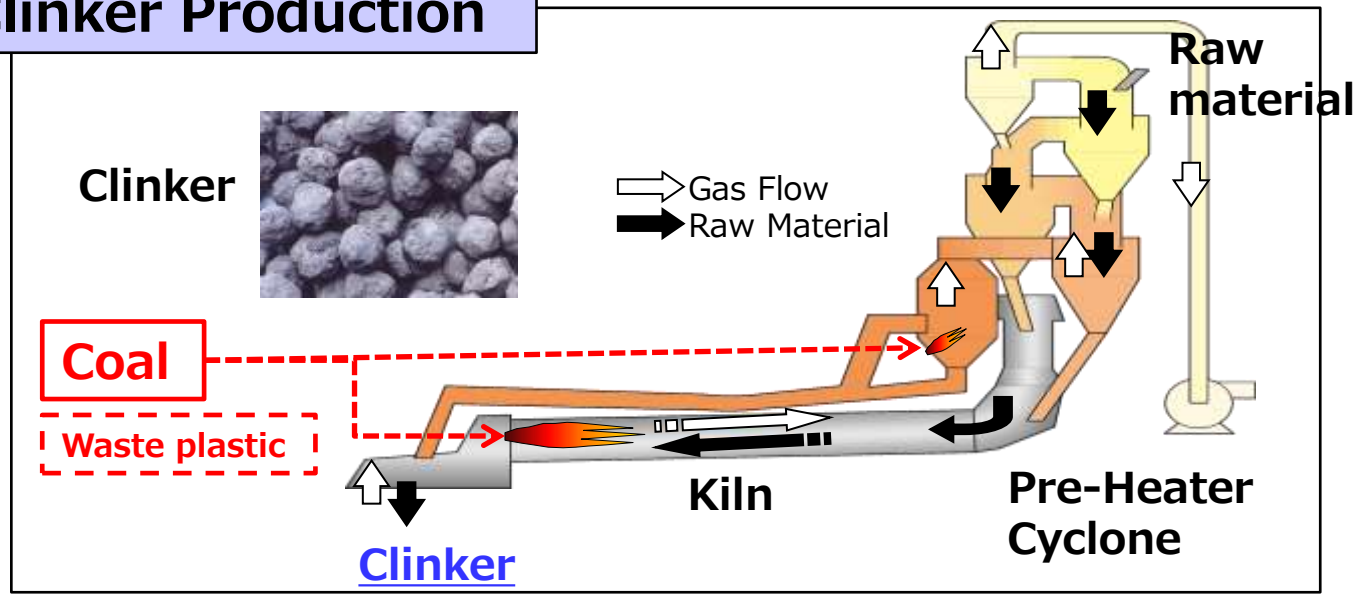
Cross-ministerial Strategic Innovation Promotion Program (SIP) “Energy Career” by Council for Science, Technology and Innovation (CSTI) in Japan

We’ve been participating in SIP “Energy Career” since 2014,
toward applying NH_3 energy for industrial furnace (cement kiln)

1. Burned clinker in electric furnace of exhaust-gas atmosphere
2. Fired NH_3 energy in test furnace
3. Fired clinker by NH_3 energy in test furnace
4. Process simulation and CFD for our commercial plant

【Background】 Cement Manufacturing Process

Clinker Production



- ✓ **Clinker** ; $CaCO_3$, Silica, Clay and Fe Source mixtures burned at 1450 °C
- ✓ **Cement** ; mixture of clinker and $CaSO_4 \cdot 2H_2O$(di-hydrated gypsum)

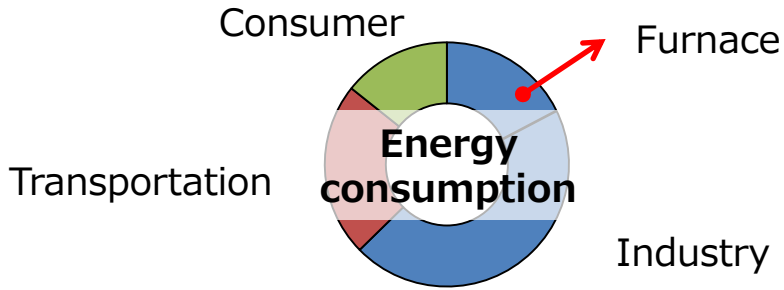
➢ Mixed NH_3 Combustion would be reduce CO_2 Emission

【Background】 Estimation CO_2 reduction in cement

Industrial furnace account for

17% Energy consumption in Japan

Agency for Natural Resources and Energy (2016),
"Japan's Energy White Paper", September



◘ Estimation CO_2 reduction effect

Based on average coal usage in cement process, estimate CO_2 reduction effect by replacing NH_3

※Following values were used for estimation
【Heat value】 Coal : 25.95, NH_3 : 18.8 MJ/kg
【Coal comp.】 C:65, H:4, O:4, N:2, Ash:25 wt%

	Average ('11-'15) (1K ton/year)
Clinker production	50,319
Coal usage	6,680
Total energy consumption	8,967

Cement Handbook, Japan Cement Association (2016)

Replaced NH_3 (cal. %)	NH_3 requirement (1K ton/year)	Coal usage (1K ton/year)	CO_2 emission (1K ton/year)	CO_2 reduction (1K ton/year)
0	0	6680	15,921	0
1	92	6613	15,761	159

➢ Replacing 1% Coal with NH_3 could reduce 160 kton-CO_2/year

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【Experiment】 Materials

Materials for clinker

- Calcium carbonate
- Silica stone powder
- Fly ash (JIS II)
- Reagent
  (Fe_2O_3, Na_2CO_3,
  K_2CO_3, $CaSO_4 \cdot 2H_2O$)

Mixed Water → Poured into mold → Drying → 105 °C, Half a day → □10mm pellets

Clinker modules for mixing ratio of raw materials

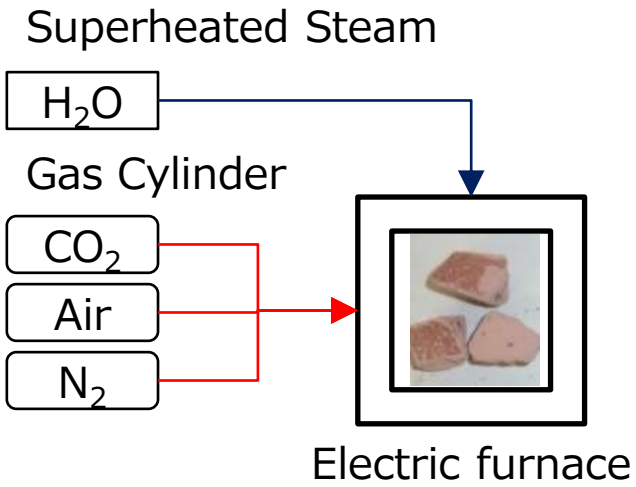
	Ex.1	Ex.2
H.M.	2.10	2.10
S.M.	2.45	2.77
I.M.	1.80	1.57

$$H.M = \frac{CaO - (0.7SO_3)}{SiO_2 + Al_2O_3 + Fe_2O_3}$$

$$S.M. = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \qquad I.M. = \frac{Al_2O_3}{Fe_2O_3}$$

【Experiment 1】 Burning clinker in electric furnace

Procedure



Combustion Conditions	Gas Conditions (Vol.%)			
	CO_2	H_2O	N_2	O_2
Coal	16.4	6.3	73.4	3.9
30%NH_3 Mixed	10.7	14.6	71.1	3.6

Calcination → 1000 °C, 30 min

Heating Up → 25 °C/min Until 1350, 1450 or 1550 °C

Retention and Quench → 0, 10 or 30 min

Analysis

Minerals (XRD/Rietveld), **free-CaO** (JCAS-01(1997))

Calculation of reaction rate (Jander equation)

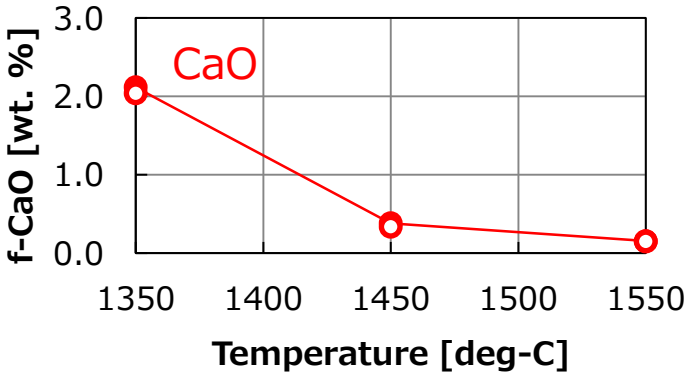
$$(1-\sqrt[3]{1-\alpha})^2 = A\exp\left(\frac{-E}{RT}\right)t$$

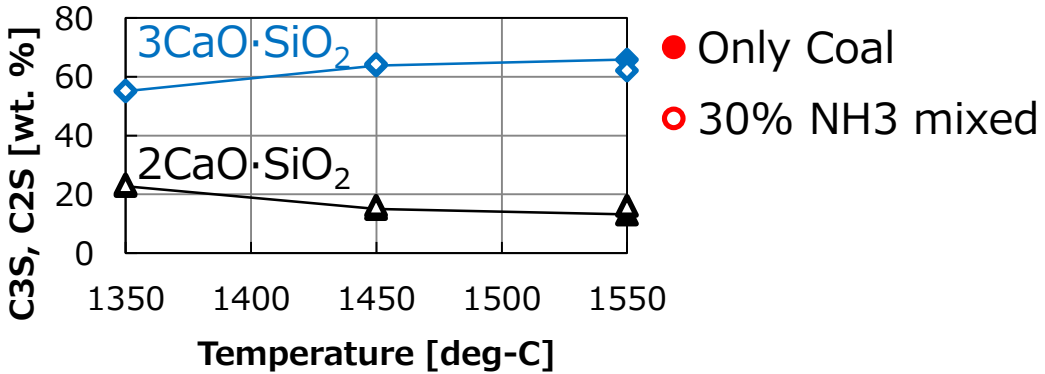
W. Jander, *Z Anorg Allg. Chem*., 163, 1 (1927)

Defined E=29.92 kJ/mol Calculated A

[Nomenclature] α: Free-CaO reaction rate (-), A: Frequency factor (1/min), T: Temperature (K), E: Activation energy (J/mol), R: Gas constant (8.314 J/(mol K)), t: Retention time (min)

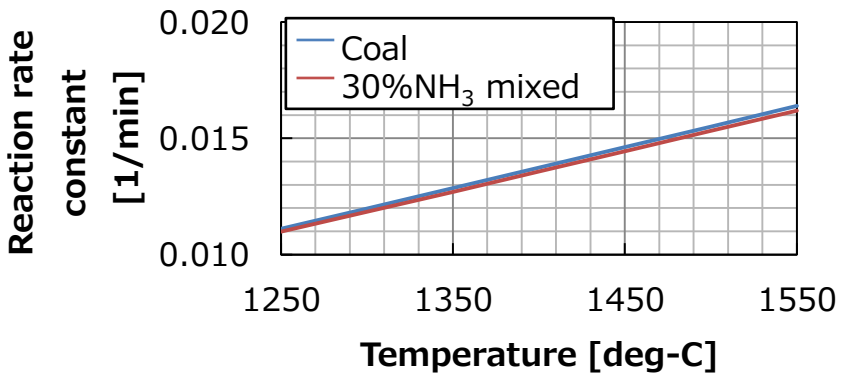
【Results】 Minerals and reaction rate in clinker





Sample picture (retention time: 10min)

	Before	1350 °C	1450 °C	1550 °C
Only Coal				
30% NH_3 mixed				



➢ Clinker minerals, reaction rate didn’t depend on the gas conditions.

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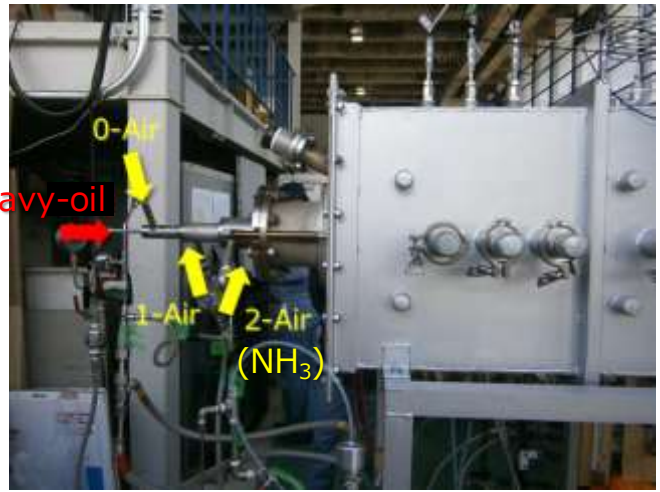
【Experiment 2】 NH_3 heavy-oil co-fired clinker

☐ Procedure

10 kW Test Furnace Inner Size (mm) : L.1500×W.300×H.300



Test furnace

Preheating → Until 600 °C, City gas

Heating Up → Until 1000 °C, Heavy-oil

Until 1400 °C, Heavy-oil or Mixed 30%NH_3

Retention → 30 min

Quench → Until <500 °C, air

Take out (Next day)

【Experiment 2】 Chemical analysis, physical testing

☐ Chemical analysis

Minerals (XRD/Rietveld)
free-CaO (JCAS-01(1997), Ethylene glycol dissolution method)

☐ Physical testing (JIS R 5201)

◆ Cement clinker
◆ $CaSO_4 \cdot 2H_2O$

Mixed → Milling → Cement

Test Piece Size (mm) : L.160×W.40×D.40

◆ Cement
◆ Sand
◆ Water

Kneading (Test Time) → Casting (20 °C, RH>50% in room) → Demolding → Curing (20 °C in water-bath) → Measure

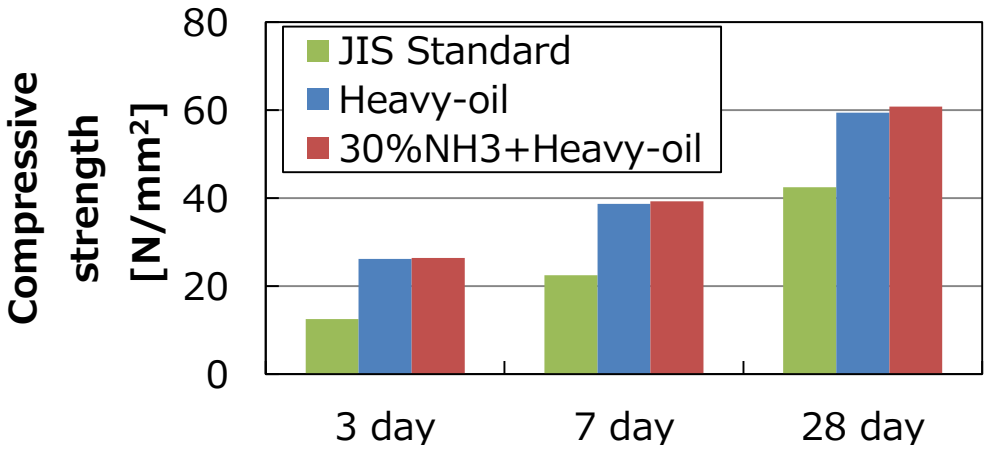
24 hour

Measured age : 3 day, 7 day or 28 day

【Results】 Clinker Minerals and Cement Strength

Firing conditions	Clinker minerals (wt.%)				
	f-CaO	C3S	C2S	C3A	C4AF
Heavy-oil	0.19	49.4	30.5	8.2	9.5
30%NH_3+Heavy-oil	0.18	50.2	29.9	8.3	9.5

C3S : $3CaO \cdot SiO_2$
C2S : $2CaO \cdot SiO_2$
C3A : $3CaO \cdot Al_2O_3$
C4AF : $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$



- f-CaO less than 0.2 wt. %, same clinker minerals
- No influence of conditions on compressive strength, satisfying JIS

Conclusion

- We’ ve done 2 basic experiment toward applying NH_3 energy for cement process
- The main findings of this work are as follows.
  - ✓ The reaction rate of clinker didn’t depend on the gas conditions (exhaust-gas atmosphere).
  - ✓ There was no difference in minerals of clinker and compressive strength of cement on the firing conditions (only heavy-oil or mixed NH_3).

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革新の心
Wings of technology
Spirit of innovation
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