

Behavior of Trace Metals in Coal Gasification with High Pressure Steam

On-Line Number 1096

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ABSTRACT

We have developed a new hydrogen production process "HyPr-RING" where high pressure steam thermochemically decomposes organic materials such as coal with a calcium-based CO₂ sorbent. In this study, the comparison of behavior of trace elements between in a batch and in a continuous reactor was studied. In the experiment with a small batch reactor, a mixture of pulverized Taiheiyo-coal and water with Ca(OH)₂ was charged into a micro reactor. The reactor was put into a fluidized sand bath and rapidly heated to a subcritical condition. In the experiment with a continuous reactor, Taiheiyo-coal was charged into the fixed bed reactor. After the pressure in the reactor system was increased, the reactor was heated to a high temperature by using an electric furnace, and high temperature steam was continuously injected into the reactor below. In both experiments, the residual solid and liquid collected were analyzed with ICP-AES. Consequently, in the batch experiment conversions of most of metals into liquid were increased with reaction temperature, while in the continuous experiment they were hardly increased with temperature. In both experiments, conversions of most of metals into liquid occurred during pyrolysis and gasification in the initial stage. As the result obtained at 973 K, 19.8 MPa and 10 minutes in the batch experiment, Al, Fe and Mo were almost in the solid, while Mg, Ti, Cu, Zn and Pb were recovered in the liquid. However, it seems that Cu, Zn and Pb were partially in gas phase during reaction because they are easier to be volatilized. As the result obtained at 973 K, 6.0 MPa and 160 minutes in the continuous experiment, most of metals were only in the solid, while Zn was detected in the liquid. These experimental results almost corresponded with results of thermodynamic equilibrium calculation.

KEYWORDS

trace metals, coal gasification, high pressure steam, hydrogen production

INTRODUCTION

From the viewpoint of depletion of fossil fuel resources and global environmental issues, clean utilization of unused carbonaceous resources such as biomass and organic wastes as well as low-rank coal should be promoted. In the energy production from the organic resources, it should be required to minimize CO₂ emissions. On the other hand, to establish a new social system with clean and efficient energy system as hydrogen-based fuel cell, stable supply of hydrogen will be an important problem. Steam gasification of fossil fuel, biomass or organic wastes is one of the key technologies for hydrogen production. However, in conventional steam gasification, a synthesis gas including H₂, CO and CO₂ is produced (e.g. Schmieider *et al.*, 2000).

The HyPr-RING (hydrogen production by reaction integrated novel gasification) method, which gasifies organic matter with high temperature and high pressure steam under the presence of calcium-based CO₂ sorbent, has been proposed (Lin *et al.*, 1999, 2001, 2002). It starts being developed with a continuous bench-scale unit with a fluidized bed reactor. Figure 1 shows the concept of HyPr-RING method. H₂ and CaCO₃ are mainly obtained as final products. CaCO₃ can be regenerated to CaO by calcination. CO₂ in high concentration can be collected. According to the thermodynamic analysis, the high-pressure conditions will be required to achieve the organic matter gasification with steam and the efficient sorption of CO₂ by Ca(OH)₂ simultaneously in a reactor.

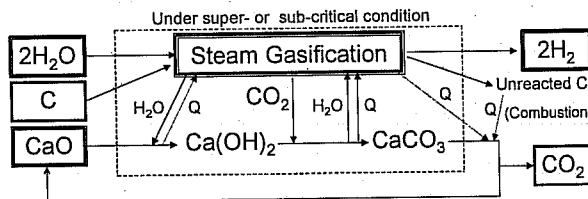


Figure 1. Concept of HyPr-RING method.

In our previous work (Kumabe *et al.*, 2003), we experimentally examined the characteristic of the initial conversions of organic matters such as coal and the composition of gaseous products during the gasification with steam in the presence of Ca(OH)₂ under the temperature of 973 K and the relatively high pressure of 20 MPa (subcritical condition) using a tubing-bomb (TB) reactor. In applying the HyPr-RING process to various organic resources, it should be important to understand the behavior of trace elements.

Here, the results of thermodynamic equilibrium calculation of trace metal for both conditions of conventional steam gasification and HyPr-RING obtained by using the commercial soft (HSC Chemistry 5) are shown in Figure 2. In both conditions, Al, Fe, Mg, Ti, Mo and Sn are in the solid phase. Most of these metals exist as oxides. These are non-volatile metals. In the condition of conventional steam gasification, Cu is changed from the solid phase to liquid and gas phases, and Zn and Pb are mainly in the gas phase. For example, Pb exists as Pb (g), Pb (l), PbO (l), Pb (s) and PbO (s). On the other hand, in HyPr-RING condition, nothing is in the gas phase, and even Cu and Zn are almost in the solid phase because HyPr-RING condition is lower temperature and higher pressure than those of conventional steam gasification. The higher temperature promotes volatile metals to the liquid or gas phase. The higher pressure promotes it to solid phase. The existence of high pressure steam hardly influences the behavior of metals because the behaviors of metals in the condition of HyPr-RING are hardly changed between with water (i.e. steam gasification) and without water (i.e. pyrolysis). Thus, the HyPr-RING process is also expected to reduce the trace elements to shift gas product.

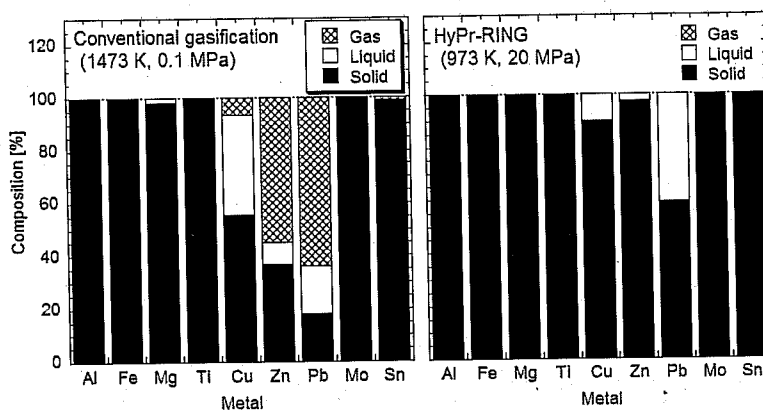


Figure 2. Results of equilibrium calculation of trace metal phase for conditions of conventional steam gasification and HyPr-RING.

1. EXPERIMENTAL

In the present study, first, the behavior of trace elements, when pulverized raw Taiheiy-coal (Japanese subbituminous coal) with or without Ca(OH)₂ was gasified with subcritical steam by using a batch reactor, was experimentally examined. However, in the batch experiment, the behavior of trace elements during real reaction cannot be investigated, because the experiment is discontinuous and

residual solid and liquid are recovered as a sample after cooling completely. Therefore, the behavior of trace elements was also investigated by using a continuous reactor, and was compared between in the batch and in the continuous experiment. Then, it was also compared between the experimental results and the thermodynamic equilibrium calculation results shown in Figure 2.

1.1 Experimental apparatus

Figure 3 shows experimental apparatuses used in the present study.

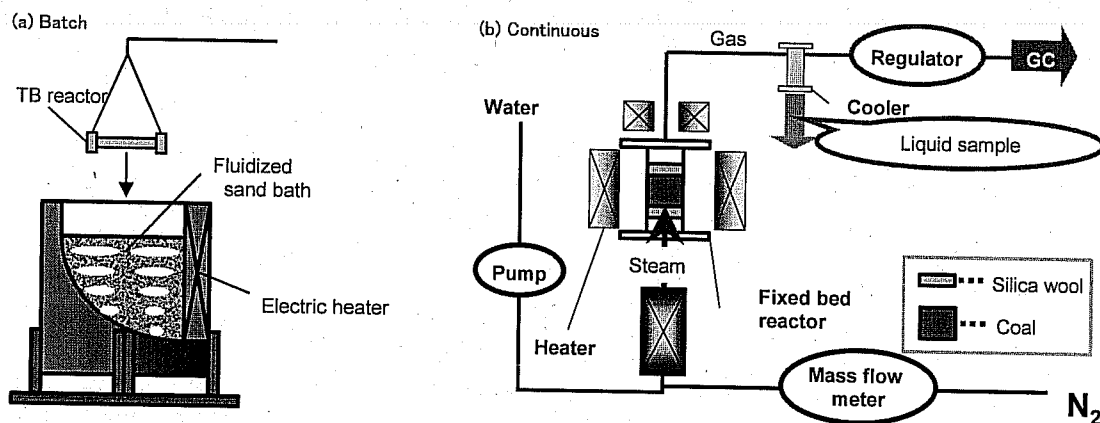


Figure 3. Batch and continuous experimental apparatuses used in the present study.

For the batch experiment, a TB reactor was used to investigate steam gasification of organic matters with $\text{Ca}(\text{OH})_2$ under high pressure with relatively rapid heating rates. The TB reactor was a seamless tube made of stainless steel (SUS-316), which had a length of 100 mm with an outer diameter of 1/2 inch, and sealed at both ends with SUS-316 caps. The reactor had a volume of 7.2 cm^3 . It was externally heated to a given temperature with a fluidized sand-bath heater, which had an inner diameter of 400 mm, a bed height of 450 mm, and a bed material of silica sand.

For the continuous experiment, a fixed bed reactor was used to investigate steam gasification of coal under high pressure. A fixed bed consisted of coal and silica wool. The reactor was made of SUS-316, which had a length of 200 mm with an inner diameter of 8.3 mm. Nitrogen gas was quantitatively fed to the reactor below under the control by using a mass flow meter (Brooks 5896C, USA). Water fed by using a pump (Nihon-seimitsu-kagaku NP-KX-100, Japan) was heated to be steam by using a ribbon heater set under the reactor, and was quantitatively fed to the reactor heated by using an electric furnace. A mantle heater (Taika-denki CCL, Japan) set on top of the reactor was used to reduce the reflux of liquid by cooling steam and gaseous products. Liquid sample was collected at a cooler set behind the mantle heater. Product gas was led to TCD-GCs (Aera M200, USA) after passing through a regulator, simultaneously controlling the pressure in the reactor system. A reaction temperature was defined as the temperature of fixed bed.

1.2 Experimental procedure

1.2.1 Batch experiment

A mixture of raw Taiheiyo-coal (0.1 g) and distilled water (0.35 cm^3) together with reagent grade $\text{Ca}(\text{OH})_2$ (0.58 g) was loaded with nitrogen in the TB reactor. The molar ratio of H_2O to C was about 3.53, and the molar ratio of Ca to C was about 1.43. The TB reactor was soaked in the fluidized sand bath and was heated to the subcritical condition (873 to 973 K and 17 to 20 MPa). As confirmed in our

previous work (Kuramoto *et al.*, 2003), using a similar TB reactor with a relatively lower heat capacity than that of the conventional autoclaves, it gives much more rapid heating. The average heating rate is approximately 330 K/min. It takes about 2 minutes to reach a desired temperature under the present experimental conditions. It is also confirmed with comparing between real observation of temperature and pressure and calculation that the target temperature and pressure in the reactor for gasification could be practically determined by the sand bath temperature and amount of water.

After a desired soaking time (1 to 10 minutes), the reactor was rapidly pulled up from the sand bath, and it was rapidly cooled to room temperature with water to quench the reaction. Then, after filtering solid residue in the reactor, the residual solid on the filter paper and the filtrate collected were analyzed with an ICP-AES (JEOL PS-1000UV, Japan). According to the analysis, the distribution of Al, Fe, Mg, Ti, Cu, Zn, Pb, Mo and Sn to solid and liquid was estimated.

1.2.2 Continuous experiment

Raw Taiheiyo-coal (0.5 g) was charged into the fixed bed reactor. After the pressure in the reactor system was increased to 6.0 MPa by nitrogen gas (50 mL/min), the bottom of the reactor was heated to 723 K by using the ribbon heater. The reactor was heated to 873 to 1073 K by using the electric furnace, and the top of the reactor was heated to 673 K by the mantle heater. Then, steam (0.25 mL/min) of 5.2 MPa was continuously fed into the reactor below. Product gas was continuously removed from the reactor system for the analysis of the concentrations of H₂, O₂, N₂, CH₄, CO, C₂H₄ and C₂H₆ in product gas by using the TCD-GCs. The liquid sampled from the cooler every 20 minutes and the residual solid in the fixed bed after the reaction for 160 minutes were analyzed with the ICP-AES. According to the analysis, the distribution of Al, Fe, Ca, Mg, Ti, Zn, Mo and Ni to solid and liquid was estimated.

1.3 Samples

Properties of pulverized raw Taiheiyo-coal (Japanese subbituminous coal) used in the batch and in the continuous experiment are shown in Table 1.

Table 1. Properties of pulverized raw Taiheiyo-coal used in the present study.

(a) used in the batch experiment

Particle size: 25-73 μm		Ash composition [wt%]	
Proximate analysis [wt%, dry basis]		Al ₂ O ₃	14.7
		Fe ₂ O ₃	4.1
Moisture	5.1	CaO	15.3
Ash	7.9	MgO	2.8
Volatile matter	51.3	TiO ₂	2.4
Fixed carbon	40.8	Cu	0.010
Ultimate analysis [wt%, dry ash-free basis]		Zn	0.002
		Pb	0.031
C	71.5	Mo	0.010
H	6.1	Sn	0.002
N	1.1	Ni	ND

(b) used in the continuous experiment

Particle size: 250-1000 μm		Ash composition [wt%]	
Proximate analysis [wt%, dry basis]		Al ₂ O ₃	17.8
		Fe ₂ O ₃	13.9
Moisture	5.3	CaO	9.4
Ash	8.2	MgO	3.0
Volatile matter	51.1	TiO ₂	1.0
Fixed carbon	40.7	Cu	ND
Ultimate analysis [wt%, dry ash-free basis]		Zn	0.013
		Pb	ND
C	71.6	Mo	0.021
H	6.1	Sn	ND
N	1.1	Ni	0.053

The reagent grade Ca(OH)₂ (Nacalai tesque, Japan) was used as the CO₂ sorbent.

2. RESULTS AND DISCUSSION

2.1 Change of each metal balance with temperature

2.1.1 Batch experiment

According to the analysis with ICP-AES, the distributions of Al, Fe, Mg, Ti, Cu, Zn, Pb, Mo and Sn to solid and liquid for the temperatures of 873, 923 and 973 K at the soaking time of 10 minutes are plotted in Figure 4.

Al, Fe and Mo were almost in the solid at each temperature, while conversions of Mg, Ti, Cu, Zn and Pb into the liquid were increased with

reaction temperature. However, it seems that Cu, Zn and Pb were in the gas phase during reaction because they are easier to be volatilized. Sn was not detected in the liquid, while Sn in the solid was decreased with temperature. Thus, some of Sn might be converted into the liquid. The behavior of most of metals was similar to the result of thermodynamic equilibrium calculation shown in Figure 2, but that of Mg and Ti was not similar. This suggests that Mg and Ti in the liquid shown in Figure 4 were not liquid phase in the reaction temperature but soluble in water after cooling. Thus, the approximate behavior of trace elements may be estimated by only thermodynamic equilibrium calculation.

The excess of the Fe yields up to 100 % seems to be caused by the elution of Fe contained in the material of reactor (SUS-316). The failure of the yields of metals except Fe seems to be due to the error values for the measurements and/or the yields in the gas not measured. In addition, the distribution of Ca contained in ash in raw Taiheiy-coal could not be estimated because raw Taiheiy-coal was gasified with steam under the presence of $\text{Ca}(\text{OH})_2$ in the batch experiment.

2.1.2 Continuous experiment

According to the analysis with ICP-AES, the distributions of Al, Fe, Ca, Mg, Ti, Zn, Mo and Ni to solid and liquid for the temperatures of 873, 973 and 1073 K at the reaction time of 160 minutes are plotted in Figure 5.

Most of metals in the continuous experiment were only in the solid at each temperature as compared to the distributions of metals in the batch experiment. The behavior of metals in the continuous experiment seems not to depend on reaction temperature. Zn in the liquid shown in Figure 5 seems to be in the gas phase during reaction, as the batch

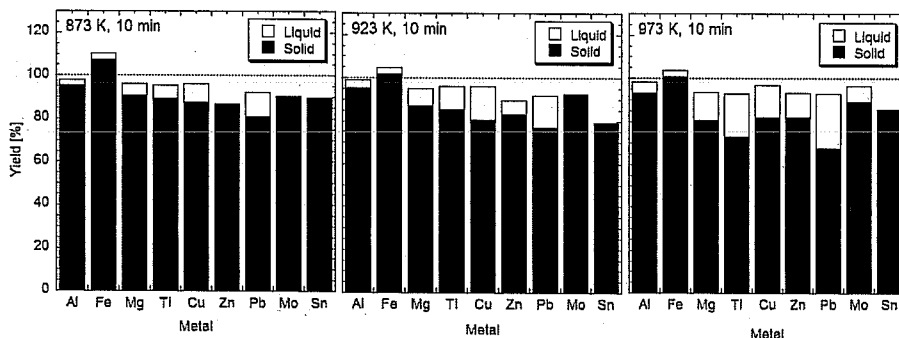


Figure 4. Change of each metal balance with temperature in the batch experiment.

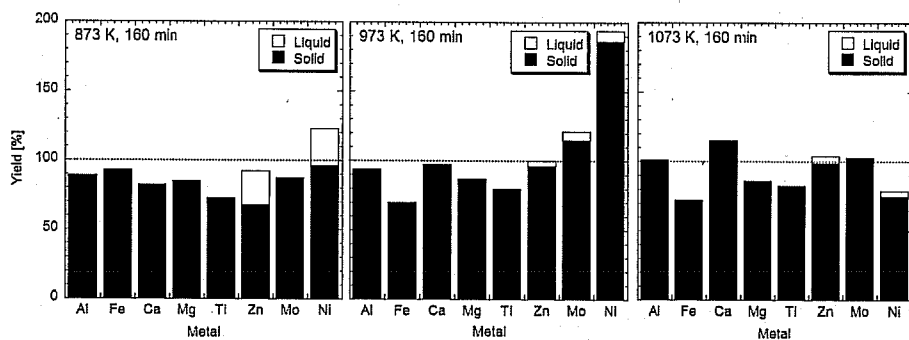


Figure 5. Change of each metal balance with temperature in the continuous experiment.

experiment. Mg and Ti were not detected in the liquid. Because there was unrecovered Mg and Ti, some of them might be converted into the liquid in the continuous experiment. The behavior of most of metals in the continuous experiment as well as in the batch experiment was similar to the result of thermodynamic equilibrium calculation.

The excess of the Ni yield up to 100 % seems to be caused by the elution of Ni contained in the material of reactor and the commingling of Ni contained in the baking inhibiting oil coated at the junction with reactor.

2.2 Change of conversions of each metal into liquid with time

2.2.1 Batch experiment

The change of conversions of Mg, Ti, Cu, Zn and Pb into the liquid for the temperature of 973 K with soaking time is plotted in Figure 6(a). In addition, the product gas distribution in condition of our previous work (Kumabe *et al.*, 2003) is shown in Figure 6(b).

As confirmed in our previous work (Kumabe *et al.*, 2003), in the initial stage within 5 minutes, H₂ and CH₄ were mainly produced because pyrolysis was more dominant than gasification with steam.

After the initial stage, H₂ was produced more than CH₄ because gasification with steam was dominant. On the other hand, in the initial stage within 5 minutes conversions of each metal into the liquid were increased with soaking time, while after the initial stage they were hardly increased. Thus, it is suggested that conversions of most of metals into the liquid occurred during pyrolysis and/or gasification in the initial stage.

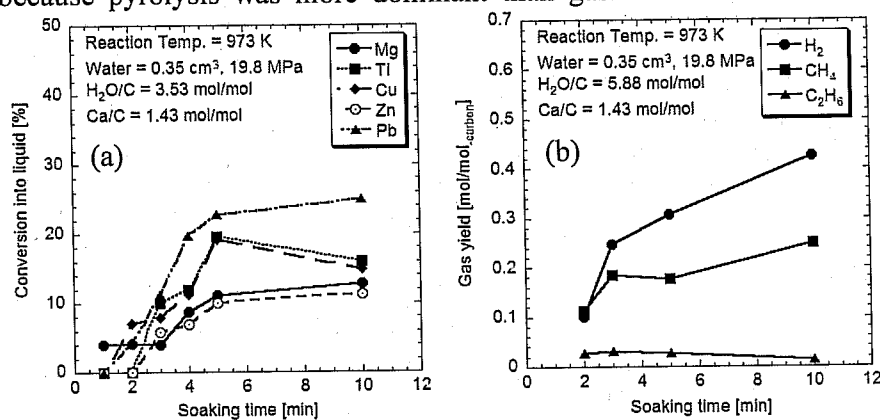


Figure 6. Changes of conversion of each metal into liquid and product gas distribution with soaking time.

2.2.2 Continuous experiment

The change of transient conversion of Zn into the liquid for the temperature of 973 K with time is plotted in Figure 7(a). In addition, the change of transient product gas simultaneously analyzed with time is also plotted in Figure 7(b).

In continuous experiment, in the initial stage within 30 minutes, CH₄, H₂ and CO₂ were mainly produced because pyrolysis was more dominant than gasification with steam. CO₂ production was caused by no addition of Ca(OH)₂. After the initial stage, about twice H₂ as production as CO₂ was mainly produced because gasification

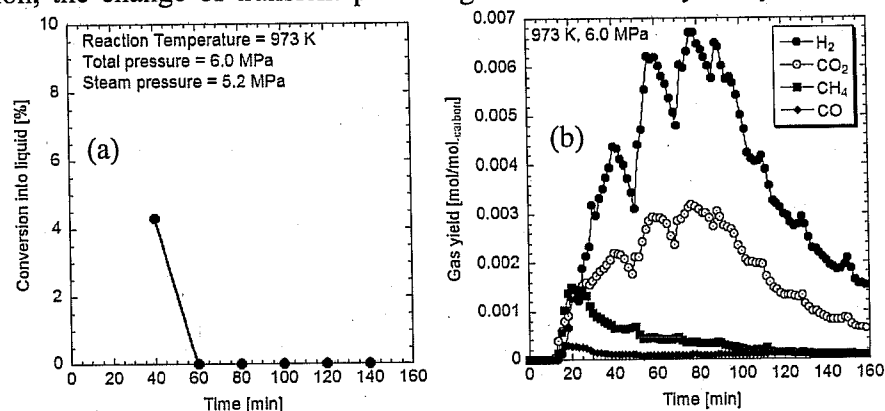


Figure 7. Changes of transient conversion of Zn into liquid and transient product gas with soaking time.

with steam due to Equation (1) was dominant.



It is because some of product gases were sampled from the cooler every 20 minutes that the yields of product gases in Figure 7(b) were rapidly decreased. On the other hand, conversion of Zn into the liquid was completed in the initial stage within 60 minutes. Thus, it is suggested both in the batch and in the continuous experiments that conversions of most of volatile metals such as Zn into the liquid occurred during pyrolysis and/or gasification in the initial stage.

2.3 Effect of Ca(OH)₂ addition on each metal balance

2.3.1 Batch experiment

The distributions of Al, Fe, Mg, Ti, Cu, Zn, Pb, Mo and Sn to solid and liquid for the temperature of 973 K at the soaking time of 10 minutes without and with Ca(OH)₂ are plotted in Figure 8.

There seems not to be so much difference of the behavior of distributions between without and with Ca(OH)₂.

2.3.2 Continuous experiment

The distributions of Al, Fe, Mg, Ti, Zn, and Mo to solid and liquid for the temperature of 873 K at the soaking time of 160 minutes without and with Ca(OH)₂ addition are plotted in Figure 9.

In both cases without and with Ca(OH)₂, most of metals were only in the solid. On the other hand, in the case without Ca(OH)₂ Zn was detected in the liquid, while in the case with Ca(OH)₂ Zn was not detected in the liquid. The thermodynamic equilibrium calculation showed that most of Zn exists as ZnO (s). This suggests that Zn was physically adsorbed by Ca of the solid. In the case with Ca(OH)₂, Mo was detected in the liquid. The thermodynamic equilibrium calculation showed that most of Mo exists as CaMoO₄ (s). This suggests that Mo in the liquid was soluble in water sampled from the cooler.

In the case with Ca(OH)₂, the excess of the Mg and Zn yields up to 100 % seems to be a trace of Mg and Zn contained in the reagent grade Ca(OH)₂.

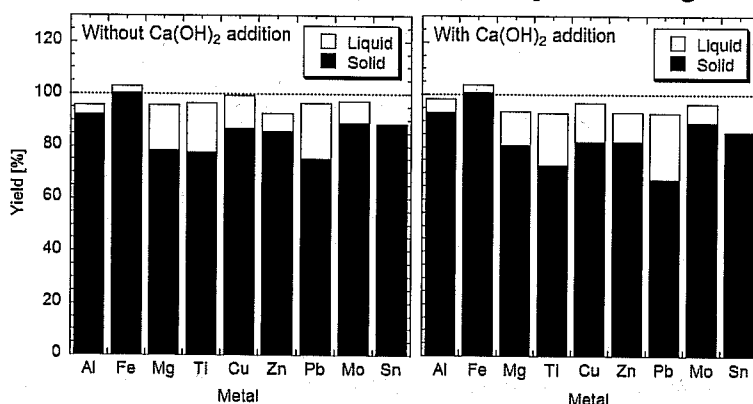


Figure 8. Each metal balance in both cases without and with Ca(OH)₂ in the batch experiment.

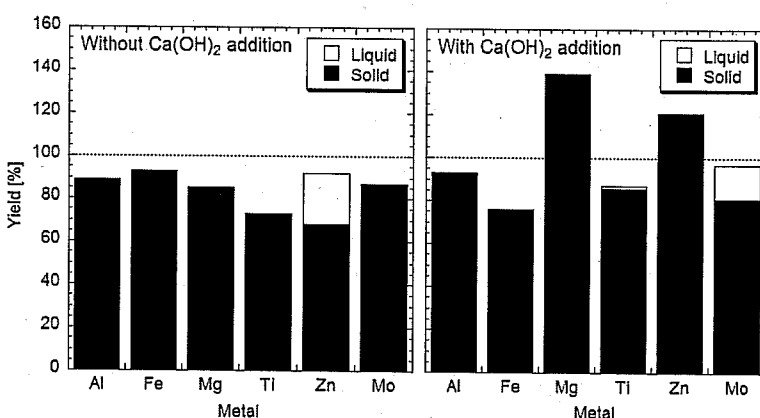


Figure 9. Each metal balance in both cases without and with Ca(OH)₂ in the continuous experiment.

CONCLUSIONS

In order to investigate the behavior of trace elements in the initial stage of pyrolysis and the second stage of char gasification for the HyPr-RING process, pulverized raw Taiheiyo-coal with or without Ca(OH)_2 was gasified with steam under high pressure conditions using both a batch and a continuous reactor. Consequently, conclusions can be derived as follows:

(1) In the batch experiment, conversions of Mg, Ti, Cu, Zn and Pb into the liquid were increased with reaction temperature. However, it seems that Cu, Zn and Pb were partially in the gas phase during reaction. The behavior of most of metals was similar to the result of thermodynamic equilibrium calculation. In the continuous experiment, Zn was recovered as the liquid. The behavior of metals in the continuous experiment as well as in the batch experiment was similar to the result of thermodynamic equilibrium calculation.

(2) Both in the batch and in the continuous experiments, conversions of volatile metals such as Zn into the liquid occurred during pyrolysis and/or gasification in the initial stage.

(3) In the continuous experiment, Zn was recovered in the liquid in the case without Ca(OH)_2 , and was not in the case with Ca(OH)_2 . The result of thermodynamic equilibrium calculation suggests that Zn was physically adsorbed by Ca of the solid.

ACKNOWLEDGMENTS

This study was financially supported by Center for Coal Utilization, Japan (CCUJ). The authors are also grateful to National Institute of Advanced Industrial Science and Technology (AIST) for supplying the raw Taiheiyo-coal and its technical support.

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