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HIGHLY ACTIVE ABSORBENT FOR SO_2 REMOVAL PREPARED FROM COAL ASH (PART 3)

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ABSTRACT

In the Philippines, the government has started to impose environmental regulations to keep its environment free from hazardous and toxic element. Among the detrimental pollutants being looked into, the government is focusing its attention to the hazardous emissions from coal-fired thermal power plants, in particular, to the reduction of SO_x *emissions. ITDI has developed a process for the production of highly active absorbents for* SO_x *removal using coal ash and limestone, raw or calcined, as its principal raw materials. In previous studies, the chemical composition, mineral composition, morphological structure and thermal history of coal ash samples were determined to find out their effects on the preparation of the absorbents for* SO_x *removal. Studies on the production of* SO_x *absorbents were conducted and the performance of these absorbents were measured. In this particular paper, the effect of sieving the coal ash samples to obtain most reactive materials will be investigated.*

I. Introduction

The clamor for environmental protection is a global concern. With increasing economic and social activities, degradation of the environment due to increased energy demand is inevitable. As oil resource is fast becoming depleted, dependence pollutants such as SO_2, NO_x, and CO_2 emissions during the combustion of these fuels is already a major concern for advanced countries. In the Philippines, the government has started to impose environmental regulations to keep its environment free from hazardous and toxic element. Among the detrimental pollutants being looked into, the government is focusing its attention to the hazardous emissions from coal-fired thermal power plants, in particular, to the reduction of SO_x emissions.

The Industrial Technology Development Institute (ITDI) of the Department of Science and Technology (DOST), through its Fuels and Energy Division (FED) had entered into a joint collaboration with Hokkaido National Industrial Research Institute (HNIRI) of the Agency of Industrial Science and Technology (AIST), Ministry of International Trade and Industry (MITI), Japan to conduct a joint research project entitled "Research on the Preparation of High Quality Absorbent for SO_x from Coal Ash". The joint project is being implemented within the framework of the Institute for Transfer of Industrial Technology (ITIT) Program organized by the International Research and Development Cooperation of AIST, MITI, Japan.

This 4-year project, which started in April 1994 and is in its final year, aims to develop a technology for the preparation of a high quality absorbent for SO_x using coal ash to control air pollution caused by coal-fired thermal power plants in the Philippines.

At present, the Philippines has four (4) existing coal-fired thermal power plants located in Batangas, Cebu and Quezon with a total rated capacity of 1460 MW. These power plants generate about 1 million metric ton of ash per year. At present, these plants do not have means of controlling sulfur emissions.

Since coal-fired thermal power plants are the main sources of sulfur emissions, efforts should be made by the government to reduce these harmful emissions. Coal production will continue to increase in the coming years as a result of the government's strong coal conversion and coal development programs. As projected in the Philippine Energy Plan (1996-2025), coal-fired power generating capacity is expected to reach 10,120 MW by the end of 2025. Although this would mean an increase in the utilization of indigenous coal, this would also increase potential sulfur emissions in the country.

Ash from the combustion of coal in electric utility boilers is one of the major wastes produced by the industry. Disposal of these materials is a major problem, however they can be potentially useful. Coal ash, which contains some free lime, can act as absorbent to capture sulfur as calcium sulfate. The quantity of sulfur that is retained in coal ash is usually too small to satisfy air pollution limits. With the use of limestone to produce high quality absorbents for SO_x additional reduction in sulfur emissions can be realized.

Limestone, another raw material for the production of absorbent is widely distributed in the country particularly in Bulacan. It is composed essentially of calcium carbonate and varying percentage of magnesium carbonate and mechanically admixed impurities of clay, sand, organic materials, iron, phosphate and other compounds. It is formed by accumulation and lithification of fragments of calcareous materials in the form of skeletons and shells that originally were deposited in water.

This paper describes the effect of sieving coal ash samples used in the preparation of absorbents for SO_x removal. Fly ash samples were sieved in order to obtain the most reactive materials for the production of SO_x absorbents. Power plants produce fly ash with varying chemical compositions which largely depends on the coal combustion conditions and the type of raw coal used. In the Philippines, the ratio of imported coal to local coal also effects the chemical composition of the fly ash produced. Because of the varying operation conditions in the production of fly ash, it is difficult to obtain reactive materials. Hence, sieving was done.

The effect of sieving fly ash samples on the efficiency of SO_x removal of the produced absorbents was investigated using two (2) reaction temperatures of 90 and 120°C. The glass content of the sieved coal samples was also related to the SO_x removal efficiency of the absorbents. The various mineral constituents of sieved and unsieved coal ash samples were also compared in order to determine and obtain the most reactive materials.

The use of SO_x absorbent from coal ash is a practical desulfurization system for a coal-fired power plant. The cost of installing a flue gas desulfurization equipment is already 35% of the cost of a power plant, excluding maintenance and operation costs. Considering that the disposal of coal ash is a major problem, their utilization in the production of absorbent for SO_x will not only protect the environment but also produce a value-added product.

2.0 Experimental Procedure

2.1 Chemical Composition

The chemical composition of seven (7) fly ash samples obtained from the Philippines, Thailand and Japan were determined using atomic absorption spectrometry and inductively coupled plasma (ICP) emission spectroscopy.

2.2 X-Ray Diffraction Intensity

The x-ray diffraction intensity of major mineral composition of seven (7) sieved and unsieved samples of fly ash obtained from Philippines, Thailand and Japan were determined. The effect of sieving on the intensity of various major mineral composition was investigated.

2.3 Determination of Glass Content

The per cent crystallinity of partly devitrified glass was determined by the x-ray diffraction method. The glass content of sieved and unsieved fly ash samples was determined and correlated with SO_2 removal efficiency.

2.4 Preparation of Absorbents

Absorbents were prepared using sieved and unsieved fly ash samples and using two (2) different preparation methods.

The preparation of absorbents using sieved fly ash samples proceed as follows: About 75 g of sieved fly ash with particle size of -53 μm is mixed with water while 44.64 g of limestone pulverized to a particle size of -106 μm is mixed with water bubbled with CO_2. The two resulting slurries are then mixed together and cured in a temperature controlled curing vessel at 90 and 120°C with continuous bubbling of CO_2 for 10 hours. The mixture is filtered and the absorbents are dried at 200 to 220°C for 2 hours.

The preparation of absorbents using unsieved fly ash samples is done using the above procedure. Two (2) reaction temperatures, 90 and 120°C, were also used.

2.5 Determination of SO_2 Removal Efficiency

The performance of the absorbents for SO_2 removal was determined using the experimental SO_2 absorption analyzer. Five (5) gram sample of absorbent is placed in a sample holder enclosed in a temperature-controlled reactor at 165°C using a thermocouple. Simulated flue gas with the following composition: 900 ppm SO_2 , 450 ppm NO, 13% CO_2 , 0.6% O, 10% N_2O and N_2 as the balance gas is mixed in a gas mixer. The gas flows from the reactor at a space velocity, SV of $162h^{-1}$. The tested gas then passes through a special type of moisture remover and analyzed simultaneously in SO_2, NO_x, CO_2 and O_2 analyzers. Gas leaks are being monitored through a pressure drop in the manometer.

The performance of the absorbents for SO_2 removal using both sieved and unseieved fly ash samples and preparation reaction temperatures of 90 and 120°C was compared.

3.0 Discussion of Results

3.1 Chemical Composition

The chemical composition of seven (7) fly ash samples obtained from the Philippines, Thailand and Japan are tabulated in Table 1.

Table 1
Chemical Composition of Fly Ash

Fly Ash No.	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)
1	47.07	30.01	4.87	4.50	1.37	0.79
2	54.01	25.38	6.01	4.63	1.00	0.60
3	48.60	25.90	10.30	4.21	1.70	2.26
4	40.78	22.50	10.10	7.43	3.79	2.06
5	59.18	30.15	5.01	0.74	0.49	1.86
6	51.04	28.31	5.03	5.56	2.04	0.77
7	46.50	27.00	10.50	4.01	2.63	2.27

1,6: Philippines, 2,5: Japan, 3,4,7: Thailand

3.2 X-Ray Diffraction Intensity

The x-ray diffraction intensity of major mineral composition of seven (7) sieved and unsieved samples of fly ash obtained from the Philippines, Thailand and Japan are tabulated in Table 2. The table shows that sieving fly ash has a remarkable effect on the chemical composition. Fly ash samples without sieving has an x-ray intensity of 200 c/s for quartz but when the samples were sieved, the x-ray intensity for quartz almost doubled to about 400-450 c/s. This means that sieving fly ash brings out the most reactive materials. Bigger particle sizes exhibited high concentration of unreactive crystalline form of quartz materials.

3.3 Effect of Sieving on SO_2 Removal Efficiency

The effect of sieving on the performance of the absorbents for SO_2 removal was investigated. Table 3 shows the glass content and SO_2 removal efficiency for unsieved fly ash samples for the test conditions using 120 (I) and 90°C (II) while Table 4 shows the glass content and SO_2 removal efficiency for sieved fly ash samples (-53 μm) for the same test conditions.

From Tables 3 and 4, it can be observed that sieved fly ash samples have higher glass content and SO_2 removal efficiency than unsieved fly ash samples. It is also observed that as the glass content increase, the SO_2 removal efficiency also increases. Figures 1 and 2 show the correlation between glass content and SO_2 removal efficiency for unsieved and sieved fly ash samples, respectively.

IV. Conclusions

Based on the results obtained, it can be concluded that using fly ash sieved to a particle size of -53 μm results in the production of high quality absorbents having a high SO_2 removal efficiency. This is because sieving produces the most reactive materials in the fly ash.

It can also be concluded that the higher the glass content of the fly ash, the better its performance on SO_2 removal.

Based on the results conducted during the last four (4) years, the production of high quality absorbents for SO_x will promote and diversify the utilization of locally available resources, namely, coal ash and limestone. Specifically, it will have the following benefits:

a. Produce SO_x absorbents with the desired specifications from local materials;

b. Utilize coal ash which otherwise will be accumulated and contribute to environmental pollution, if not utilized or disposed;

c. Adapt cheap and simple processes, hence are economically feasible;

d. Utilize CO_2 (waste gas from combustion) resulting in the abatement of air pollution;

e. Utilize by-products such as the spent absorbent as raw materials in the preparation of highly active absorbents and for other applications.

References

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2. Chu, P.; Rochelle G.T. (1989). Removal of SO_2 and NO_x from Stack Gas by Reaction with Calcium Hydroxide Solids. JAPCA, vol. 39, pp.175-179.
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Table 2a:
X-ray Diffraction Intensity of Major Mineral Composition in Fly Ash

Fly Ash No.	Particle Diameter (um)	Intensity (Full Scale: 200 c/s)				
		Quartz	Mullite	Hemalite	Gehlenite	Anorthite
1	No sieve	213	217	17	13	17
	+250	457	130	17	13	39
	-250~+150	361	178	26	17	13
	-150~+106	222	213	17	17	13
	-106~+75	191	200	13	13	17
	-75~+53	217	200	17	13	13
	-53~+45	183	208	17	17	17
	-45~+32	196	222	13	17	13
	-32	191	196	13	9	13
2						
	No sieve	214	220	34	109	85
	+250	442	216	30	113	79
	-250~+150	358	211	31	99	81
	-150~+106	226	194	36	105	81
	-106~+75	214	182	33	101	88
	-75~+53	203	184	28	104	85
	-53~+45	209	180	22	98	82
	-45~+32	201	182	25	99	86
	-32	196	177	20	95	85
3						
	No sieve	335	54	250	116	105
	+250	489	41	263	109	112
	-250~+150	446	20	249	106	103
	-150~+106	418	34	252	99	107
	-106~+75	381	26	251	104	100
	-75~+53	347	44	248	101	101
	-53~+45	248	31	241	98	99
	-45~+32	201	21	238	96	94
	-32	195	21	242	99	88

Table 2b: (Continuation of Table 2a): X-ray Diffraction Intensity of Major Mineral Composition in Fly Ash

Fly Ash No.	Particle Diameter (um)	Intensity (Full Scale: 200 c/s)				
		Quartz	Mullite	Hemalite	Gehlenite	Anorthite
4	No sieve	319	47	113	108	385
	+250	679	71	121	103	369
	-250~+150	384	63	109	115	374
	-150~+106	360	50	116	109	370
	-106~+75	248	46	119	101	377
	-75~+53	235	29	122	106	368
	-53~+45	210	31	115	111	372
	-45~+32	219	31	120	115	375
	-32	205	30	118	104	368
5						
	No sieve	222	302	73	35	141
	+250	1135	339	59	31	147
	-250~+150	410	327	64	29	132
	-150~+106	413	331	55	27	139
	-106~+75	405	344	51	31	134
	-75~+53	380	321	48	24	130
	-53~+45	260	325	48	27	129
	-45~+32	176	320	45	25	131
	-32	181	313	41	25	127
6						
	No sieve	257	107	26	24	20
	+106	1422	96	22	22	17
	-106~+75	413	124	17	17	17
	-75~+63	339	130	13	17	11
	-63~+53	170	107	11	13	26
	-53~+45	163	113	17	15	17
	-45~+38	165	107	9	9	13
	-38	152	109	17	24	15
7						
	No sieve	434	27	161	29	126
	+250	1825	34	149	35	111
	-250~+150	1559	30	156	31	109
	-150~+106	1216	27	151	33	112
	-106~+75	838	32	150	30	107
	-75~+53	357	28	144	26	96
	-53~+45	320	24	140	28	103
	-45~+32	283	22	145	24	94
	-32	268	26	136	25	96

1,6- Philippines; 2,5-Japan; 3,4,7- Thailand

Table 3: Glass Content and SO_2 Removal Efficiency
Using Unsieved Fly Ash Samples

Fly Ash No.	Glass (%)	SO_2 Removal Efficiency	
		I	II
1	80-83	99	78
2	80-85	92	82
3	70-73	71	53
4	65-70	64	48
5	60-65	59	36
6	58-64	52	29
7	47-53	28	11

	Reaction Temperature (°C)	Reaction Time (hr)	Fly Ash/CaO (wt.%)
I	120	10	75/25
II	90	10	75/25

Testing Condition of SO_2 Absorption
Absorption Temperature 165°C
SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%
O: 6%, N_2O: 10%, N_2: Balance Gas

Table 4: Glass Content and SO_2 Removal Efficiency Using Sieved Fly Ash Samples

Fly Ash No.	Glass (%)	SO_2 Removal Efficiency	
		I	II
3	77-81	85	72
4	71-76	74	60
5	65-68	58	43
6	66-68	61	40
7	51-57	33	21

	Reaction Temperature (°C)	Reaction Time (hr)	Fly Ash/CaO (wt.%)
I	120	10	75/25
II	90	10	75/25

Testing Condition of SO_2 Absorption

Absorption Temperature 165°C
SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%
O: 6%, N_2O: 10%, N_2: Balance Gas

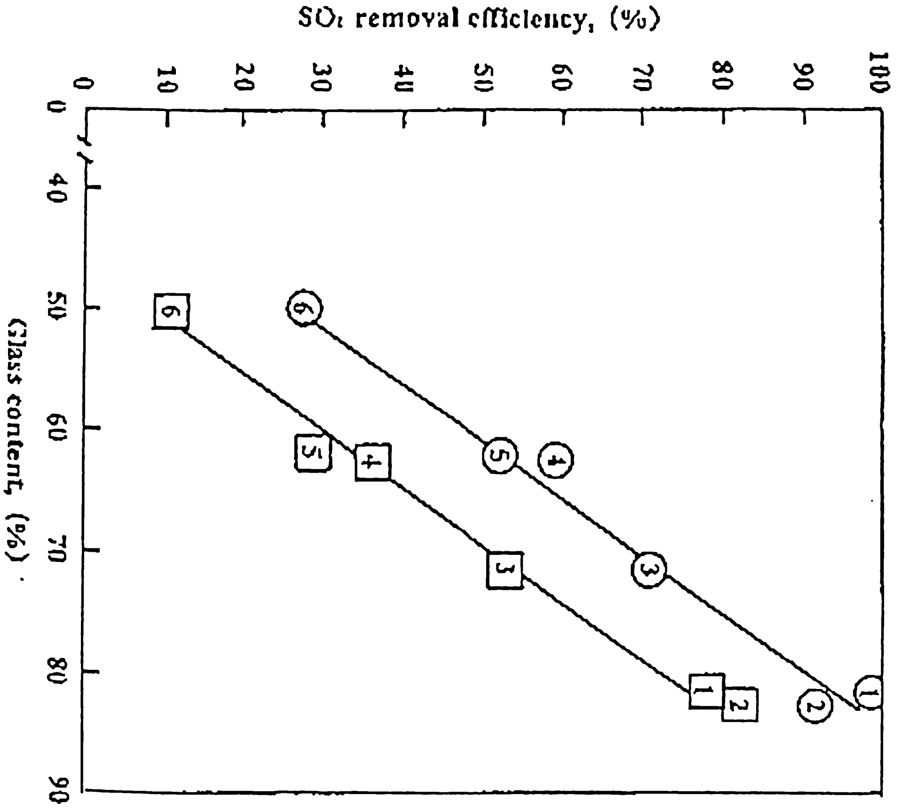

Figure 1. Correlation Between SO_2 Removal Efficiency and Glass Content Using Sieved Fly Ash Samples

Fly ash/CaO = 75/25 wt%
Curing time: 10 hrs, Curing temperature: O; 120°C, ; 90°C,
Absorption condition
SO_2: 900 ppm, NO:450 ppm, CO_2: 13%, O_2:6%, H_2O:10%
N_2: balance gas
Reaction temperature: 165°C

5:Philippine, 3, 6: Thailand, 4: Japanese

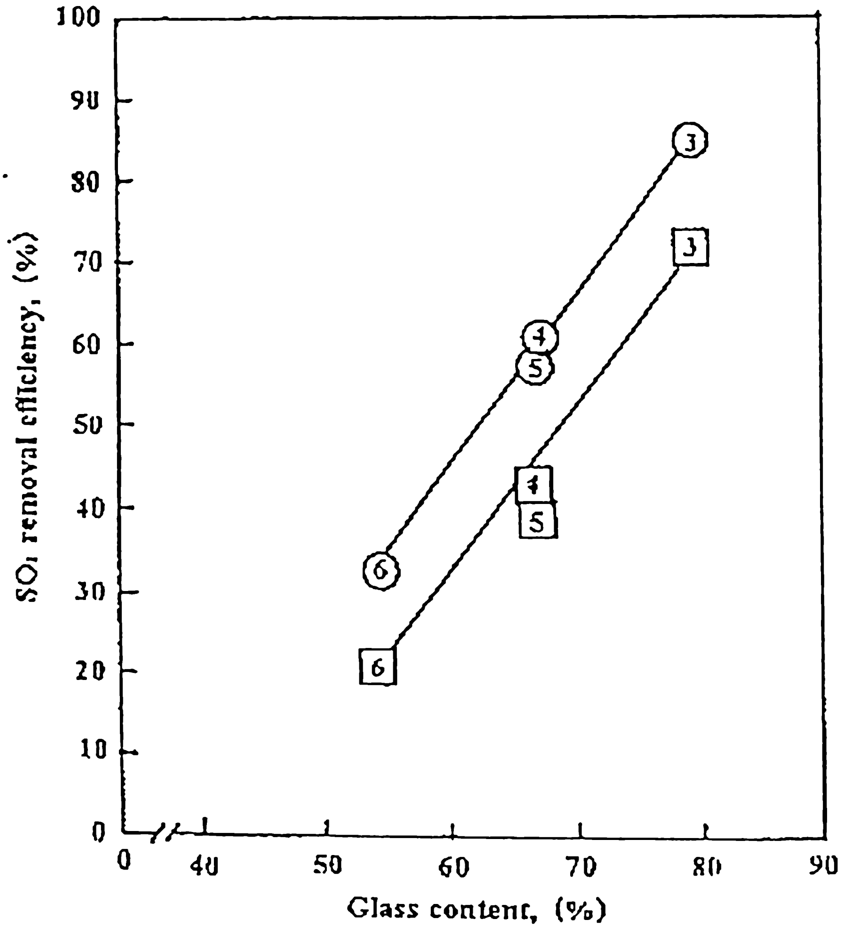

Figure 2. Correlation Between SO_2 Removal Efficiency and Glass Content Using Unsieved Fly Ash Samples

Fly ash/CaO = 75/25 wt%

Curing time: 10 hrs, Curing temperature: O; 120°C, ; 90°C,

Absorption condition

SO_2: 900 ppm, NO:450 ppm, CO_2: 13%, O_2:6%, H_2O:10%
N_2: balance gas

Reaction temperature: 165°C

1,5:Philippine, 3, 6: Thailand, 2,4: Japanese