

STUDIES ON THE FUSIBILITY OF COAL ASH

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ABSTRACT

A study, which aims to develop a technology for the preparation of a high quality adsorbent for SO_x using coal ash to control air pollution caused by coal-fired thermal power plants in the Philippines, is currently being jointly undertaken by ITDI and HNIRI. During its first year of implementation, the physical, chemical and thermal characteristics of Philippine and Japanese coal ash samples were determined. Results show that Philippine coal ash samples are of the silicoaluminous type while that of the Japanese coal samples are of the aluminosiliceous type. Three (3) common major elements, namely, quartz, mullite and hematite are found in all coal ash samples. A correlation between the melting point and chemical composition of the coal ash samples shows that the coal ash samples having a low acid-base index resulted in high melting points.

INTRODUCTION

Worldwide awareness for a clean and better environment is increasing everyday. In the Philippines, the government is also becoming aware of keeping its environment free from hazardous and toxic pollutants, hence, environmental regulations are slowly being imposed. Among the detrimental pollutants being looked into, the government is focusing its attention to the hazardous emissions from coal-fired power plants, in particular, to the reduction of sulfur emissions.

The Industrial Technology Development Institute (ITDI) of the Department of Science and Technology (DOST) through its Fuels and Energy Division (FED) has entered into a joint collaboration with the Hokkaido National Industrial Research Institute (HNIRI), Agency of Industrial Science and Technology (AIST), Ministry of International Trade and Industry (MITI), Japan. The joint research project entitled "Research on the Preparation of High Quality

Adsorbent for SO_x from Coal Ash" is being implemented within the framework of the Institute for Transfer of Industrial Technology (ITIT) Program organized by the International Research and Development Cooperation Division of AIST, MITI, Japan.

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

At present, there are two (2) coal-fired power plants in the Philippines which are sources of coal ash. These power plants are located in Naga and in Calaca. The Naga Coal Thermal Plant, located in Cebu, has a capacity of 55 MW designed to burn 550 tons of coal a day. For every ton of coal burned, 0.19 ton of ash is produced consisting of about 15% bottom ash and 85% fly ash. The Calaca Coal Thermal Plant, located in Batangas, is a 300 MW power plant that requires 3,000 tons of coal per day and produces about 200,000 tons of ash per year. Some of these coal ash are being disposed to cement manufacturers and used as a raw material in cement production.

Currently, these coal-fired power plants do not have a means for controlling its 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 in the country. In the Philippine Energy Plan (1993-2000), it has been projected that an additional 2800 MW of coal-fired thermal power plants will be installed in the year 2000. Although this would mean an increase in the utilization of indigenous coal, this would also increase potential sulfur emissions in the country. Therefore, technologies on sulfur reduction should be developed.

Coal ash, which contains some free lime, can act as a sorbent to "fix" 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 coal ash to produce a high quality sorbent for SO_x, additional reduction in sulfur emissions can be realized.

MATERIALS AND METHODS

Collection of Coal Ash Samples

Three (3) coal ash samples from the Philippines, three (3) from Japan and a standard reference sample of coal fly ash were used in the experiments.

The Philippine coal ash samples were collected from Calaca thermal power plant while the Japanese coal ash samples were collected from Naie and Tomato power plant stations. The standard reference coal ash sample was obtained from the National Institute of Standards and Technology, U.S. Department of Commerce.

Chemical Composition

The chemical composition of the coal ash samples was determined using an atomic absorption spectrophotometer. In addition, the moisture content and surface area of the coal ash samples were also determined.

X-ray Powder Diffraction

To determine the mineral constituents of the coal ash samples, x-ray powder diffraction analysis was carried out. X-ray diffraction profiles were determined by the use of a Rigaku X-ray Diffractometer Model HV21.

Scanning Electron Microscope

The microstructure of the coal ash samples was observed through a JEOL Scanning Electron Microscope Model JSM-TSO using an acceleration voltage of 20 kV. Through this microscope, the surface phenomena of the coal ash samples were observed.

Thermal Analysis

Thermal analysis was carried out for the seven (7) coal ash samples using a Rigaku Thermoflex unit with α -Al₂O₃ as reference sample. The coal ash sample was heated up to 1500°C at a heating rate of 10°K/min under air atmosphere, TG range of 20 mg full scale and DTA range of \pm 50 μ V.

Both thermogravimetry (TG) and differential thermal analysis (DTA) were conducted. The TG curve shows the weight loss pattern of the sample as temperature is increased while DTA shows a series of peaks, the position of which is determined by the chemical composition and crystal structure of the substance and the area of which is related to the energy involved in the occurring reaction.

For the DTA curves, the sintering, softening, melting point and fluidization temperatures were read.

Melting Point Determination

The melting point was determined according to Japan Industrial Standard (JIS) M-8801 and American Society for Testing Materials (ASTM) D-271-48. Finely ground coal ash samples were pressed into standard mold to form a slender triangular cone or pyramid, 19 mm in height with 6.4 mm in the edges of base regular triangle. The cones were set vertically upon a ceramic base and inserted into an electric furnace and heated at 10°C/min from room temperature to 900°C. After about 90 minutes, heating rate was changed to 5°C/min from 900 to 1600°C, the furnace maximum temperature. Temperatures are measured by a thermocouple.

Using the JIS method, softening, melting point and fluidization temperatures were recorded while for the ASTM method, initial deformation, softening, hemisphere and fluidization temperatures were recorded.

The ASTM method defines the initial deformation temperature (IDT) as the temperature at which a standard pyramid of ash just begins to fuse or show evidence of deformation at the top as it is being heated. The softening temperature, usually called the fusion temperature, of an ash, corresponds to an observed condition between initial deformation and fluidity where the height of ash cone is equal to the width of the sample. The hemisphere temperature is read when the cone has further deformed to the point where it assumes a hemispherical shape and its height equals

half its width. Both softening and hemisphere temperatures are related to conditions at which the ash shows a greatly accelerated tendency to mass together and stick in large quantities to heat exchange surfaces. The fluid temperature is the temperature at which the test cone flattens out to a pancake shape. For the JIS method, the softening temperature is similar to that of IDT and melting point to hemisphere temperature. Fluidization temperature is the same for both JIS and ASTM methods.

RESULTS AND DISCUSSION

Chemical Composition

The chemical composition of the different coal ash samples is shown in Table 1. It can be seen that Japanese coal ash samples contain relatively larger amounts of the oxides of Si, Al and Fe but smaller amounts of CaO and MgO compared to the Philippine coal ash samples. Minor trace elements such as Na₂O, K₂O and TiO₂ are found in the range of 4.76 - 4.99% for Philippine coal ash and 4.24 - 6.74% for Japanese coal ash.

Table 1
Chemical Composition of Coal Ash Samples

COMPONENTS	PHILIPPINE SAMPLES			JAPANESE SAMPLES			STANDARD REFERENCE COAL ASH (1633 a)
	FLY ASH	CINDER ASH	CLINKER ASH	NAIE FLY ASH	NAIE CLINKER	TOMATO ASH	
SiO ₂ , %	47.07	48.66	48.07	57.56	60.10	53.31	48.78
Al ₂ O ₃ , %	30.01	24.83	26.12	23.25	22.76	23.67	27.02
Fe ₂ O ₃ , %	4.87	7.89	7.92	4.06	4.62	6.31	13.44
CaO, %	4.50	5.89	6.47	2.42	2.65	3.62	1.55
MgO, %	1.37	1.81	1.60	1.56	1.61	1.17	0.75
Na ₂ O, %	1.15	1.21	1.28	0.96	0.95	0.50	0.23
K ₂ O, %	0.79	0.77	0.63	3.17	2.94	1.01	2.26
TiO ₂ , %	1.45	1.20	1.33	1.05	0.78	1.56	1.33
T O T A L :	91.21	92.26	93.42	94.03	96.41	91.15	95.36
C, %	5.25	11.00	4.02	0.95	4.49	1.24	nd
S, %	0.16	0.17	0.07	0.06	0.02	0.16	0.18
Moisture, %	0.30	0.37	0.22	0.02	0.14	0.08	nd
Surface area, sq. M/g	2.70	13.30	1.30	13.20	4.30	3.30	nd

nd - no data

It can also be observed that Philippine coal ash samples contain large amounts of total carbon ranging from 4.02 to 11.00% while total carbon for Japanese coal ash samples range from 0.93 to 1.24% except for Naie clinker ash which contains about 4.49% C. The amount of sulfur is quite low ranging from 0.02 to 0.17% for both Philippine and Japanese coal ash samples.

Considering the classification established by Voina and Todor (1978), the Philippine coal ash samples and the standard coal ash sample are of the silicoaluminous type while that of the Japanese coal ash samples are of the aluminosiliceous ashes. The classification established by

Voina and Todor (1978) considers the ratio between SiO_2 and Al_2O_3 as well as the quantities of CaO and SO_3 . Aluminosiliceous ashes are those with $\text{SiO}_2/\text{Al}_2\text{O}_3 > 2$ and $\text{CaO} < 15\%$ while silico aluminous ashes are those with $\text{SiO}_2/\text{Al}_2\text{O}_3 < 2$ and $\text{CaO} < 15\%$.

X-ray Powder Diffraction

Figure 1 shows the x-ray diffraction pattern for the coal ash samples. The occurrence of the major and minor elements are shown in this figure and are numbered as follows:

- | | | |
|--------------|-----------------|-------------------|
| 1. Quartz | 6. Portlandite | 11. Plagioclase |
| 2. Mullite | 7. Feldspar | 12. Cristobalite |
| 3. Hematite | 8. Wollastonite | 13. Melilite |
| 4. Corundum | 9. Lime | 14. Metakaolinite |
| 5. Magnetite | 10. Anhydrite | |

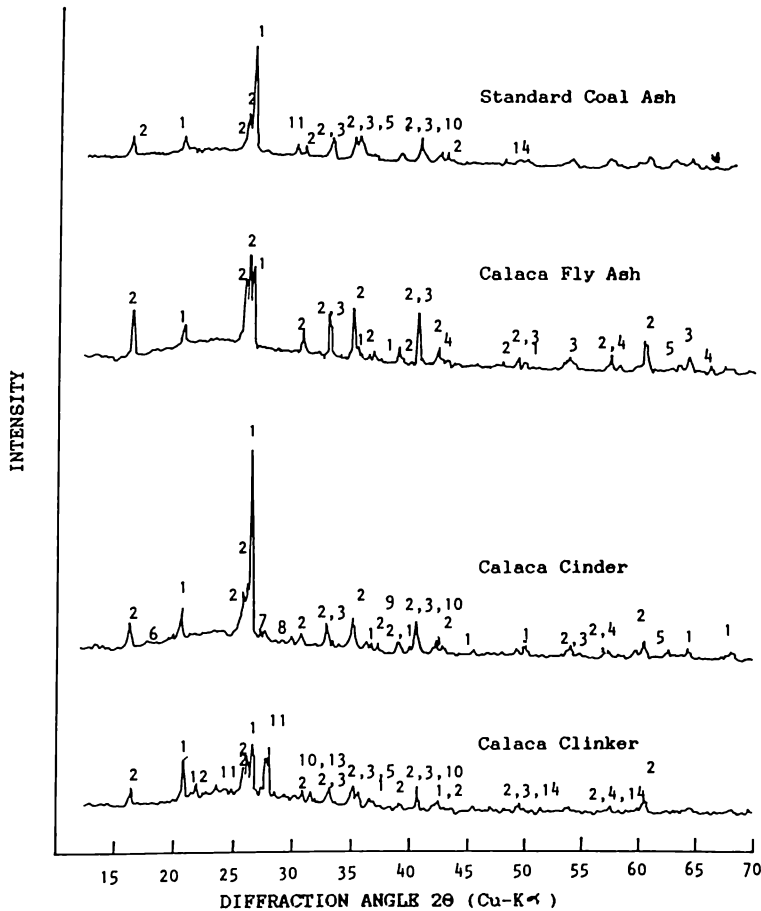


Figure 1a
X-Ray Diffraction Pattern for Standard Coal Ash, Calaca Fly Ash, Calaca Cinder and Calaca Clinker

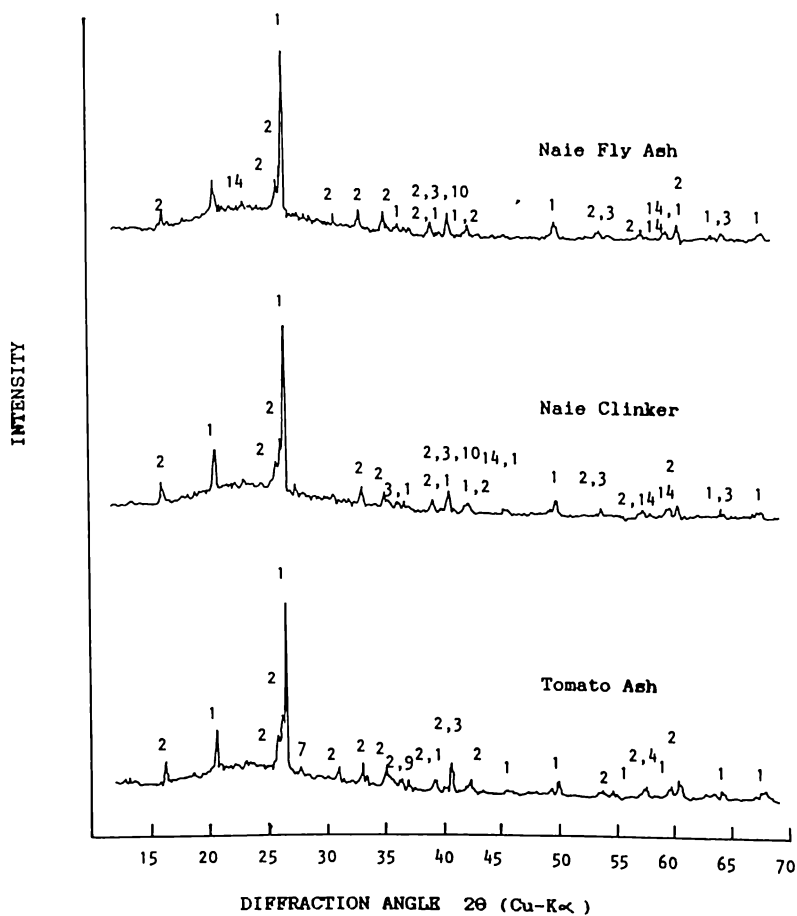


Figure 1b
X-Ray Diffraction Pattern for Naie Fly Ash,
Naie Clinker and Tomato Ash

It has been observed that the common major elements found in coal ash samples include quartz, mullite and hematite. This is confirmed in Figure 2 where a comparison of the intensity of five (5) major elements such as quartz, mullite, hematite, gehlenite (melilite) and lime found in the coal ash samples is shown.

Table 2 enumerates the major, minor and trace elements identified in the coal ash samples.

Scanning Electron Microscope

The microstructures of the coal ash samples are shown in Figure 3.

INTENSITY

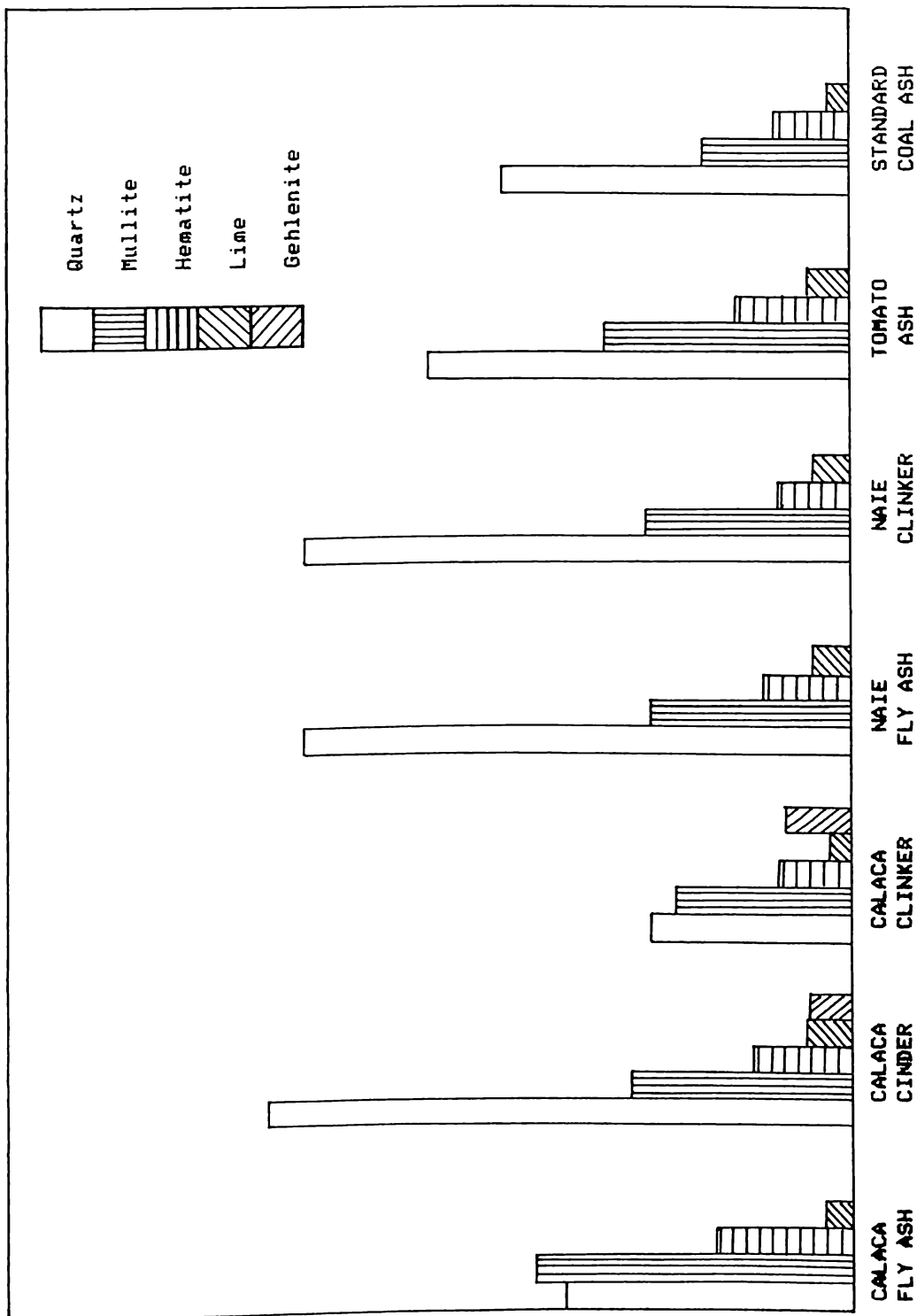


Figure 2
X-Ray Diffraction Line Intensity of Major Elements in Coal Ash

Table 2
Major, Minor and Trace Elements Identified in the Coal Ash Samples

COAL ASH SAMPLES	MAJOR ELEMENTS	MINOR ELEMENTS	TRACE ELEMENTS
Calaca Fly Ash	Quartz, Mullite Hematite, Corundum	Calcite, Feldspar, Wollastonite, Portlandite, Lime, Magnetite, Larnite, Anhydrite	Plagioclase, Spinel Ferrian, Brucite
Calaca Cinder Ash	Quartz, Mullite, magnetite, Lime, Wollastonite	Hematite, Calcite, Plagioclase, Corundum, Feldspar, Anhydrite	Melilite, Larnite, Brucite, Barite, Pyrrhotite, Metakaolinite, Spinel Ferrian, Periclase
Calaca Clinker Ash	Quartz, Mullite, Plagioclase, Mellite, Calcite, Metakaolinite, Cristobalite, Barytocalcite, Hematite, Feldspar	Anhydrite, Lime, Magnetite, Gypsum, Monticellite, Wollastonite,	Barite, Witherite, Corundum, Larnite, Portlandite, Spinel Ferrian, Tridymite
Naie Fly Ash	Quartz, Mullite, Hematite	Calcite, Lime, Feldspar, Gypsum, Portlandite, Metakaolinite, Plagioclase	Wollastonite, Magnetite, Anhydrite
Naie Clinker Ash	Quartz, Mullite, Hematite	Calcite, Feldspar, Plagioclase, Lime, Portlandite, Metakaolinite, Gypsum	Wollastonite, Magnetite, Anhydrite, Larnite
Tomato Ash	Quartz, Mullite, Hematite, Lime Periclase	Wollastonite, Tridymite, Larnite, Magnetite, Corundum	Geothite, Rutile, Monticellite, Plagioclase, Anhydrite, Feldspar
Standard Coal Ash (1633a)	Quartz, Mullite, Hematite, Corundum, Magnetite	Wollastonite, Lime Periclase, Calcite, Monticellite	Metakaolinite, Larnite

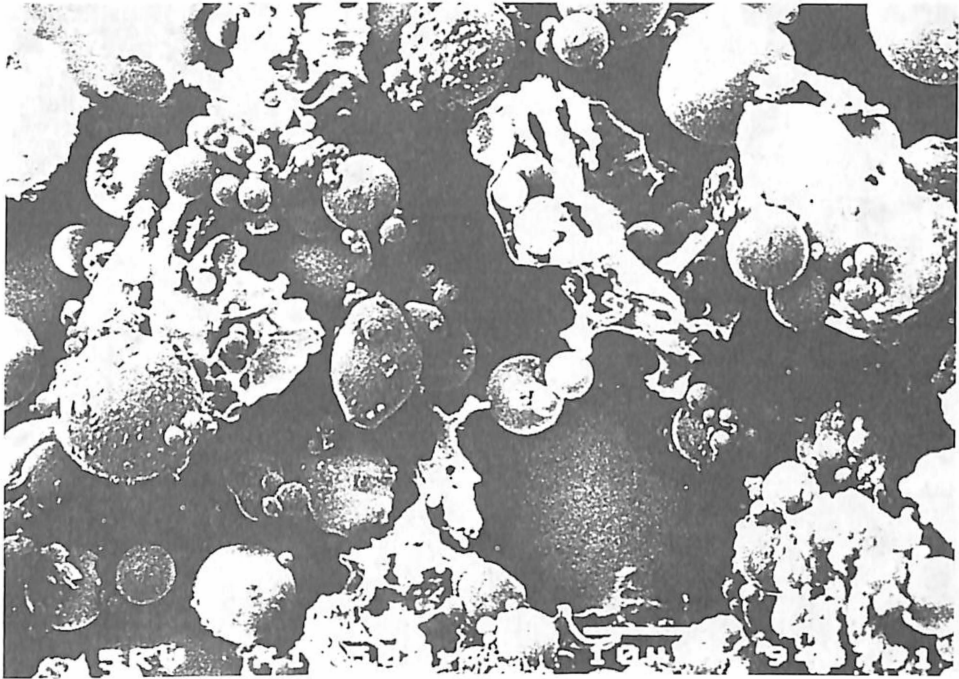


Figure 3a
Surface of the Calaca Fly Ash in SEM

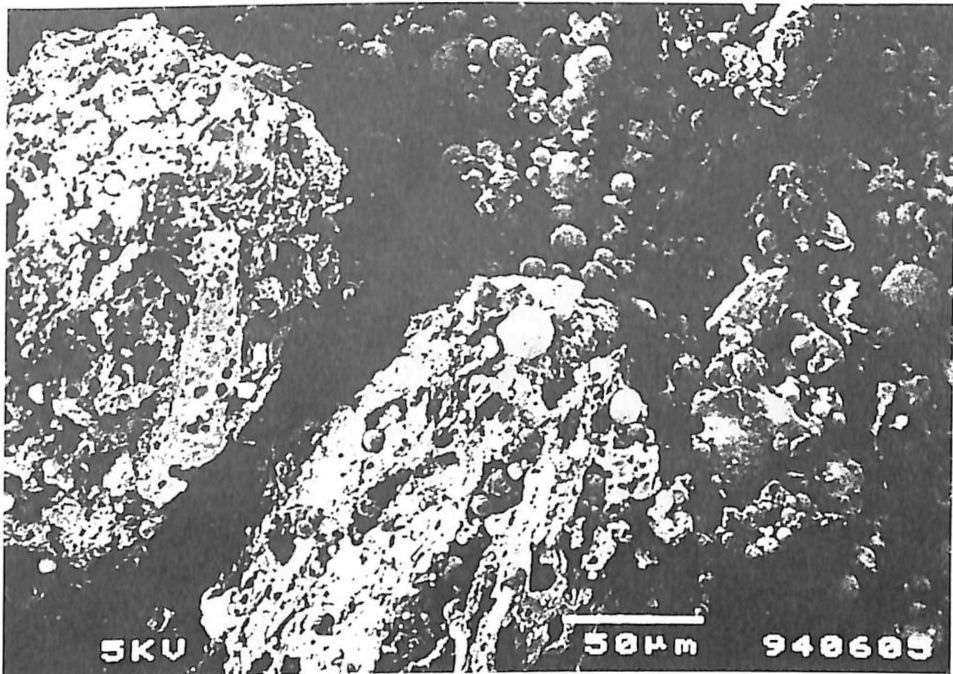


Figure 3b
Surface of the Calaca Cinder in SEM

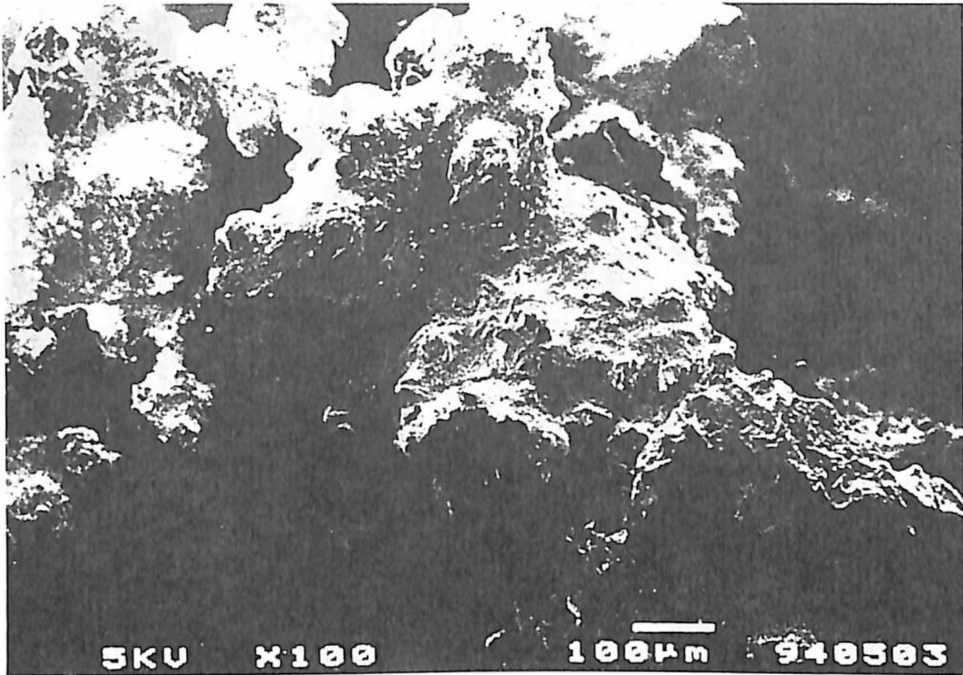


Figure 3c
Surface of the Calaca Clinker in SEM

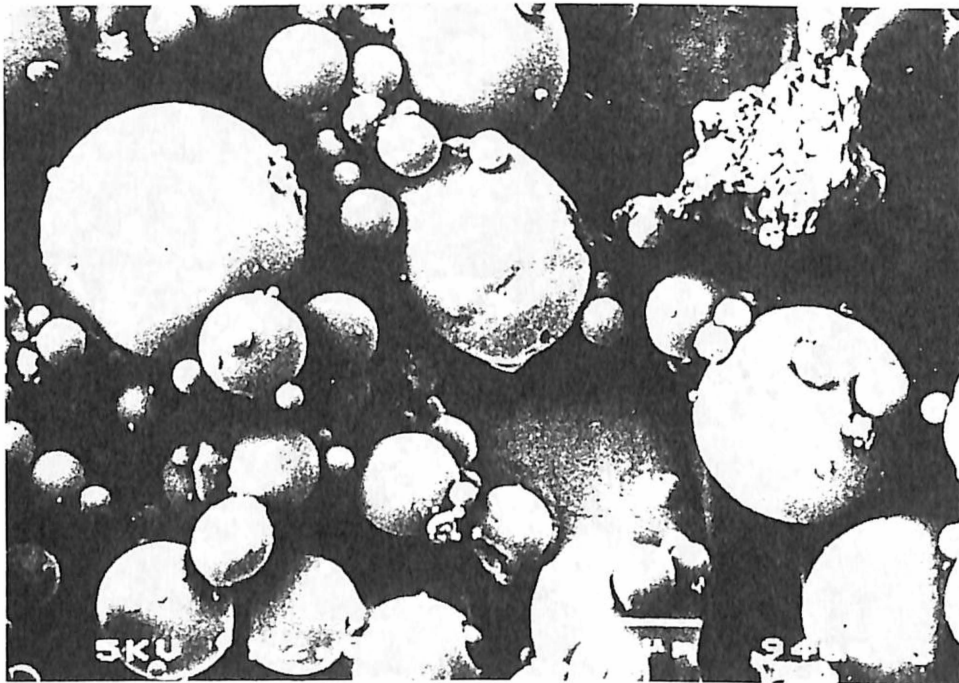


Figure 3d
Surface of the Naie Fly Ash in SEM

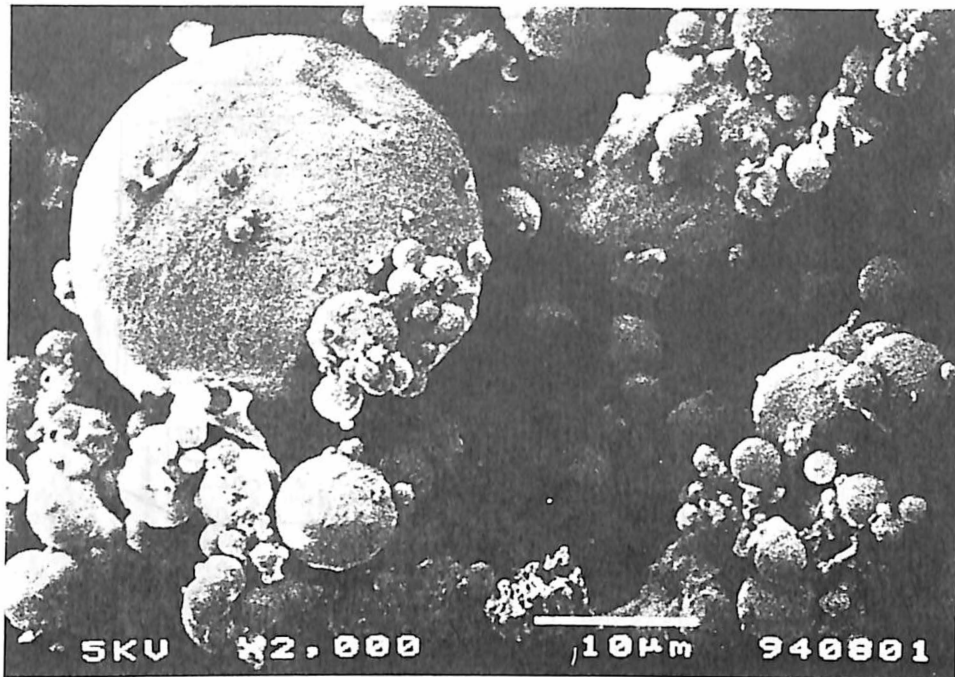


Figure 3e
Surface of the Standard Coal Ash in SEM

Thermal History

Figure 4 shows the TG-DTA curves obtained for the coal ash samples. It depicts the weight loss pattern and the different endothermic and exothermic reactions which occur during the heating of the coal ash samples.

For the Philippine coal ash samples, the total weight loss is observed to be in the range of 2 to 21.5% while for the Japanese coal ash samples, total weight loss ranging from 0 to 2% is observed. The standard coal ash sample has a total weight loss of about 2.2%. This shows that the Philippine coal ash samples contain a larger amount of organic substances, mainly unburned carbon, than that of the Japanese coal ash samples.

The DTA curves for both the Philippine and Japanese coal ash samples exhibit the same pattern. At first, endothermic effects are observed in the temperature range between room temperature (24°C) to about 200°C for all coal ash samples except for Calaca clinker. This means that the coal ash samples contain water which is either physically absorbed or fixed in the tobermorite gels. Tobermorite gels are calcium silicate hydrates which are formed by the hydration of dicalcium or tricalcium silicate at or near ambient temperatures.

As the temperature is increase, oxidation, thermal decomposition, transformation and reaction between components occurred.

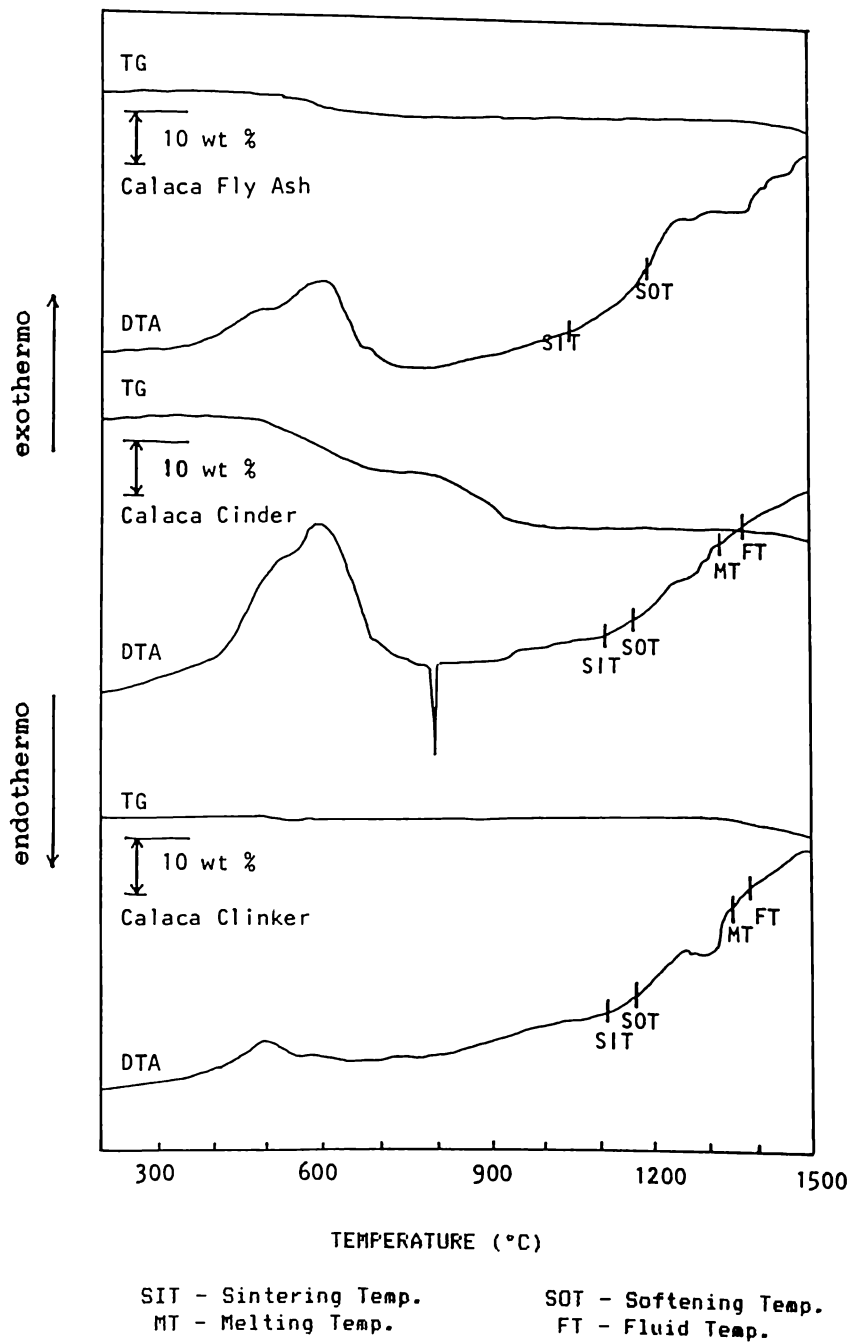
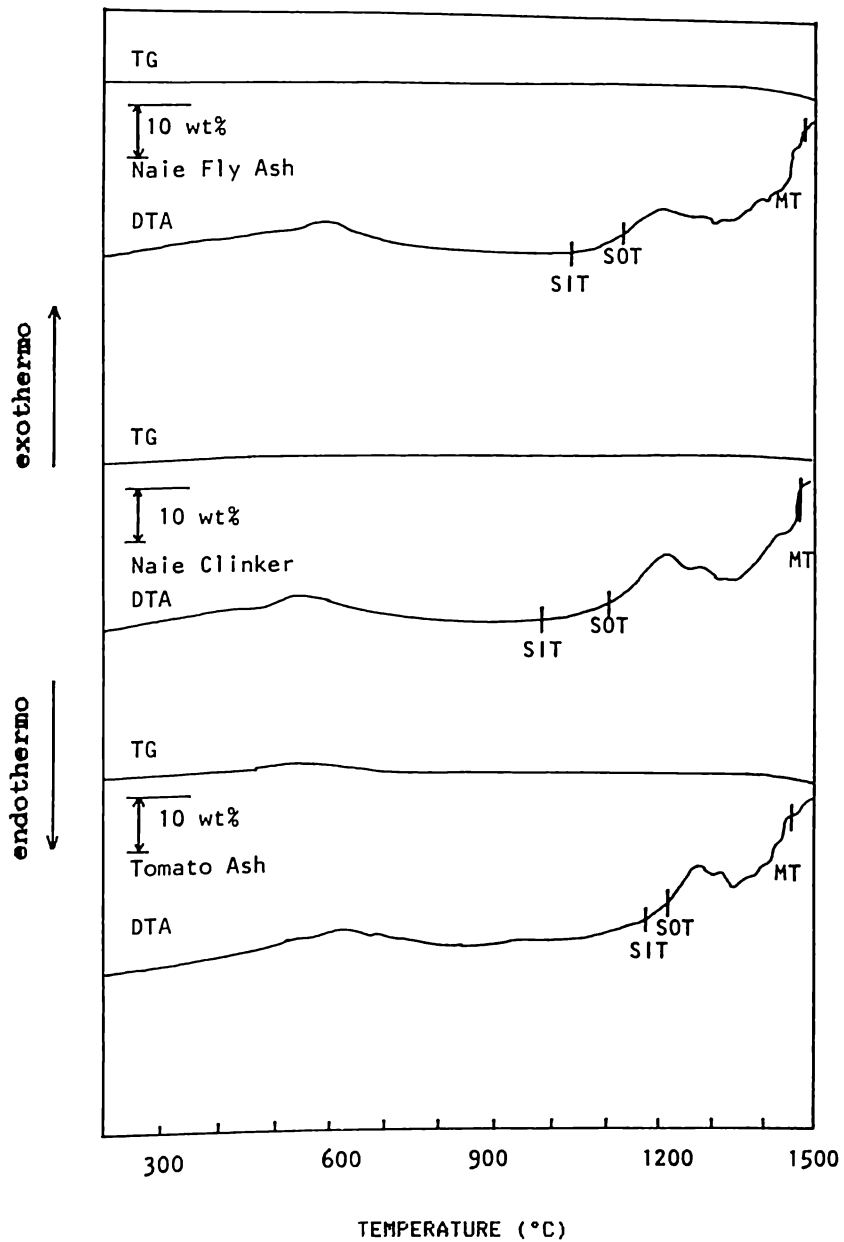


Figure 4a
Thermal Analysis of Calaca Fly Ash, Calaca Cinder and Calaca Clinker

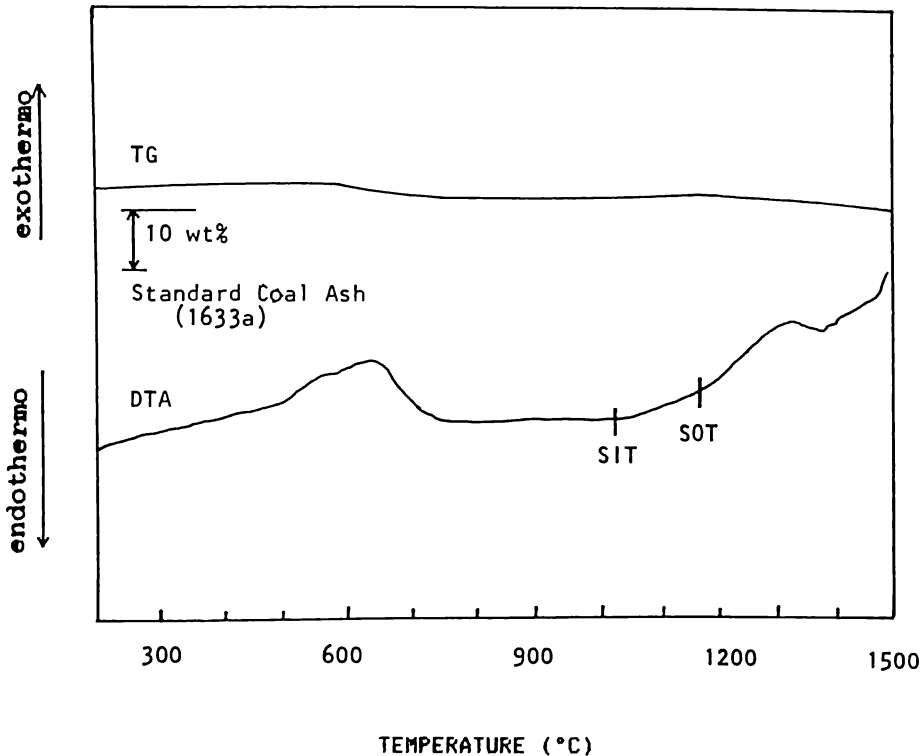
Reference Sample: α - Al_2O_3
 Program Rate: 10°C
 Atmosphere: Air



SIT - Sintering Temp. SOT - Softening Temp.
 MT - Melting Temp.

Figure 4b
Thermal Analysis of Naie Fly Ash, Naie Clinker and Tomato Ash

Reference Sample: α - Al_2O_3
 Program Rate: $10^\circ C$
 Atmosphere: Air



SIT - Sintering Temp. SOT - Softening Temp.

Figure 4c
Thermal Analysis of Standard Coal Ash

Reference Sample: α - Al_2O_3
 Program Rate: 10°C
 Atmosphere: Air

In the temperature region of 300 to 700°C, exothermic effects due to the oxidation of organic substances are observed for all coal ash samples. Weight loss which corresponds to this burning of organic substances vary and their differences are attributed to the varying amount of noncombustibles that did not burn completely during combustion. Iron compounds such as pyrite and siderite are also oxidized at this temperature region producing hematite.

Lime (CaO), a compound significant in the capture of SO_x , readily undergoes recarbonation in an atmosphere of carbon dioxide at a temperature slightly below the decomposition temperature of calcite (CaCO_3). Calcite begins to decompose thermally at a temperature greater than 700°C while anhydrite (CaSO_4), found in small quantities, thermally decomposes to CaO and SO_3 at a temperature greater than 1000°C.

The presence of periclase and brucite in the coal ash samples indicates that the oxide and hydroxide of magnesium do not readily carbonate. Likewise, the carbonation of the hydroxide of

calcium (portlandite) does not readily carbonate. Once the decomposition of Ca(OH)_2 commences, which is at about 600°C , the carbonation of CaO rapidly becomes dominant.

Polymorphic transformations of SiO_2 and possibly the loss of hydroxyl groups (OH) from kaolinite $[\text{Si}_2\text{Al}_2\text{O}_5][\text{OH}]_4$, which is an endothermic reaction, occurs at a temperature range greater than 700°C .

From the DTA curves, sintering occurs at a temperature range of 1000 to 1110°C for Philippine coal ash samples and 980 to 1170°C for Japanese coal ash samples. Softening occurs at a temperature range of 1150 to 1190°C for Philippine coal ash samples and 1105 to 1220°C for Japanese coal ash samples. Melting point occurs at a temperature range from 1320°C to greater than 1500°C . Fluidization temperature occurs at a temperature greater than 1500°C except for Calaca cinder and Calaca clinker which occurs at a lower temperature.

Table 3 shows the sintering, softening, melting and fluidization temperatures read from the DTA curves for all coal ash samples.

Table 3
Temperatures Read from TG-DTA Curves ($^\circ\text{C}$)

COAL ASH SAMPLES	SINTERING TEMP.	SOFTENING TEMP.	MELTING TEMP.	FLUID TEMP.
Calaca Flys Ash	1034	1190	> 1500	> 1500
Calaca Cinder	1104	1160	1320	1365
Calaca Clinker	1105	1155	1340	1373
Naie Fly Ash	1030	1130	1480	> 1500
Naie Clinker	980	1105	1490	> 1500
Tomato Ash	1168	1215	1455	> 1500
Standard Coal Ash	1018	1160	> 1500	> 1500

Table 4
Temperature Results from Electric Furnace (°C)

COAL ASH SAMPLES	IDT	SOFTENING	HEMISPHERE	FLUID
	SOFTENING*	TEMP.	MELTING*	FLUID*
Calaca Fly Ash	1195	1483	1535	1556
Calaca Cinder	1196	1306	1321	1363
Calaca Clinker	1185	1317	1330	1375
Naie Fly Ash	1120	1412	1462	1530
Naie Clinker	1098	1400	1430	1506
Tomato Ash	1216	1403	1423	1463
Standard Coal Ash	1163	1489	1495	1510

* JIS Method

Melting Temperatures

Table 4 shows the results of the melting point determination according to ASTM and JIS methods. All coal ash samples have melting point greater than 1320°C. Calaca fly ash has the highest melting point followed by the standard coal ash sample while Calaca cinder and Calaca clinker have the lowest melting point among the coal ash samples.

The correlation between the melting point and the chemical composition of the coal ash samples has been looked into by plotting the melting point against an acid-based index as shown in Figure 5. The acid-based index describes the ratio of the alkaline earth compounds to the acidic compounds and is computed as follows:

$$acid - base \text{ index} = \frac{\%CaO + \%MgO + \%Na_2O + \%K_2O}{\%SiO}$$

From Figure 5, it is observed that a coal ash sample having a low acid-base index will have a high melting point while high acid-base index would indicate low melting point.

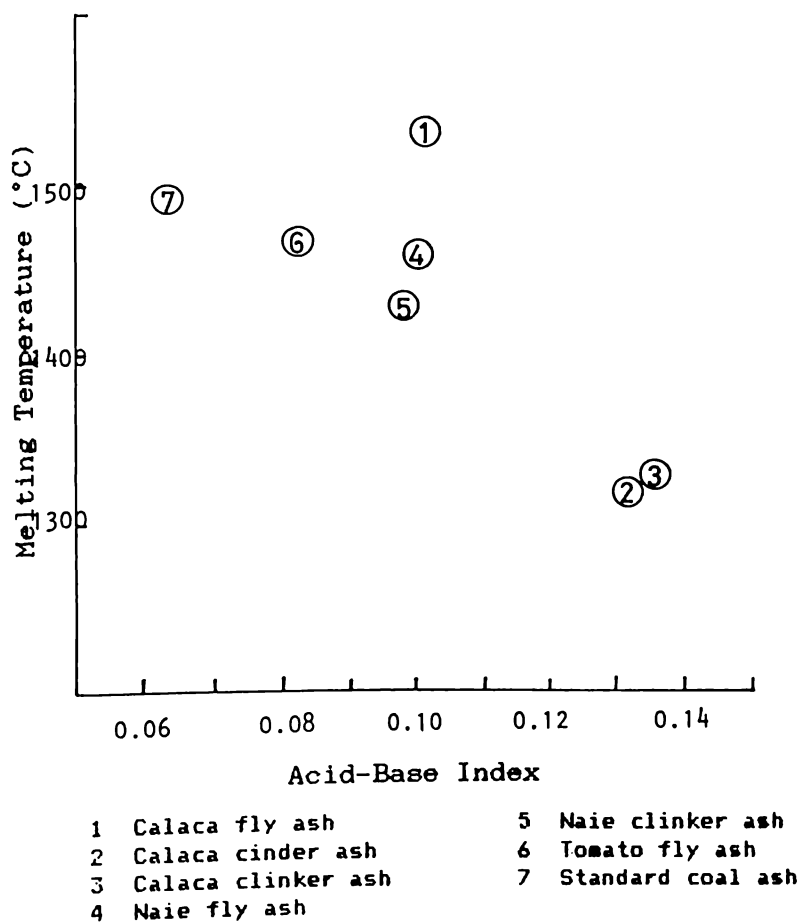


Figure 5
Correlation Between an Acid-Based Index
and Melting Temperature of Coal Ash

CONCLUSIONS

In the preparation of a high quality adsorbent for SO_x using coal ash as the starting material, it is, indeed, important that the physical, chemical and thermal characteristics of the coal ash be known. From the foregoing results and discussion of the experiments conducted on the characterization of coal ash, the following were the conclusions reached:

- a) As compared to the Japanese coal ash samples, the Philippine coal ash samples contain relatively smaller amounts of the oxides of Si, Al and Fe but larger amounts of CaO and MgO. Minor trace elements of Na_2O , K_2O and TiO_2 are found in the magnitude of less than 5%.

- b) The Philippine coal ash samples are of the silicoaluminous type while that of the Japanese coal samples are of the aluminosiliceous type.
- c) There are three (3) common major elements found in all the coal ash samples and these are quartz, mullite and hematite.
- d) Sintering of all coal ash samples begin at about 1000°C while softening starts at about 1100°C.
- e) Melting point and fluid temperatures are highest for Calaca fly ash while lowest for Calaca cinder and Calaca clinker.
- f) The correlation between the melting point and chemical composition of the coal ash samples shows that the coal ash samples having a low acid-base index resulted in high melting points.

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