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## A study of ash deposits on the heat exchange tubes using SDT/MS and XRD techniques

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### Abstract

Four ash samples which were deposited on four different locations in the atmospheric fluidized bed combustor, FBC, system at the TVA Shawnee Steam Plant near Paducah, KY, were employed in the present study. The SDT/MS and XRD techniques were applied to identify the sample composition and the mechanism that form the deposits. The major compound in the deposits from convection pass inlet, superheater and multiclone inlet was  $\text{CaSO}_4$ , and the predominant minor compound was  $\text{CaO}$  in the samples. Also,  $\text{CaS}$  was found in the deposits from superheater by XRD analysis. In the case of recycle feed pipes,  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  were the major components, and  $\text{CaSO}_4$  and  $\text{CaO}$  the predominant minor compound in the deposits. The combined SDT/MS with XRD results are useful techniques for identification of unknown ash samples. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Thermal analysis; Ash; FBC

### 1. Introduction

Ever since the steam-raising process was introduced as a means of generating electricity in the beginning of this century, the combustion system technology has been improved remarkably and the capacity of the combustor has increased largely. However, the fireside problem of the combustion system is still troublesome. The formation of deposits is responsible for adding maintenance, reducing the rate of heat transfer and affecting the combustion efficiency. It has been estimated that fireside problems collectively cost the electrical generating industry \$4 billions per year. The nature of deposits varied significantly with the change in the combustor system and the steam-raising fuel employed. The fireside problems are very com-

plex phenomena, depending on the transformation of the inorganic components (found in the impurities in fuels) upon heating and cooling; the chemical reaction between gas, liquid and solid phase in motion, and at rest; the existence of non-equilibrium conditions usually associated with supercooling; and the attachment of impurities to surfaces and the detachment of deposited liquids and solids [1]. Even in the same steam-generator, the components and severity of the deposits are different throughout the furnace with the change of surface temperature, flame temperature, absorption rates, direction of gas flow, mineral composition, and oxygen level of the flue gas in contact with the heat-transfer surface [1]. Under such a circumstance, a thorough understanding of the deposits is essential to control the fireside problem. Numerous techniques are now available for characterizing the fireside phenomena. Among them, thermal analysis is

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a powerful tool for identification of the composition of the deposits.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are the most widely used thermal analysis techniques based on the change of weight or energy as a function of temperature. The physical and chemical changes that a sample undergoes during heating are characteristics of the material being used. By measuring the temperature at which such a reaction takes place and the heat involved in the reaction, the compounds present in the sample can be determined. Thermal analysis systems work well on most mineral species that give distinguishable thermal response at distinct temperatures. However, the signal generated may be altered and masked if a mixture of minerals is present or no definite thermal response is given if a thermally inert substance is tested. In such cases, XRD is another recommendable technique for identifying the presence of the mineral species in their crystalline form in a concentration of a few weight percent or greater.

In the present work, the four deposits samples provided by the Tennessee Valley Authority were examined in an SDT/MS system and an XRD instrument. Information about the components of the deposits was obtained and the possible mechanisms for the formation of deposits at specific conditions were proposed.

These four samples represented the different areas at which the hard deposits were observed. The temperatures at the deposit formation sites are:

Convection pass inlet-gas, 760–1040°C, tube ca. 440°C

Superheat2-gas, 790–900°C, tube ca. 495°C

Multiclone inlet-gas and surface 345–400°C

Recycle feed pipes, 175–230°C

The superheat scale deposit forming was only observed during period when there was high CO emission. The recycle pipe deposits were produced during a period that 20–50% petroleum coke burned.

## 2. Experimental

The samples appear as dark grey or brown in color, irregular in masses and shapes. Prior to examination in

this study, the samples were grounded and passed in an 8-mesh sieve.

### 2.1. SDT/MS technique

A number of pure compounds as reference materials, as well as deposits samples were tested.

An approximately 10 mg sample was placed in a platinum pan and analyzed on an SDT (simultaneous TGA&DTA) 2960 interfaced to a Fisons VG Thermolab mass spectrometer by means of a heated capillary transfer line. The Fisons unit is based on a quadrupole design with a 1–300 atomic mass units (amu) mass range. The sample gas from the interface was ionized at 70 eV. The system was operated at a pressure of  $1 \times 10^{-6}$  torr.

The samples were heated at 20°C/min from room temperature to 1490°C in dynamic nitrogen atmosphere. The DTA reference was 10 mg of pure aluminum oxide.

### 2.2. XRD technique

The XRD diagrams were obtained with a Phillips X-pert X-ray diffraction system using  $\text{CuK}\alpha$  radiation. The XRD patterns were identified with a database of over 80 000 inorganic compounds.

## 3. Results and discussions

The results of the elemental analysis (LECO CHN analyzer and ICP-AES) are summarized in Table 1.

Thermogravimetric analysis (TGA) was used to characterize the various types of ash deposits, illustrated in Fig. 1, and qualitatively shows that there are large differences in the thermal behavior between different samples. The overlay of DTA curves of four deposit samples indicated their different characteristic temperatures, as shown in Fig. 2.

From the endothermic peak at around 1230°C in the DTA curve and the weight loss during 1150–1450°C in the TGA curve, it was determined that all of the four samples consist of  $\text{CaSO}_4$ . The endothermic peak at about 710°C and the weight loss from 500° to 850°C indicate the presence of  $\text{CaCO}_3$  in the deposits from convection pass inlet, multiclone inlet and recycle pipes. Moreover, in the case of the last two samples

Table 1  
Element Analysis of four samples

	Convection (%)	Superheat2 (%)	Multiclone (%)	Recycle (%)
Carbon	2.28	0.313	1.34	3.292
Sulfur	11.12	15.56	8.86	5.54
Calcium	35.33	25.92	37.27	41.19
Magnesium	1.18	0.79	1.00	1.50
Iron	1.52	2.16	4.82	1.54
Aluminum	1.39	2.36	1.88	0.63
Silicon	2.00	3.71	2.44	0.69

from the low temperature sites,  $\text{Ca}(\text{OH})_2$  and a small amount of moisture were detected. The latter is associated with the endothermic peak at  $\approx 420^\circ\text{C}$  and a weight loss beginning at ca.  $350^\circ\text{C}$ .

In order to confirm the above information, pure compounds were tested under the same conditions, for example:  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$  and  $\text{CaSO}_4$ . The TGA and

DTA curves obtained show close agreement with the corresponding composition in the deposits.

Figs. 3–6 present the MS spectrum of the four deposit samples. It can be seen clearly that the  $\text{H}_2\text{O}$  peak ( $m/z=18$ ), associated with the decomposition of  $\text{Ca}(\text{OH})_2$ , appears at around  $400^\circ\text{C}$ ; the  $\text{CO}_2$  peak ( $m/z=44$ ), representing calcination of  $\text{CaCO}_3$ , appears

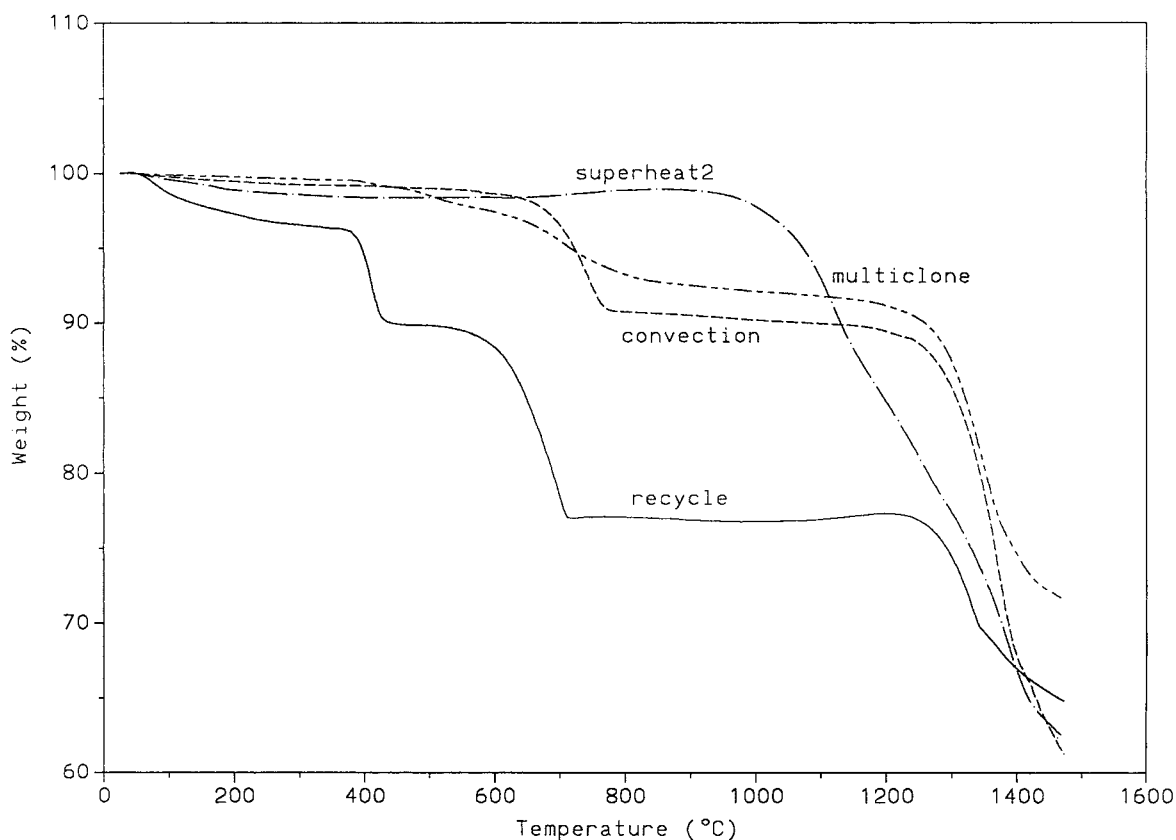


Fig. 1. TGA of various types of ash deposits: ramp  $20^\circ/\text{min}$  upto  $1490^\circ\text{C}$ , in nitrogen atmosphere.

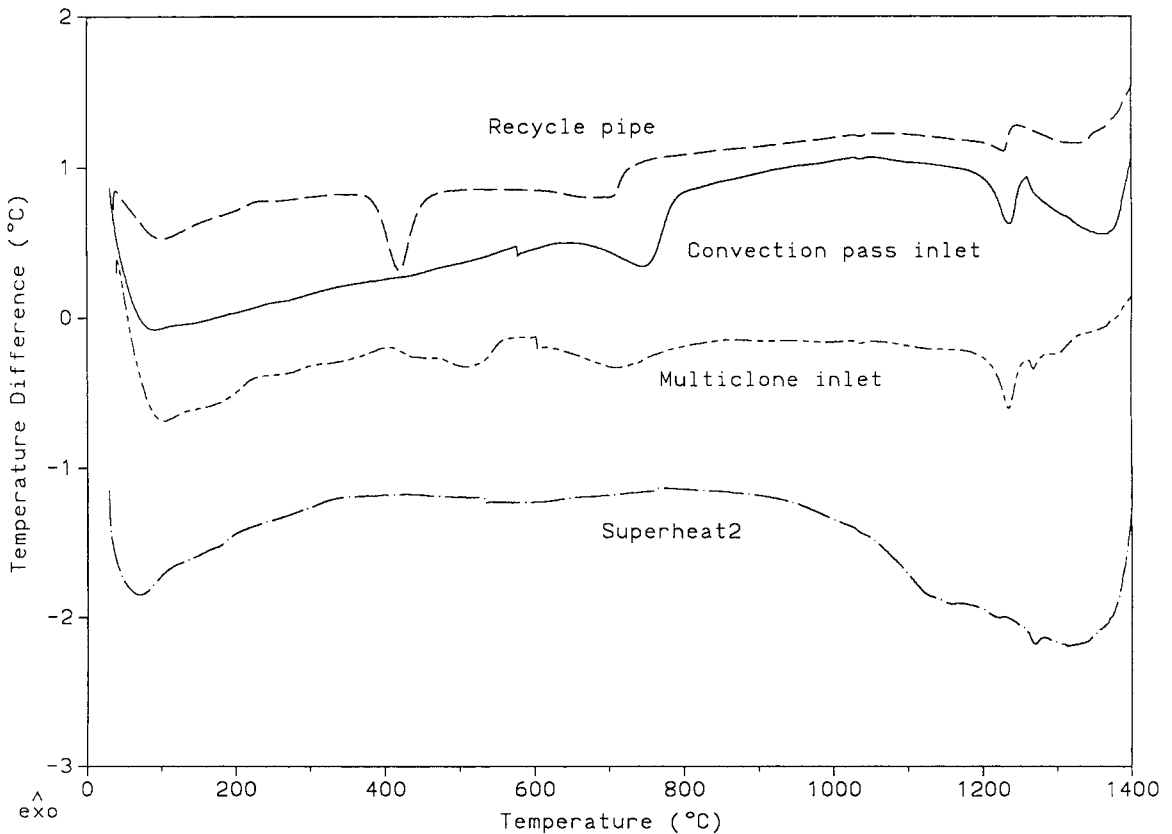


Fig. 2. Comparison of DTA curves of four deposits: ramp 20 C/min upto 1490°C, in nitrogen atmosphere.

at ca. 700°C; and the SO<sub>2</sub> peak ( $m/z=64$ ), due to sulfate decomposition, appears at a temperature >1100°C. This is in good agreement with the information obtained from TGA and DTA curves.

The ICP analysis shows the existence of some minor or trace elements in the deposits, such as Mg, Fe, Si and Al. The XRD analysis confirmed their existence as the oxide form: Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and MgO, except for Al. These components derived mainly from the fuel-ash components and, in some cases, the material used in bed start-up. Other more complicated complex salts could not be determined in this study.

The proportions of Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> and CaSO<sub>4</sub> in the deposits are obtained by multiplying the weight loss over its decomposition step by the ratio of the molecular weight of the evolved gas species to that of parent compounds, respectively. The fraction of CaO existing in the deposits is calculated from the differ-

ence between residue weight and the weight of CaO produced by the decomposition of calcium-based compounds and the determined minor species. The calculation of CaS also relies on the element analysis of total calcium and sulfur in the deposits and the information from TGA curves. Some minor species were not identified, the quantities of these substances are normally so small that their presence makes little difference in the overall results. The possible compounds and their weight percent in the four samples are listed in Table 2.

### 3.1. The major component of the deposits

Thermal analysis and XRD data indicated the major components in each deposit. As shown in Fig. 7, CaSO<sub>4</sub> and CaO are confirmed to be present in all the four samples. Similar to the thermal analysis information, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> are found in the

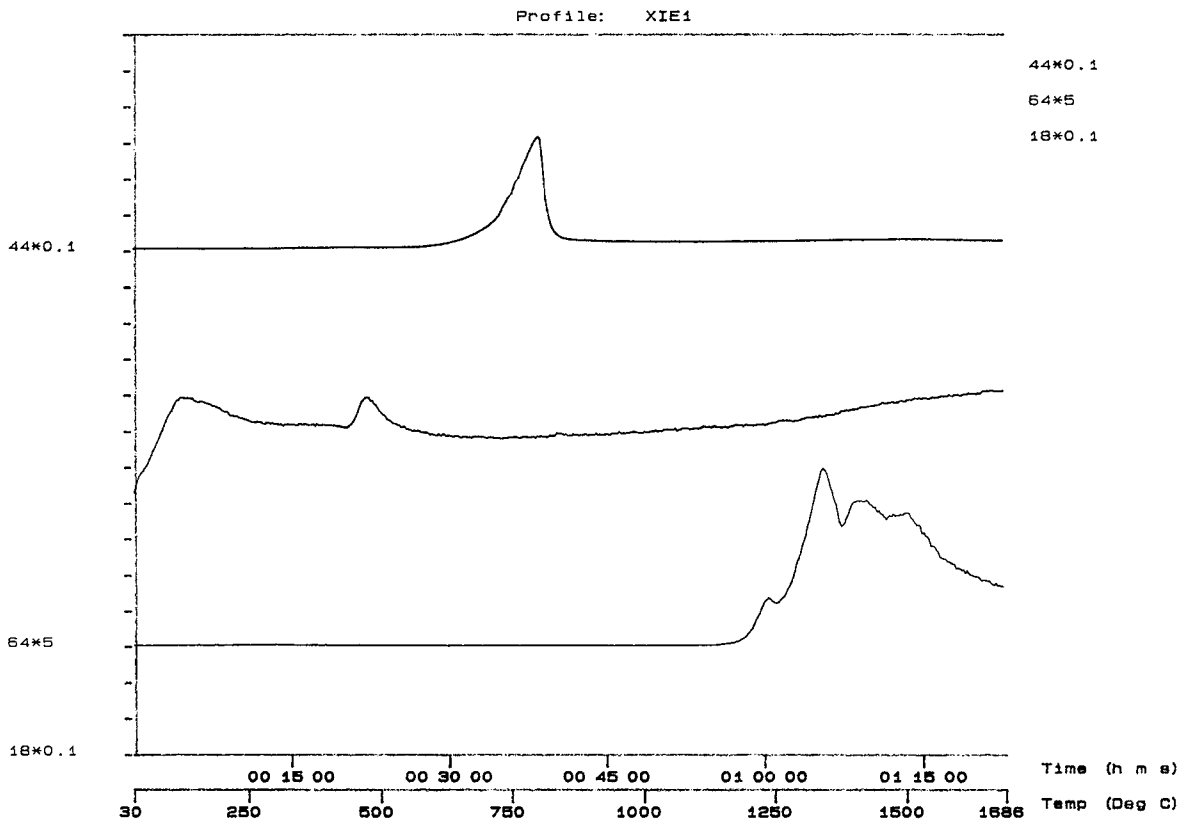


Fig. 3. MS spectrum of deposit from recycle feed pipe.

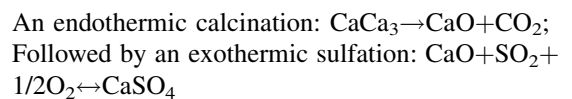
Table 2  
The possible compounds in each sample

Sample	Convection (%)	Superheat 2 (%)	multiclone (%)	recycle (%)
Moisture				3.68
Ca(OH) <sub>2</sub>			7.07	26.48
CaCO <sub>3</sub>	17.8		11.72	29.32
CaSO <sub>4</sub>	57.12	76.79	43.59	22.13
CaO	14.21	8.74	22.59	3.37
CaS		5.00		
SiO <sub>2</sub>	4.28	7.94	5.22	1.48
Fe <sub>2</sub> O <sub>3</sub>	2.17	3.09	6.88	2.20
MgO	1.97	1.31	1.67	2.50

samples taken from low-temperature sites and confirmed by XRD data analysis.

The addition of limestone or other calcium-based sorbent to coal is a well-established method for desulfurization in solid-fuel thermal power station [2]. Limestone injected into a combustor is rapidly cal-

cined into calcium oxide which, in turn, absorbs sulfur dioxide in the absence of oxygen in a two-step process:



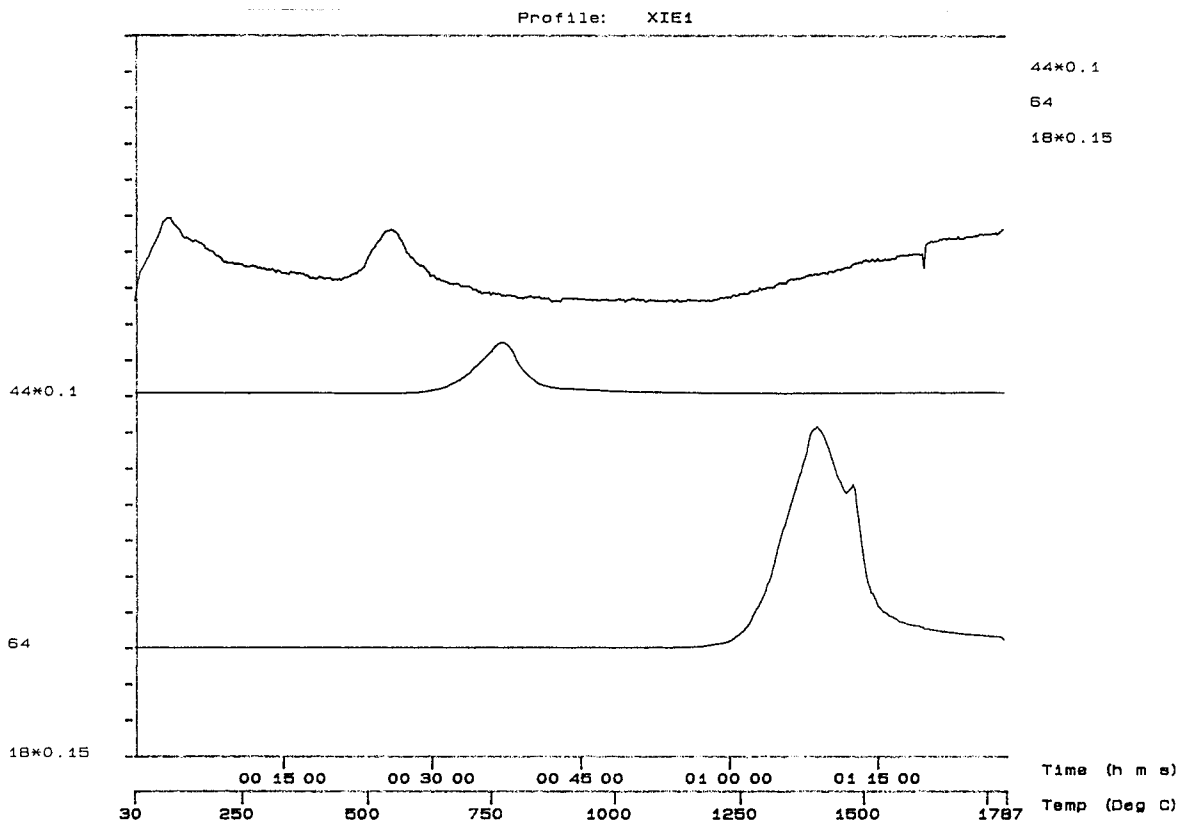


Fig. 4. MS spectrum of deposit from multiclone inlet.

The latter is a reversible reaction, where the forward reaction is dominant at a temperature of ca. 850°C, a temperature at which most fluidized bed combustors (FBCs) operate. However, because of the presence of an outer sulfate layer which blocks the access of  $\text{SO}_2$  to the unreacted  $\text{CaO}$ , conversion of  $\text{CaO}$  is limited to <45% [3]. Consequently, the ash in the combustor usually contains uncalcined limestone,  $\text{CaSO}_4$ , and  $\text{CaO}$ . The excess free lime reacts readily with the possible moisture in the combustor to form  $\text{Ca}(\text{OH})_2$ , another possible component of the ash. At temperatures >400°C, the decomposition of  $\text{Ca}(\text{OH})_2$  becomes prevalent. It explains why only the deposits from low-temperature sites may contain  $\text{Ca}(\text{OH})_2$ .

Calcium-sulfate-bonded deposit is important in systems using finely ground limestone for sulfur capture. In a recent study, the presence of  $\text{CO}_2$  and  $\text{SO}_2$  facilitated the sintering of calcium-bonded

deposits [2]. It is a two-step process, beginning with the sintering of  $\text{CO}_2$  at a temperature as low as 300°C, resulting in the formation of calcium carbonate and reaching a maximum of 750°C just before the decomposition of  $\text{CaCO}_3$ . The process begins again with the formation of  $\text{CaSO}_4$  [4]. Although  $\text{CaSO}_4$  has a reported melting point of 1448°C, some scientist considered that the heat of formation may raise the temperature sufficiently to cause a sticky surface [5]. Actually, the process of deposits formation is directly associated with the degree of sintering of crystalline solids. The latter can be measured by the Tammann temperature, a temperature corresponding to about one-half the absolute melting point of the chemical compound [5]. The melting point of  $\text{CaSO}_4$  will give a Tammann temperature at 860°C [2]. It is reasonable to conclude that, at a typical FBC temperature (~850°C), the sintering of calcium sulfate product layer is

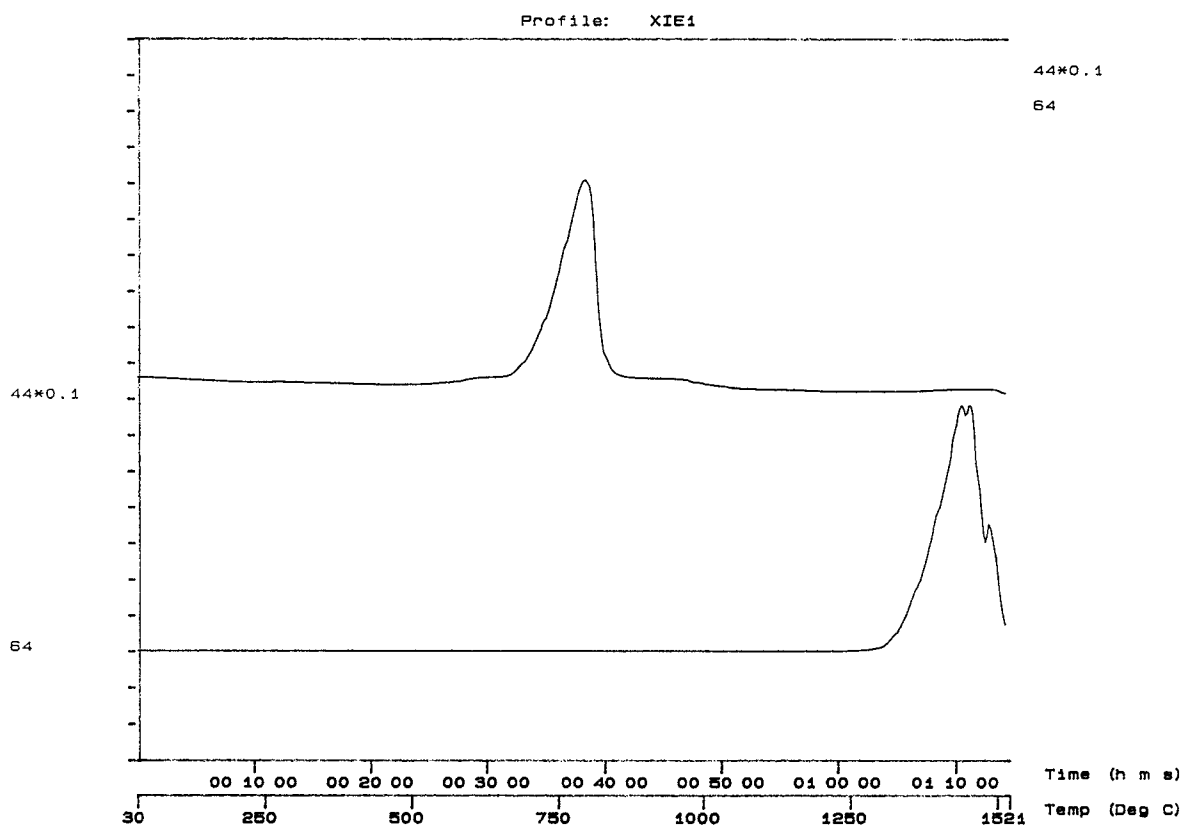


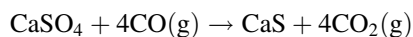
Fig. 5. MS spectrum of deposit from convection pass inlet.

becoming appreciable, and can provide a sticky surface to bond fly-ash particles on the tube surface and furthers deposit formation.

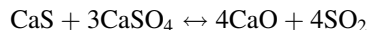
### 3.2. The deposits from superheat scale

As already noted, the deposits from superheat scale were only observed when there was a high CO emission. This is an interesting phenomena.

On comparison, it is found that CaO was present in all the samples, as determined by the XRD technique, whereas CaS was found only in the deposit from the superheat scale. It has been reported that under oxidizing conditions, sulfur is captured as CaSO<sub>4</sub>. Under local O<sub>2</sub>-lean conditions and in the presence of CO, sulfur is captured as calcium sulfide via the following reaction [6]:



XRD analysis indicated that calcium sulfate is the major component in superheat scale deposits. However, the comparison of TGA curves of the four samples revealed that the decomposition temperature of calcium sulfate in the deposit from superheat scale is lower than that of others. It was attributed to the reaction between CaS and CaSO<sub>4</sub>. When a mixture of these two compounds is heated in an inert atmosphere to temperatures >830°C, the apparent solid–solid reaction takes place as follows [7]:



The above reaction also causes the formation of a melt in the calcium sulfide/calcium sulfate system. This low-melting eutectic bond fly-ash particles to each other on the tube surface, and increase deposits formation [8].

In our experiments, the decomposition process of the CaS/CaSO<sub>4</sub> system has been investigated by TGA

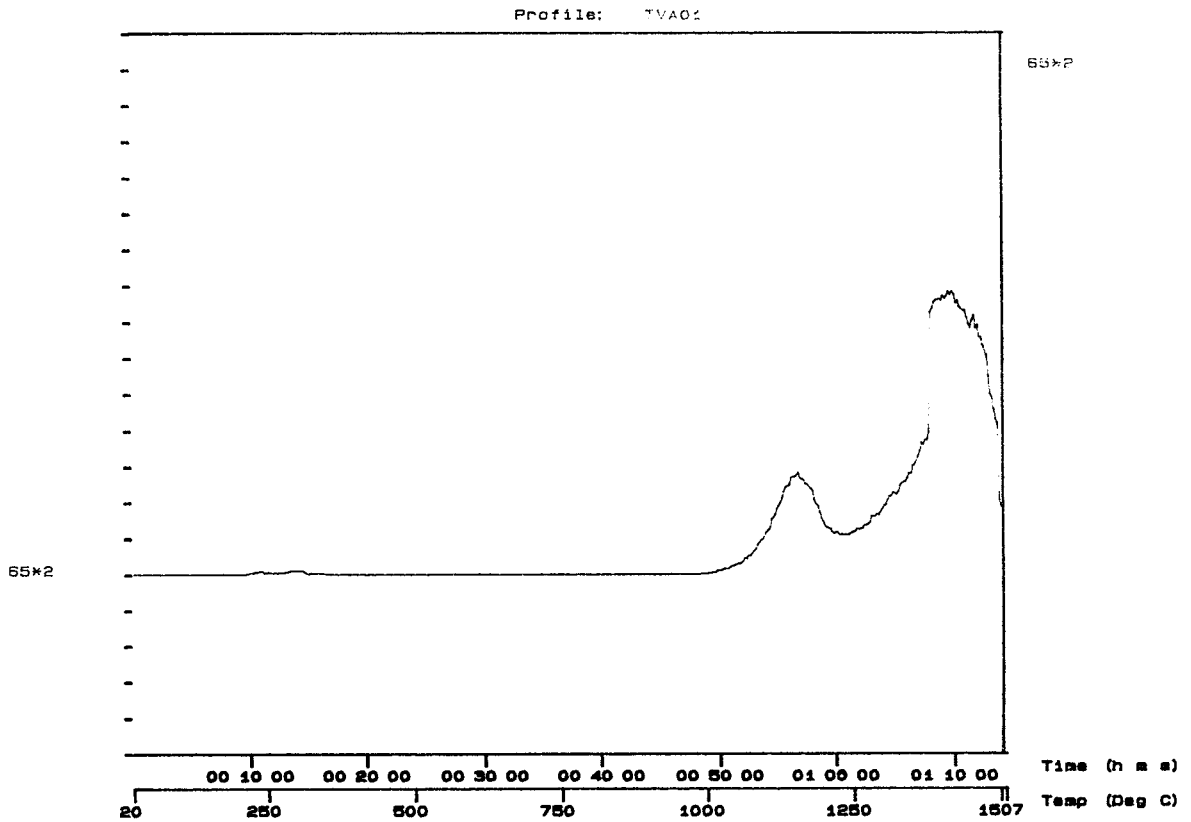


Fig. 6. MS spectrum of deposit from superheater.

using a synthetic blend as well as real deposit ash (see Fig. 8).

From the above information, it can be concluded that CaS exists in the deposit from the superheater as a consequence of high CO emission, and the low-melting CaS/CaSO<sub>4</sub> system resulting in the formation of deposits.

### 3.3. Possible mechanism for the formation of deposits from recycle pipe

Petroleum coke has by-products containing a high fraction of amorphous carbon from the refining operation. These were found to be a viable fuel for generating electricity from steam. On account of their uniformity, they are easy to feed and maintain under a steady state. Unlike coal, petroleum coke is very low in volatiles, low in ash, and contains

minerals not found in coal, such as vanadium and nickel. The latter may introduce new problems when burned [9]. The literature attributes the corrosion and fouling of a boiler fired with residual oil to sodium, vanadium and sulfur in the oil [10]. In particular, vanadium can cause additional concerns of molten-ash agglomeration in the combustor due to molten-ash samples. Fouling occurs when the V<sub>2</sub>O<sub>5</sub> condenses on fly-ash material composed of refractory oxides, such as Fe<sub>2</sub>O<sub>3</sub>, at temperatures above the melting point of V<sub>2</sub>O<sub>5</sub> (690°C). Counter-diffusion of the two components at the particle surface produces a sticky surface, giving the particle a high potential for sticking [11]. Even if the concentration of V<sub>2</sub>O<sub>5</sub> is as low as 4000 ppm, it may cause fouling of the combustor.

When, however, properly handled and fired, petroleum coke can tolerate high vanadium levels because of suppression of the oxidation of vanadium to its



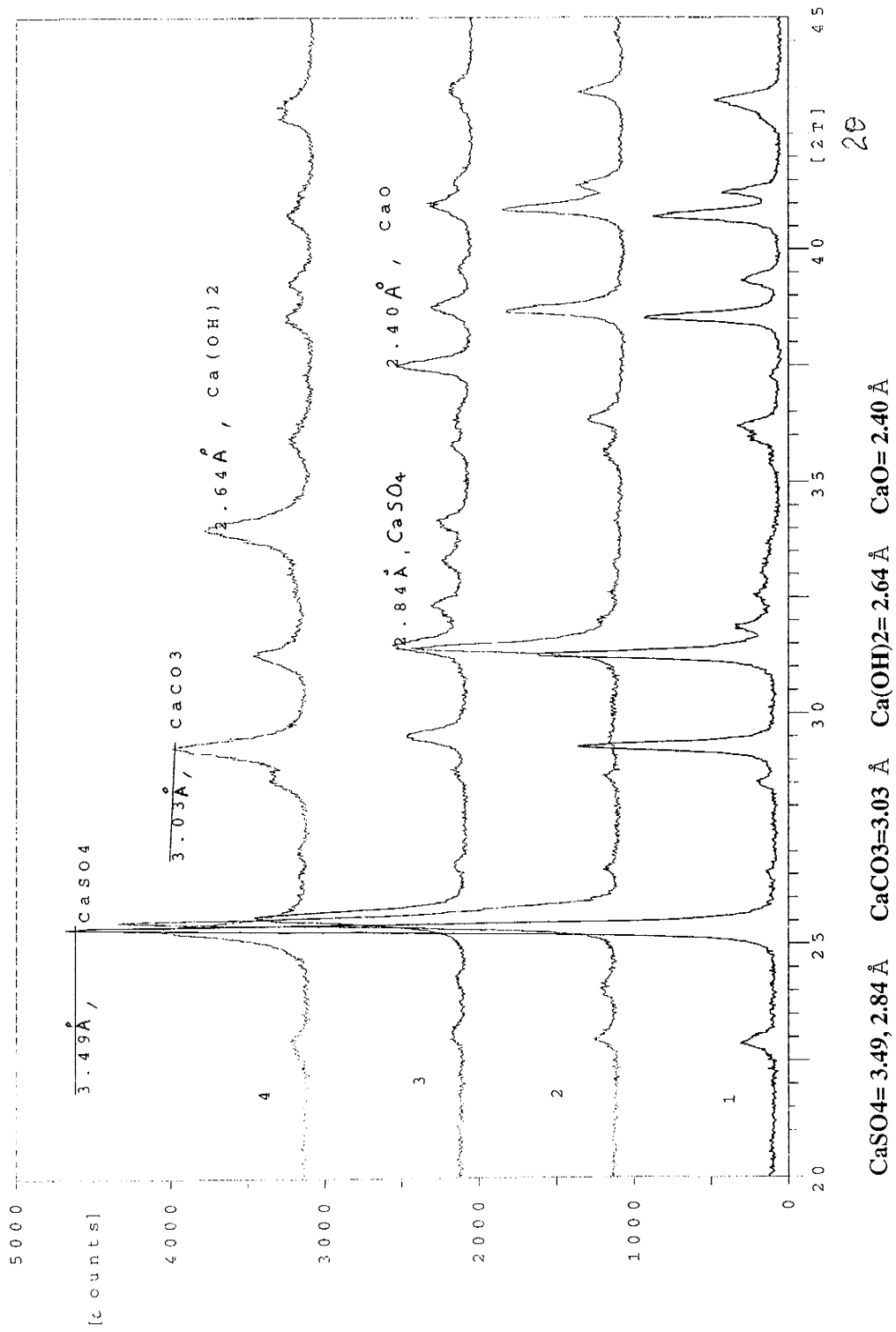


Fig. 7. Major components of the deposits by XRD analysis.

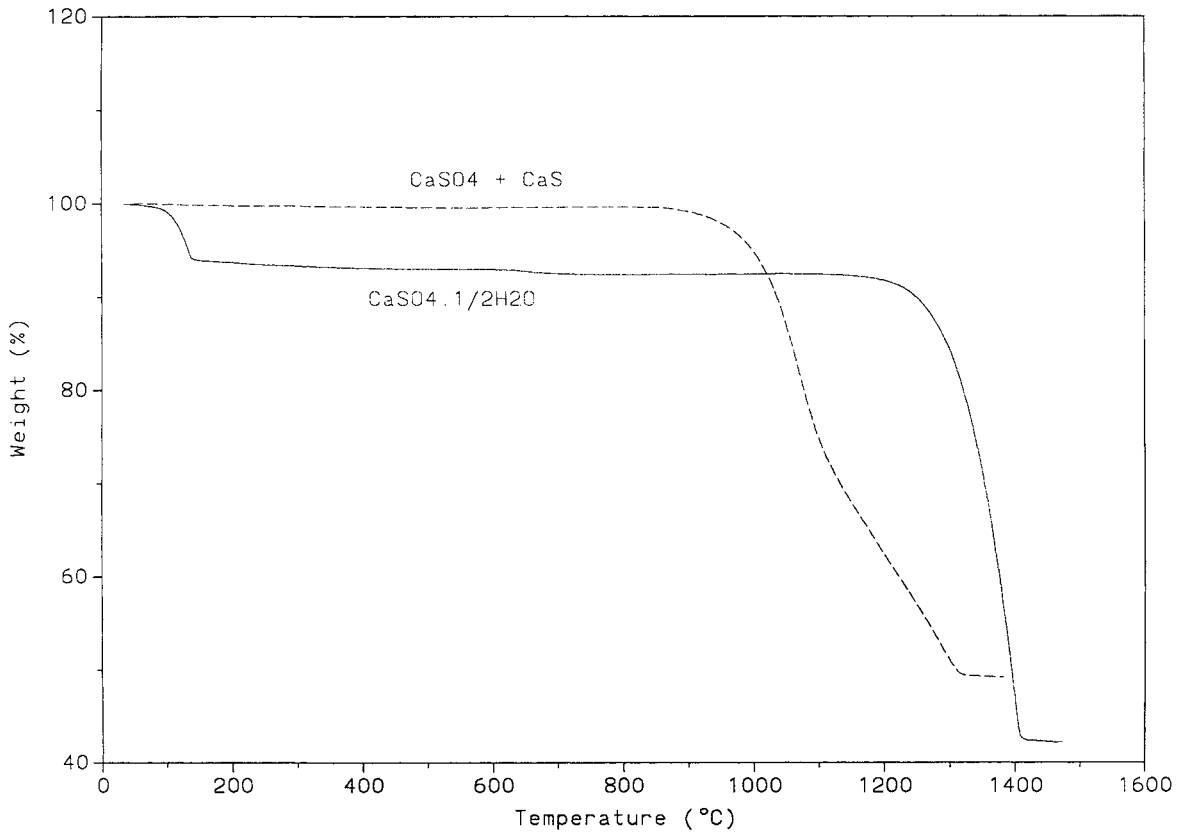


Fig. 8. Comparison of thermal behavior of pure  $\text{CaSO}_4$  and  $\text{CaSO}_4/\text{CaS}$  system: ramp  $20^\circ\text{C}/\text{min}$  upto  $1490^\circ\text{C}$  in nitrogen.

highest oxide state.  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_4$  have very high melting temperatures and are innocuous with regard to the formation of fireside problems [12].

In the sample taken from the recycle feed pipe, 1000 ppm V was detected, that corresponds to 1780 ppm  $\text{V}_2\text{O}_5$  as determined by our ICP analysis. However, further study is needed to confirm the mechanism of the formation of deposits in the recycle feed pipes.

#### 4. Conclusions

Thermal analysis is a desirable technique in determining the composition of complicated ash deposits. Moreover, combined with other techniques, it can provide useful information to propose the mechanism of the formation of deposits.

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