

Characterization of the ash deposits from AFBC system using thermal techniques

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Abstract

Deposit formation is considered as an important problem challenging the improvement of coal-combustion performance. Deposits usually result from the thermal decomposition of coal-borne mineral matter followed by impact and adhesion along the hot gas pathway. Several ash deposit samples collected from the heat exchange tube in the Atmospheric Fluidized Bed Combustor (AFBC) at Western Kentucky University, were used in the present study. The SDT-MS and XRD techniques were employed to examine the sample composition and the mechanism responsible for the deposit formation. This work especially concentrated on the investigation of the chlorine containing species and the behavior of chlorine during the heat treatment. It was proved that the alkali or alkali earth chloride would vaporize significantly under the tested condition, and these compounds were likely responsible for the deposit formation. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

For the next two or three decades, coal is possibly to remain the most important fuel for electrical power generation, industrial or municipal purposes in United States and many other countries. A large variety of studies have been made in order to improve the coal-combustion, conditions and performances. One of the big issues that continue to draw the researchers' attention is the control of deposit formation during the coal combustion.

According to the general understanding, the mineral impurities present in coal are mainly responsible for the fireside problems. Deposition can be considered as a sequence of events consisting of particle arrival and

adherence. The inorganic constituents in coal are transformed into fly ash particles, which may deposit on the heat transfer surfaces of a combustor. Fireside deposits reduce the heat transfer from the hot flue gas to the water-steam cycle leading to the decreased output efficiency for the boiler. In some instances, several types of deposits would cause the increase of corrosion on the heat transfer surfaces [1]. As stated by Bryers, the complexity of fouling and slagging is compounded by the fact that fireside problems cannot be simply represented by a single rate of deposition on a target by ash characterized by a single elemental analysis. Individual species behave differently during combustion and their subsequent flight through the steam generator, depending on various parameters, such as direction of gas flow, oxygen level of the flue gas or surface temperature [2]. A better understanding of deposit composition and the mechanism responsi-

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ble for the deposit formation is essential to the efforts for alleviating the deposit formation.

The thermal analysis technique was utilized in the present study to characterize the deposits, also to explore the mechanism for deposit formation. Especially, this work focuses on the thermal behavior of chlorine containing species in the deposits. Chlorine became a severe problem for furnace walls and superheaters while firing pulverized coal and was believed to be responsible for high-temperature corrosion. Three major forms for the occurrence of chlorine in coal have been proposed: inorganic chlorides, organochlorine compounds and chloride ions in brines and other waters associated with coal [3]. Under combustion conditions, most of chlorine was released as HCl. Through the reaction of UCl on sodium or potassium oxide, the alkali chloride was then produced. Also, alkali chloride is able to vaporize directly from fuel as a consequence of its appreciable vapor pressure. There is a general agreement that alkali compounds play an important role in the deposit formation. The evolved gas analysis was used to monitor the release of chloride ions upon heating the deposit samples, for the purpose of understanding the form of chlorine in the ash particles.

2. Experimental

The deposit samples were collected from the bench AFBC system in Western Kentucky University after the completion of 3-day combustion tests for co-firing coal with PVC and wood pellets. Therefore, unlike the deposits sampled from other tests burning pure coal, a high chloride concentration is found in the deposit samples.

The tested deposits were taken from heat exchanger tube in dense zone. The temperature of the flue gas at the deposit formation sites is 850°C, and temperature of tube surface is about 90°C. The samples are soft, and appear as powder with a dark gray color.

Five standard chlorides, including CaCl₂, KCl, NaCl, MgCl₂ and FeCl₃, were prepared and examined under both inner (N₂) and oxidation (air) atmosphere.

2.1. SDT/MS technique

An approximate 40 mg sample was placed in a platinum pan on a SDT (simultaneous TGA &

DTA) 2960 and was heated from ambient temperature at 20°C/min from ambient temperature to 1300°C in a dynamic high purity helium atmosphere. The evolved gas was analyzed by a Fisons VG Thermolab Mass Spectrometer interfaced to the SDT 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, and the system was operated at a pressure of 1×10^{-6} Torr.

2.2. XRD technique

The XRD diagrams were obtained through a Philips X-pert X-ray diffraction (XRD) system equipped with Cu K radiation. The XRD patterns were identified with a database of over 80000 inorganic compounds.

3. Results and discussions

3.1. Characterization of evolution of chloride from the standard materials

In order to have a better understanding in the evolution of chloride from ash deposits, the standard chloride mixtures were examined using SDT-MS techniques under both inner and oxidation atmosphere. The most possible chlorides existing in the deposit were: CaCl₂, KCl, NaCl, MgCl₂ and FeCl₃, on the basis of elemental analysis and possible mechanism. Therefore, all these five chlorides were selected as the standard chloride to investigate the decomposition of chloride in high temperature.

Based on the results from TGA experiments as illustrated in Fig. 1, almost all the chlorides were evaporated in the high temperature in both inert and oxidation atmosphere. The weight loss in both the atmospheres showed similar results, 86.23 and 87.63%, respectively. As shown in the DTA curve, there are almost no effects of atmosphere on the release or evaporation of chlorides.

Fig. 2 showed the MS spectrum of chloride ($m/z=35, 37$) and chlorine ($m/z=72, 74$) released from the standard mixture chlorides in the air atmosphere. Five chlorides peaks can be clearly identified from MS spectrum and they are corresponded with five standard chlorides selected in the experiments. The evaporation of five standard chlorides in inert atmosphere also showed a similar trend. Although it is still difficult to

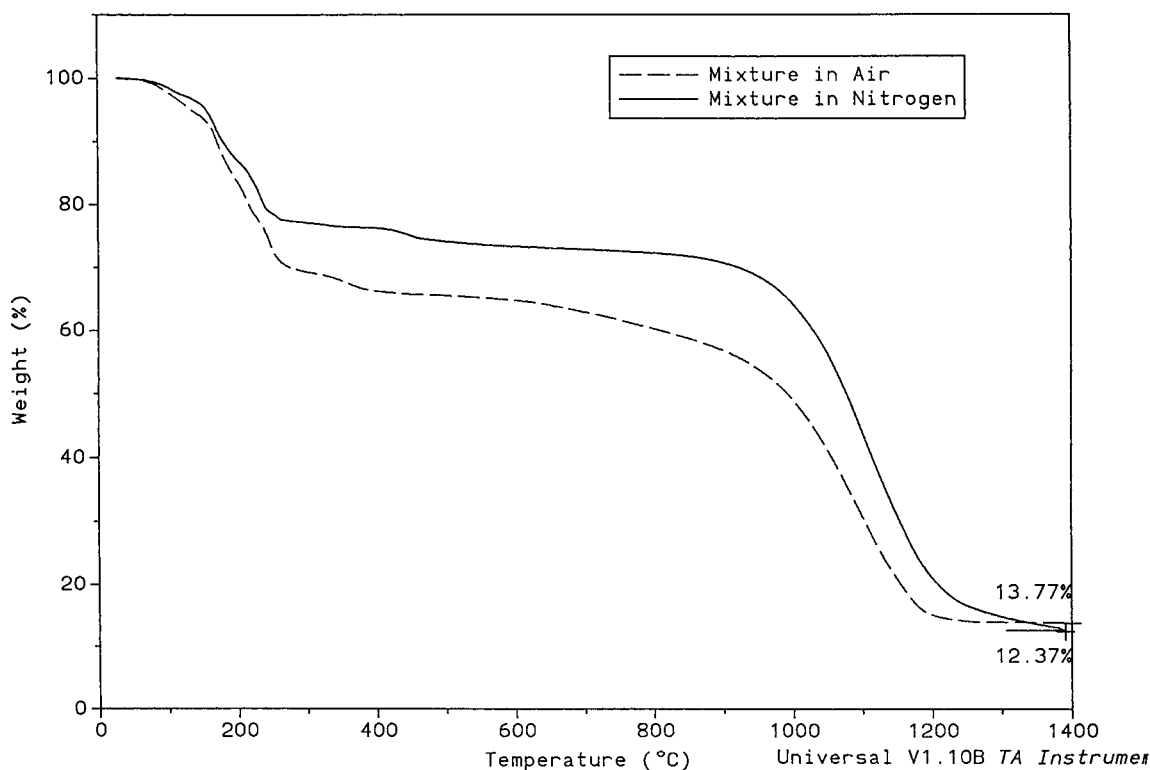


Fig. 1. Comparison of TG curve of chloride mixture in air and nitrogen atmosphere.

exactly identify what kinds of chloride presented in ash samples from SDT/MS techniques due to the shift of melting point of chlorides when the other kinds of salt also presented in the ash samples [4], the MS spectrum, at least, will shed a light on the way of how many chlorides presented in the testing samples and it is possible to identify them when using SDT/MS techniques combined with the other techniques, such as XRD. The melting point of CaCl_2 , KCl , and NaCl are quite similar, 772, 776, and 801°C, respectively, the evolving chloride peak ($m/z=35, 37$) can still be well separated in the MS spectrum as shown in Fig. 2. Therefore, it is suggested that SDT/MS technique is a reliable and useful technique in examining chlorides presented in the ash samples, especially when it is coupled with the other techniques.

3.2. Determination of components of deposit

As shown in the TGA curve in Fig. 3, the sample continued to lose weight since it was heated from

ambient temperature. No apparent stages to separate the weight change due to reaction of one individual compound, however, the DTG curve (Fig. 1) helped us to identify the decomposition process for the different compound. The weight loss before 100°C resulted from the loss of absorbed moisture, which can be inferred from the water ($m/z=18$) peak appearing around 100°C in the MS spectrum (Fig. 4). The weight loss at 570°C was attributed to the decomposition of $\text{Ca}(\text{OH})_2$, which is supported by the DTA characteristic peak and the corresponding water peak in the MS spectrum. The presence of CaCO_3 was proved by the DTA peak at 785°C and the release of CO_2 ($m/z=44$) at the same temperature range as reflected from MS spectrum. Likewise, CaSO_4 was identified using the same approach.

The XRD results also render a strong evidence for the existence of CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 and CaSO_4 in the deposit. In addition, XRD analysis found the substantial amount of KCl present in the deposit sample. Unfortunately, presence of CaCl_2 can not

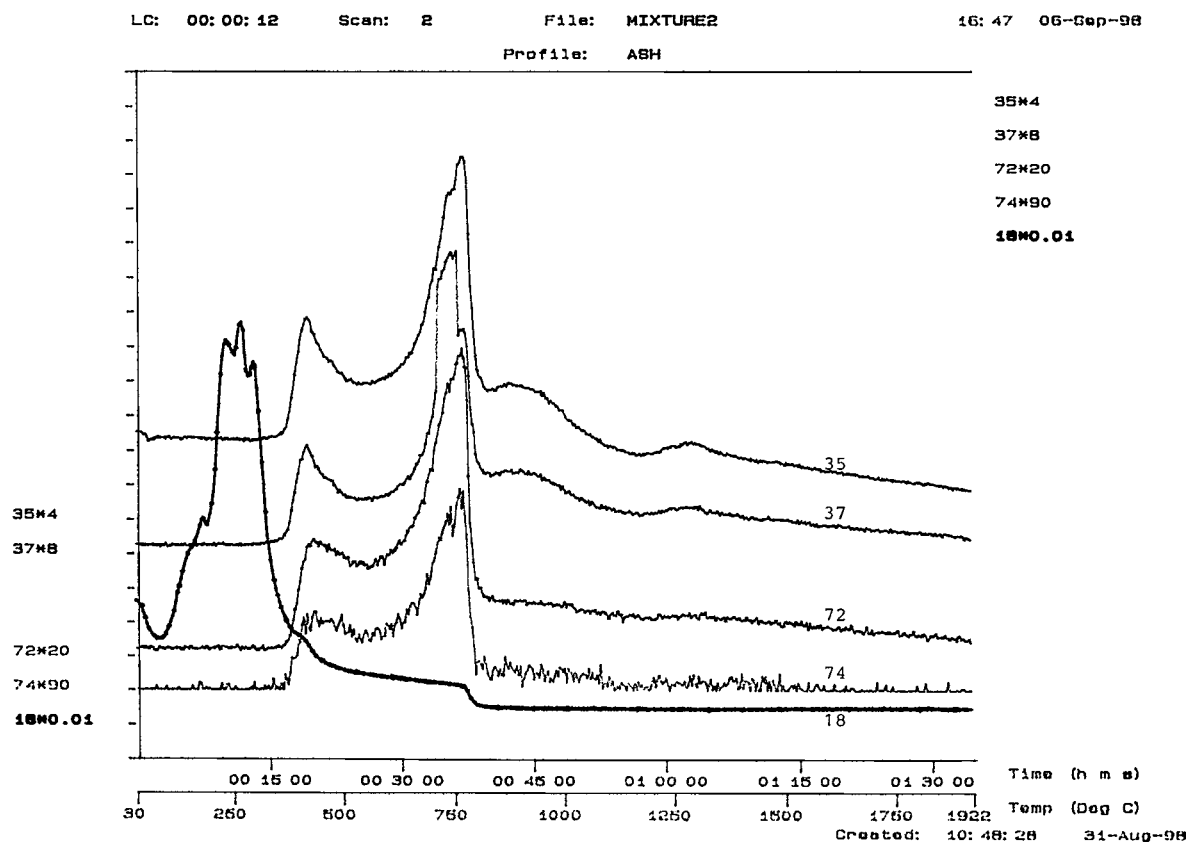


Fig. 2. MS spectrum of chloride mixture pyrolysis under air atmosphere.

be confirmed from XRD diagram, because the major line of CaCl_2 was blocked by that of CaCO_3 . As determined by the IC (ion chromatography) analysis, the concentration of chloride ion in the tested deposit sample was over 17% by weight. The elemental analysis also revealed appreciable amount of Na. It is very possible that sodium presents in the deposit in the form of NaCl. However, such compound has not been found from XRD analysis. This maybe ascribed to the detection limit of XRD instrument, which is 5% by weight. Another possible reason is that the chlorine presents in the complex salt rather than the simple salt. The alkali chloride may bond with alumina or silica to form some kind of product in a complicated form, which is out of the range of this study.

Evolved gas analysis aids in obtaining a comprehensive understanding of the behavior of chlorine-containing species. As illustrated in the MS spectrum, the $m/z=35, 37$ curve, which represents the chloride

ion signal, kept straight before 700°C , and leveled up thereafter. Upon a closer look, it can be found that four different overlapping peaks appear at the temperature range from 700 to 1300°C . It may indicate that the chloride ion is released from four different chlorine-containing species or from different mechanisms. In order to prove that assumption, the SDT/MS tests on the pure chloride salts were carried out.

Five chlorides most possibly existing in the deposit were: CaCl_2 , KCl, NaCl, MgCl_2 and FeCl_3 , on the basis of elemental analysis and possible mechanism. Despite the melting temperature of different metal chloride varies, a common phenomenon was observed for all of the tested chlorides. In an inert atmosphere, once temperature exceeded its melting point, the chloride began to vaporize, as reflected from the weight loss in the TGA curve. This phenomenon is also inferred from the MS spectrum that the chloride peak ($m/z=35, 37$) and the corresponding metal ion

Sample: Ash17
Size: 43.1429 mg

TGA-DTA

File: D:\TA\SDT\DATA\ASH17N.005
Operator: xiew
Run Date: 18-Jun-98 14:36

Comment: 1450@20-30 in UHP He

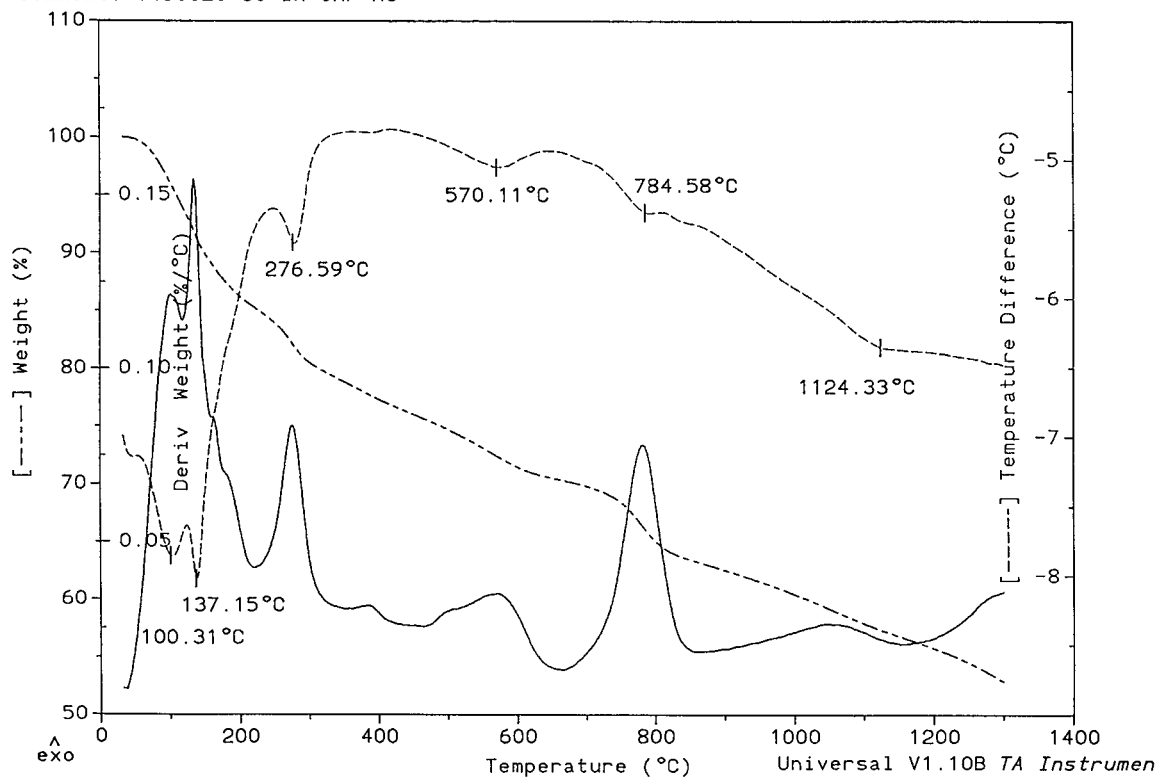


Fig. 3. TG curve of sample ash17 in nitrogen atmosphere.

peak occurred at the temperature above the melting temperature of tested material. It is reasonable to assume that if these chlorides present in the combustor, they are easily volatilized at the combustion condition.

Since melting temperature of investigated substance is strongly dependent on the presence of other salts, it is not suitable using the melting effect exhibiting in the DTA curves for the identification of the chloride [4]. However, as shown in Fig. 2, metal ion peaks: such as Ca ($m/z=40$) and K ($m/z=39$), were observed in the same temperature range as where the chloride ion released, it is suggested that there are appreciable amounts of CaCl_2 and KCl present in the deposit.

Fig. 5 illustrates the MS spectrum of the release of gases when ash deposit was heated in air atmo-

sphere. The same phenomenon was observed in air atmosphere as that of nitrogen atmosphere. Chloride vaporized when the heating temperature is over their melting point. There were also four different overlapping peaks presented in Fig. 5, and indicated, at least, four kinds of chloride-containing species existing in the ash deposit sample. As discussed above, atmosphere has no effect in the release of chloride-containing species from the samples investigated.

3.3. Mechanism responsible for the deposit formation

Both the SDT/MS analysis and XRD results revealed the presence of large amount of calcium containing species in the deposit, the compounds were

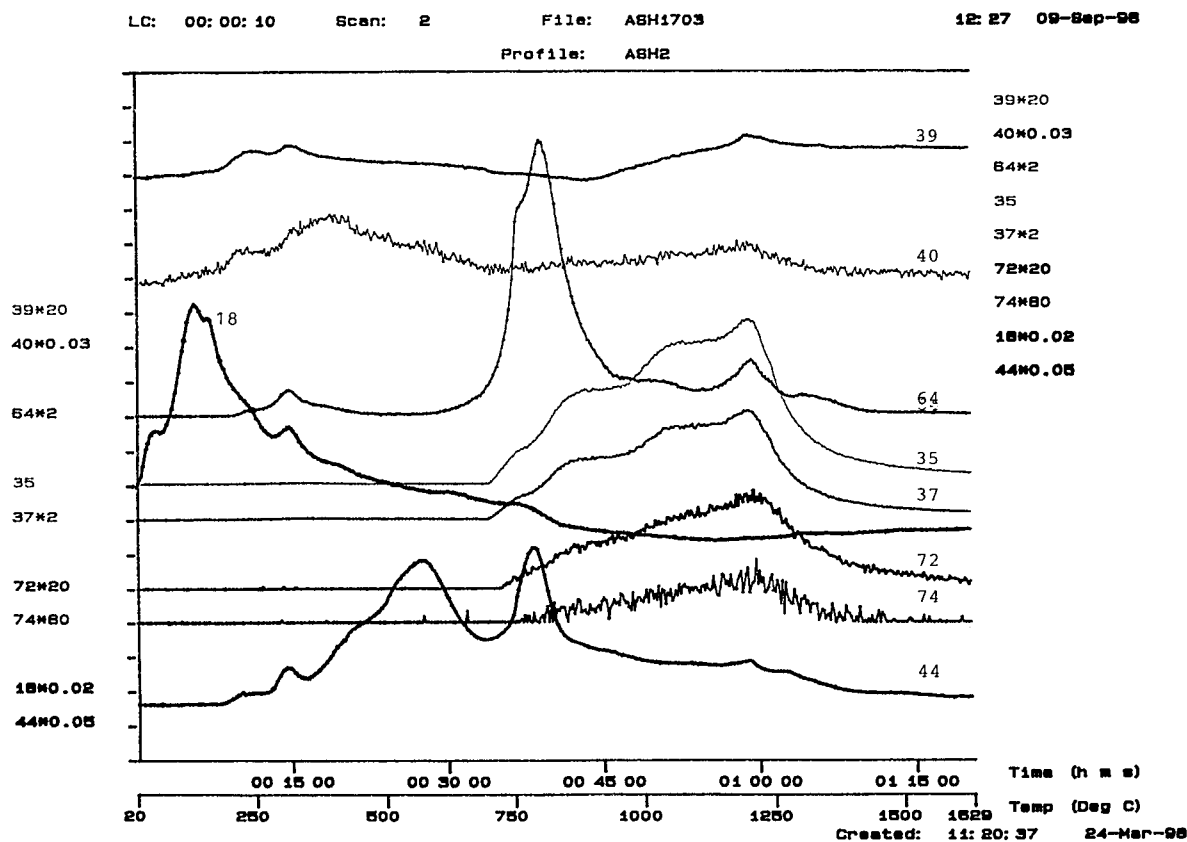
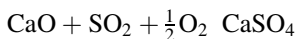


Fig. 4. MS spectrum of sample ash17 in nitrogen atmosphere.

produced as a result of the addition of limestone for the desulfation of the coal-fired boiler. Once limestone is injected into the combustor, it will decompose to CaO and CO₂. CaO is capable of absorbing SO₂, thus CaSO₄ is formed through the following reaction.



Free lime is also utilized to absorb the HCl in the combustor, as:



Unlike burning pure coal, the co-firing test involved in this study was characterized by the high chlorine concentration in the fuel. The source of chlorine are both inorganic, primarily as NaCl present in coal and limestone, and organic, of which polyvinyl chloride plastic is the primary item.

NaCl is a predominant form of sodium in coal; in contrast, potassium in coal occurs largely as non-volatile aluminosilicates. However, potassium can be released from silicates as KCl through exchange reactions with NaCl vapor. Since both NaCl and KCl have appreciable vapor pressure (0.4 and 0.7 kPa, respectively, at 1173 K) at the fluidized-bed combustion temperature range, their vapors are expected to be in the flue gas of AFBC [5]. Numerous studies have revealed that the sodium vapor emission from the combustor is NaCl [6,7]. Thermodynamic calculations also indicated that gaseous NaCl and KCl are the major sodium and potassium carriers, respectively, present in the flue gas of a fluidized-bed combustion of coal [5]. It is generally accepted that alkali metal sulfates, which can be formed by the reactions of alkali chlorides with gaseous sulfur compounds, may react as liquid 'glue' binder to promote inorganic

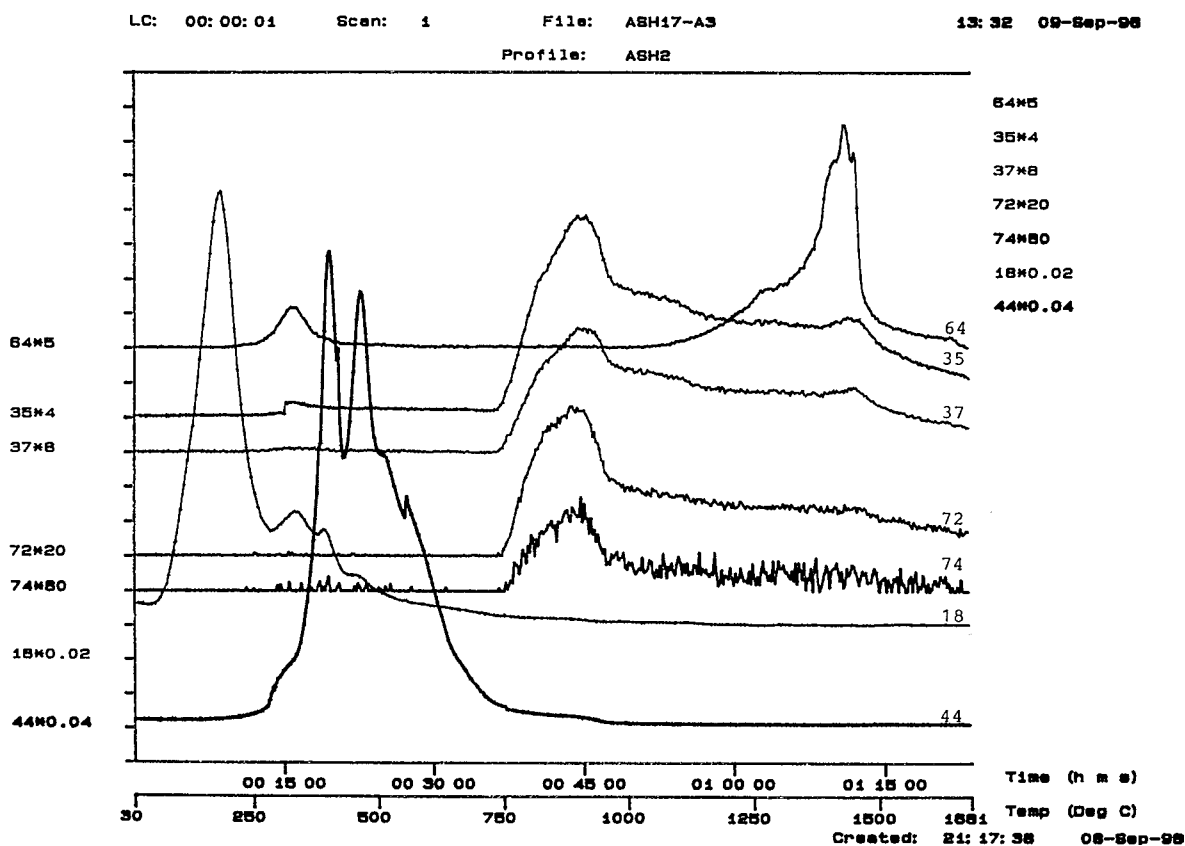


Fig. 5. MS spectrum of sample ash17 in air atmosphere.

deposit formation [8]. However, in this case which has a high concentration of chlorine in the fuel, alkali chloride is likely governing the deposit formation. It is suggested that as the vapor of the alkali chloride reaches the cooler tube surface on the bed heat exchanger, the vapor will directly condense and provide a sticky layer on the tube surface for the further adhesion of bed ash particles.

4. Conclusions

1. Combining the XRD results and SDT/MS analysis, the major constituents of the ash deposit are identified.
2. Evolved gas analysis (TG/MS) provided substantial evidence for the form of chloride present in the deposit sample.

3. It is observed that under laboratory conditions, some metal chloride possibly present in the coal-combustor, such as: CaCl_2 , KCl , NaCl , MgCl_2 and FeCl_3 would begin to vaporize at the temperature above its melting point. The alkali chloride vapor is likely responsible for the deposit formation on the cool surface of the bed heat exchange tubes.
4. SDT/MS technique has a potential ability to identify the chloride presented in the ash samples when combined with other techniques.

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