BEHAVIOR OF ASH-FORMING MINERAL MATTER IN COAL DURING CHEMICAL CLEANING WITH MOLTEN CAUSTIC

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ABSTRACT

Coal-derived mineral matter, obtained by low-temperature ashing of Kentucky No. 11 coal, as well as mineral-grade samples of quartz, illite, kaolinite, and pyrite, were treated with various ratios of molten caustic (NaOH, KOH, and 1:1 NaOH-KOH mixtures) at 370°C for 1-2 hours to study the nature of reaction products obtained under the conditions of chemical cleaning of coal by the molten caustic leaching (MCL) process. Under these conditions, most of the reactions of minerals with caustic were very rapid, being complete in less than 10 minutes. The reaction products were characterized by x-ray diffraction, thermogravimetric analysis, atomic absorption spectrophotometry, and chemical analysis. The nature of these products was related to the stoichiometry of the reaction and was useful in explaining the process chemistry and in developing regeneration schemes for the spent caustic.

INTRODUCTION

The reaction of pyrite and coal with molten caustic has been studied first by Masciantonio (1) and then by Meyers and Hart (2) as a potential basis for the chemical cleaning of coal. It became rapidly obvious that molten caustic leaching (MCL) is of unparallelled effectiveness for removing sulfur and ash-forming minerals from coal, leading to the development of the Gravimelt Process by TRW (3-7). The process has been shown to be especially effective for the removal of organic sulfur (7-9).

However, to make this process economical, spent caustic will have to be regenerated for recycling. And to propose and test reactions for the regeneration of caustic, the nature of the reaction products anticipated in the spent caustic needs to be known. Thus, it is important to study the reactions of ash-forming minerals, present in coal, with molten caustic under conditions similar to those of the MCL process. We have undertaken such a study using quartz, kaolinite, illite, and pyrite as the major minerals found in coal and testing coal-derived mineral matter in the form of a low temperature ash.

EXPERIMENTAL

Materials

Quartz (St. Peters sand); kaolinite ($Al_2Si_2O_5(OH)_4$) from Twiggs Company, Georgia; illite ($KAl_2[Si_3AlO_{10}(OH)_2]$, 85% pure, from Ward's Natural Science Establishment, Inc.; and pyrite, both mineral-grade and coal-derived, were used in this study. The low temperature ash (LTA) of a Kentucky No. 11 coal was prepared by using standard procedures. Reagent-grade NaOH and KOH were powdered for easy mixing. Because of

its higher moisture content, the KOH was dried by heating above 410°C for several hours. The powdered NaOH and heated KOH contained 3% and 7% moisture, respectively, as determined by titrimetric assay or TGA.

Procedures and Analyses

Experiments were performed by mixing 1.5 g of quartz with powdered NaOH, KOH, or a 1:1 NaOH + KOH mixture using caustic-to-quartz mole ratios of 2:1, 4:1, 6:1, and 8:1. Similarly, 2 to 3 g each of kaolinite and illite were mixed with appropriate amounts of the above caustics to obtain caustic-to-clay mole ratios of 5:1, 10:1, 15:1, and 20:1. The mixtures of caustic and minerals were heated in an Inconel crucible at 370°C for 2 hours under a slow purge of helium. The reaction products were removed from the crucible while hot and then transferred to a glove box for cooling. The reaction mixture was powdered in an inert atmosphere of a glove box, and the powders were analyzed by x-ray diffraction (XRD) with a Picker x-ray diffractometer using Mo K_α radiation. All the time, the samples were protected from moisture during the analysis by purging the sample holder with nitrogen.

Products from the reaction of quartz with 1:1 NaOH + KOH were also washed with methanol to remove excess caustic. The residues were then dissolved in water and analyzed for Na and K by ion chromatography (IC). These data were used to calculate the Na_2SiO_3 and K_2SiO_3 mole fractions in the reaction products as a function of caustic-to-quartz mole ratio in the original mixture.

In addition, the reactions of quartz, kaolinite, illite, pyrite, and the low temperature coal ash with NaOH, KOH, or 1:1 NaOH + KOH mixtures were studied by thermogravimetric analysis (TGA) using a DuPont 951 Thermogravimetric Analyzer. The samples were prepared by mixing the appropriate amount of caustic with mineral matter or coal ash to achieve the desired caustic-to-mineral mole ratio (6:1 for quartz, 20:1 for kaolinite and illite, 10:1 for pyrite, and 2:1 for the LTA). For a typical TGA experiment, 30-50 mg of the sample mixture (mineral plus caustic) was transferred to the TGA pan and heated continuously, or isothermally at 370°C, under a nitrogen purge (50 mL/min.). The reaction products were subsequently washed with methanol or water, and the washed products were analyzed by chemical methods and by XRD.

RESULTS AND DISCUSSION

Reactions of Caustic with Quartz

An x-ray diffraction pattern of the reaction product obtained by heating a 2:1 NaOH-to-quartz mixture at 370°C for 2 hours is shown in Figure 1. The main product has been identified as sodium metasilicate (Na_2SiO_3). A small amount of unreacted quartz was also present. At higher NaOH-to-quartz ratios, the reaction product was mostly sodium orthosilicate, Na_4SiO_4 (a representative XRD pattern of this product is shown in Figure 2). Also, unreacted NaOH was present at the higher NaOH-to-quartz mole ratios. The reactions can be described by the following equations:

$$SiO_2 + 2\ NaOH \xrightarrow{370°C} Na_2SiO_3 + H_2O\uparrow \qquad \text{(Eq. 1)}$$

$$SiO_2 + 6\ NaOH \xrightarrow{370°C} Na_4SiO_4 + 2\ NaOH + 2\ H_2O\uparrow \qquad \text{(Eq. 2)}$$

where 2 or 4 moles of NaOH react with 1 mole of quartz to form Na_2SiO_3 or Na_4SiO_4, respectively, and water is also one of the products. The products are consistent with the equilibrium diagram of the Na_2O - SiO_2 system which shows the formation of Na_2SiO_3 and Na_4SiO_4 with a richer Na_2O content in the reaction mixture (10). Although Kautz et al. (11) have found Na_4SiO_4 and $Na_6Si_2O_7$ as products in the NaOH - Na_2SiO_3 - SiO_2 reaction system, the absence of $Na_6Si_2O_7$ in our study is probably due to our lower temperature.

When KOH was used as the caustic, potassium metasilicate, K_2SiO_3, was the main reaction product at all KOH-to-quartz mole ratios. A representative XRD pattern of the reaction product obtained at the 6:1 KOH-to-quartz ratio is shown in Figure 3. This reaction can be shown by the following equation, in which only 2 moles of KOH are used for each mole of quartz to result in K_2SiO_3, water, and unreacted KOH:

$$SiO_2 + 6\ KOH \xrightarrow{370°C} K_2SiO_3 + 4\ KOH + H_2O\uparrow \qquad \text{(Eq. 3)}$$

The other potential product, potassium orthosilicate (K_4SiO_4), was not found. It is also not listed in the powder diffraction file.

When the 1:1 NaOH + KOH mixture was employed in the reactions with quartz, the products were a mixture of only Na_2SiO_3 and K_2SiO_3. Surprisingly, no Na_4SiO_4 was found in the reaction products when both NaOH and KOH were present, even at higher caustic-to-quartz ratios. Thus, 2 moles of the mixed caustic were always used up in the reaction for each mole of quartz.

From the IC results for Na and K, obtained during the analysis of the reaction products from treating quartz with various amounts of the 1:1 NaOH + KOH mixtures, the relative amounts of Na_2SiO_3 and K_2SiO_3 were calculated. The data for Na and K, converted to Na_2SiO_3 and K_2SiO_3, respectively, are shown in Figure 4 as a function of the amount of caustic. As can be seen, the ratio of Na_2SiO_3 to K_2SiO_3 increased with increasing caustic-to-quartz mole ratio, indicating that under these conditions quartz forms preferentially Na_2SiO_3. This unforeseen result has implications for chemical coal cleaning by MCL, since the spent caustic will be enriched in KOH, thus requiring less makeup KOH to maintain the 1:1 NaOH-KOH ratio in the mixed caustic used for leaching.

Reactions of Caustic with Clays

The clay minerals kaolinite and illite reacted with molten NaOH to form $NaAlO_2$ and Na_2SiO_3 at all NaOH-to-clay mineral ratios, i.e., 5:1, 10:1, 15:1, and 20:1. A representative XRD pattern of the NaOH-kaolinite reaction product at the 20:1 ratio is presented in Figure 5. Unreacted kaolinite, or illite, was observed in the product when reaction mixture contained 5:1 NaOH-to-clay ratio, and unreacted NaOH was found at 15:1 and 20:1 NaOH-to-clay ratios.

The reactions of excess NaOH with kaolinite and with illite can be shown by equations 4 and 5, respectively:

$$Al_2Si_2O_5(OH)_4 + 20\ NaOH \xrightarrow{370°C} 2\ NaAlO_2 + 2\ Na_2SiO_3 + 14\ NaOH + 5\ H_2O\uparrow \quad \text{(Eq. 4)}$$

$$KAl_2[Si_3AlO_{10}(OH)_2] + 20\ NaOH \xrightarrow{370°C} 3\ NaAlO_2 + 3\ Na_2SiO_3 + 11\ NaOH + 5\ H_2O \quad \text{(Eq. 5)}$$

Similarly, kaolinite and illite reacted with molten KOH to form the analogous products $KAlO_2$ and K_2SiO_3 at all caustic-to-clay ratios. A representative XRD pattern of the products of the KOH-illite reaction at a 20:1 KOH-to-clay ratio is shown in Figure 6.

Reactions of Caustic with Pyrite and LTA

The reaction of pyrite with molten NaOH has been studied by Chiotti and Markuszewski (12). They have proposed equation 6 under reducing and equation 7 under non-reducing conditions:

$$2\ FeS_2 + 11\ NaOH + 1/2\ C \longrightarrow 4\ Na_2S + 2\ NaFeO_2 + 1/2\ Na_2CO_3 + 5\ 1/2\ H_2O \quad \text{(Eq. 6)}$$

$$FeS_2 + 5\ NaOH \longrightarrow 1\ 5/6\ Na_2S + 1/6\ Na_2SO_3 + 2\ 1/2\ H_2O \quad \text{(Eq. 7)}$$

In both cases, Na_2S and $NaFeO_2$ were the main reaction products, and approximately 5 moles of NaOH were used for the reaction with 1 mole of pyrite.

The mineral matter in the low temperature ash (LTA) of coal is composed mostly of quartz, pyrite, and clay minerals. Therefore, the anticipated products from molten caustic reaction with low temperature ash are Na_2SiO_3, $NaAlO_2$, Na_2S, and $NaFeO_2$, and the analogous potassium salts K_2SiO_3, $KAlO_2$, K_2S, and $KFeO_2$. No XRD patterns were obtained, however, since the amount of LTA sample was too small.

TGA Studies

The mineral-caustic reactions were also studied by TGA. For the reaction of quartz with caustic, the TGA in Figure 7 shows an incipient reaction at about 240°C, a more vigorous reaction at 310°C, and completion at 340°C. The TGA curves for the caustic reactions with other minerals were comparable. The isothermal plot (wt. % vs. time) at 370°C indicated that the reaction at this temperature was very fast and was completed in less than 10 minutes. The amount of weight loss, due to water evolved in this reaction, also supports the formation of Na_4SiO_4 and K_2SiO_3 as the main products of reactions with NaOH and with KOH, respectively, at 6:1 caustic-to-quartz ratios.

Figure 7 shows the isothermal TGA plots of the reactions of NaOH with low temperature ash (Kentucky No. 11 coal) and with mineral-grade pyrite. Both reactions were also very fast and were completed within 10 minutes.

Similarly, the clay minerals kaolinite and illite and a coal-derived pyrite reacted very fast with molten NaOH. Again, the reactions were completed in less than 10 minutes. Comparable results were obtained using KOH and the 1:1 NaOH + KOH mixture as the caustic.

CONCLUSIONS

This study shows that coal mineral matter can react with fused or molten caustic at 370°C in a much shorter time of heating than that commonly used in the MCL process for chemical cleaning of coal. The reaction products are mostly Na_2SiO_3, $NaAlO_2$, Na_2S and $NaFeO_2$ plus the analogous potassium compounds when a 1:1 NaOH + KOH mixture is employed as the molten caustic. It is, therefore, possible to calculate the amount of caustic that will be used up in reactions with mineral matter in a particular coal.

These reaction products are water-soluble, but they can form insoluble complex aluminosilicates when present together. Such insoluble aluminosilicates are expected to form during the countercurrent washing with water, and they will probably stay with the coal and the sodium carbonate (13). Fortunately, these are soluble in acid (aqueous H_2SO_4 or HCl) and, therefore, can be removed during the subsequent acid-washing step. Soluble silicates could then be removed from the waste streams by liming to form the insoluble calcium silicate.

ACKNOWLEDGMENTS

Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Assistant Secretary for Fossil Energy through the Pittsburgh Energy Technology Center. We gratefully acknowledge some experimental assistance from John Finn and helpful discussions with Dr. Premo Chiotti, Dr. Colin Chriswell, and Dr. Kenneth Windom.

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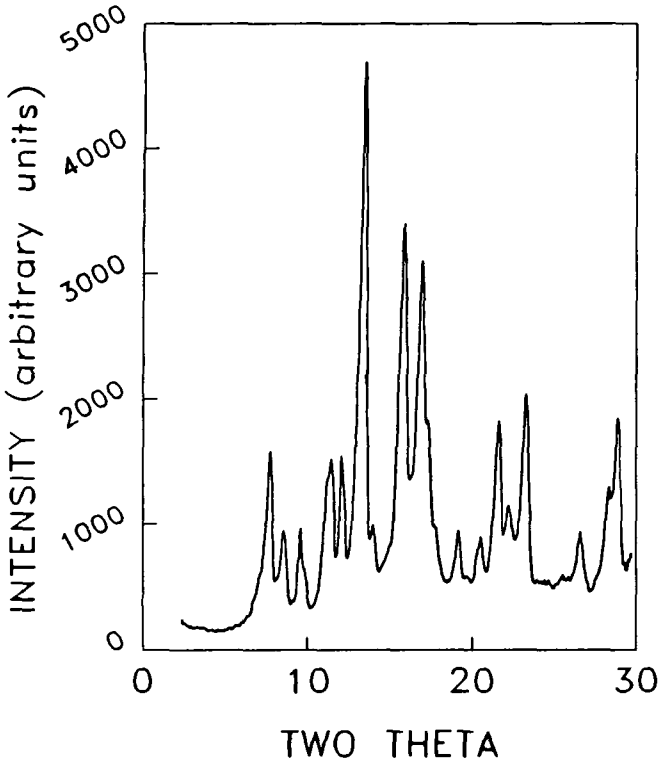

Figure 1. Typical XRD pattern for products from the reaction of SiO_2 with NaOH.

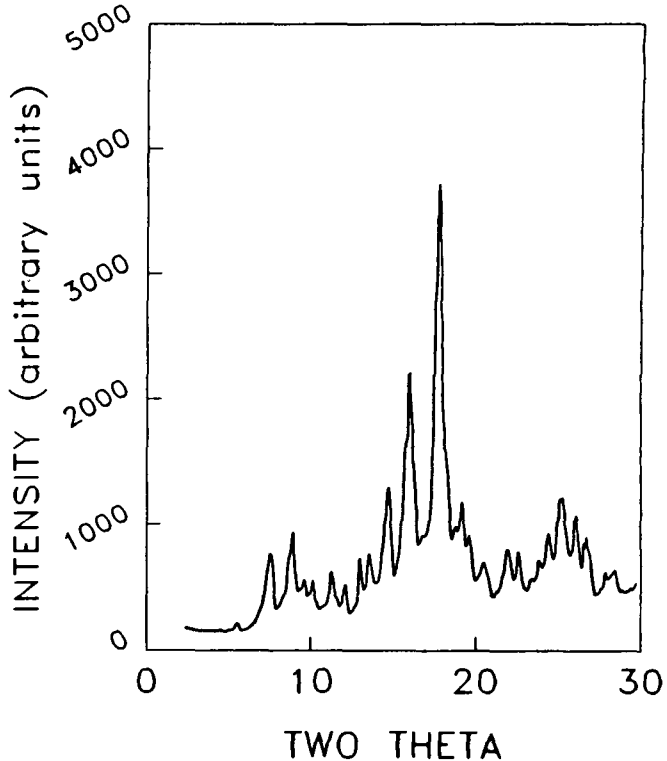

Figure 2. Typical XRD pattern for products from the reaction of SiO_2 with excess NaOH.

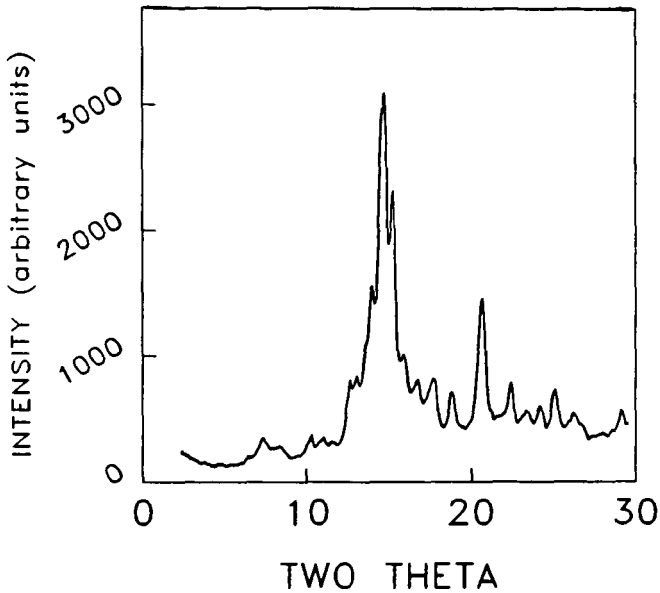

Figure 3. Typical XRD pattern for products from the reaction of SiO_2 with excess KOH.

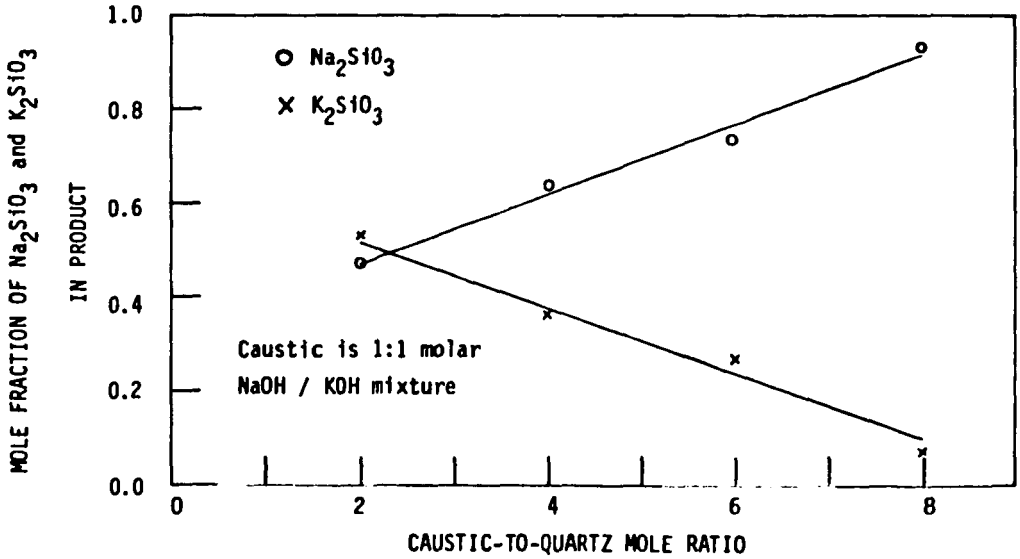

Figure 4. Mole fraction of Na_2SiO_3 and K_2SiO_3 in the product from the reaction of caustic with quartz.

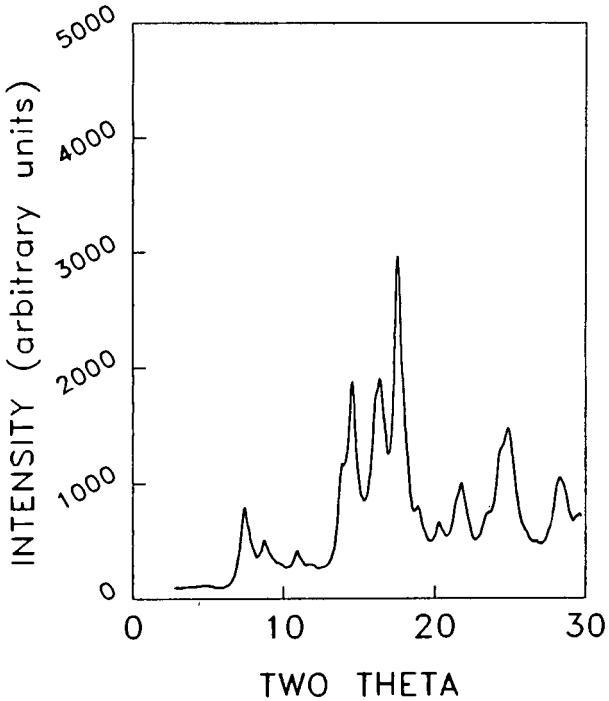

Figure 5. Typical XRD pattern for products from the reaction of kaolinite with excess NaOH.

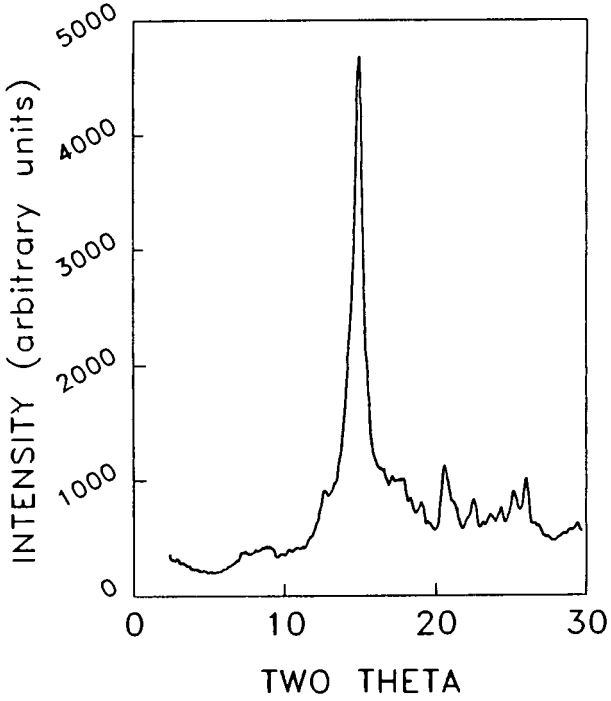

Figure 6. Typical XRD pattern for products from the reaction of illite with excess KOH.

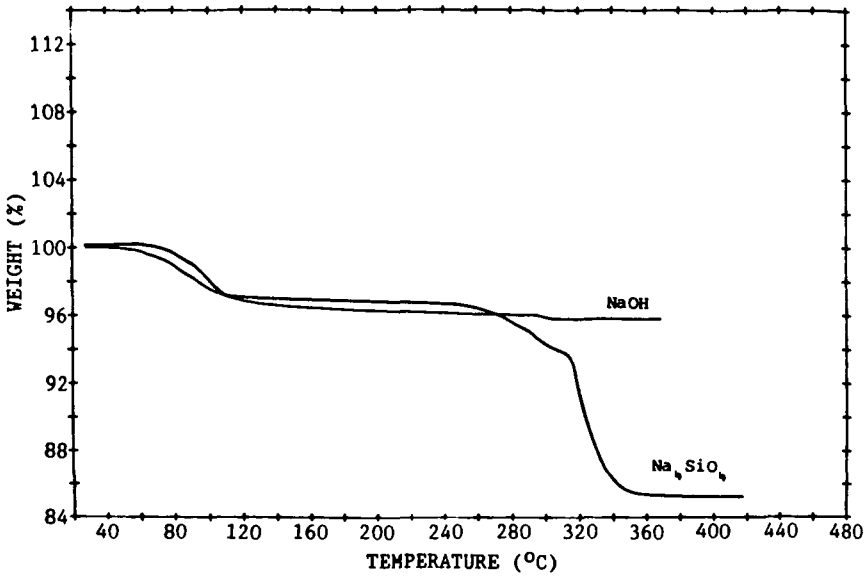

Figure 7. TGA results for the reaction of quartz with NaOH.

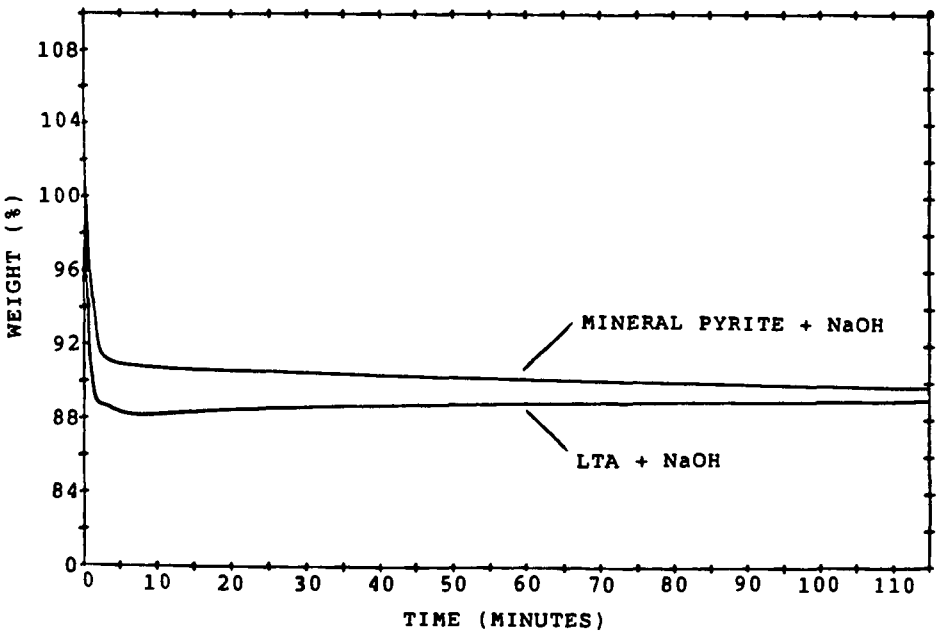

Figure 8. Isothermal TGA curves for the reaction of NaOH with mineral-grade pyrite and a low-temperature coal ash.