Effect of Selected Minerals on High Temperature Properties of Coke

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Abstract

Selected minerals were added to an industrial coal blend and coked to determine whether elements in different mineral forms change coke properties. Mineralogy can influence dilatation, fluidity, coke texture, and catalyze gasification reactions of carbon at 1100°C and 1500°C.

Introduction

Coke properties are important for the efficient operation of the blast furnace. It must supply carbon for the combustion and reduction process while remaining large and relatively unreactive as it passes through the blast furnace. Blast furnace performance has been related to the strength of coke as measured by standard tumbler tests at ambient temperatures (e.g., micum, ASTM) and coke strength after reaction (CSR) to CO_2 at 1100°C.

Although several papers have shown that the CSR test does not simulate the reaction and degradation of coke in the blast furnace (1,2); the test is related to blast furnace performance (2, 3) and considered a good relative indicator of coke quality in the chemical reserve zone of the blast furnace. Several models or formulas have been developed to predict CSR from coal properties and have been reviewed in the literature (4, 5). Earlier Canadian research has shown that ash chemistry, coal rank and thermal rheological properties must all be considered to accurately predict CSR properties for Canadian and some Appalachian coals, thus:

$$CSR = 52.7 + 0.0822\,(c+d) - 6.73\,(MBI)^2 + 14.6\,Ro, \quad \text{where}$$

MBI estimates the ratio of basic/acid oxides in coke from coal chemistry:

$$MBI = \frac{100 \times \%\ ash \times [Na2O + K2O + CaO + MgO + Fe2O3]}{[(100-VM)x(SiO2 + Al2O3)]}$$

Sensitivity analysis of these equations shows that a change in ash chemistry (i.e. minerals) in coal can play a dominant role in determining the CSR of cokes. The formulas imply that all basic oxides in the coke contribute equally to CSR. Selected minerals were added to an industrial coal blend and carbonized to determine how an element in different mineral forms can affect coke properties.

Experimental

Minerals (0.2-2%) crushed to -60 mesh were added to an industrial coal blend and carbonized in CANMET's 460 mm wide (350 kg) pilot coke oven. Minerals and chemicals included: kaolin, quartz, plagioclase, orthoclase, muscovite, bauxite, rutile, apatite, gypsum, calcite, aluminum oxide, magnesium oxide, lime, pyrite, siderite, hematite, magnetite, and sulphur.

Carbonization trials were carried out over several months. Sufficient quantities of coal were crushed and prepared to complete four to five carbonization tests. The base blend consisted of Appalachian coals supplied by two Canadian steel company members of the Canadian Carbonization Research Association (CCRA). The base blends contained 25% of low volatile coal and 37.5% each of two high volatile coals. Fourteen identical base blends were prepared, eight of which were carbonized without mineral additions.

Complete chemical, physical, and XRD mineralogical analysis of the cokes and their ashes were completed. Cokes were tested for CSR and reactivity properties and heat treated at 1500 °C in an inert atmosphere for two hours.

Results

Table 1 shows the changes that occurred in the quality of the coal and coke for the base blends during the programme. The Gieseler plasticity and dilatation properties of the coal deteriorated somewhat but the size, stability, hardness, textures and CSR of the coke remained nearly constant (CSR S=1.27). Some deterioration in CRI of the coke was observed and accounts for a relatively large variance (S= 2.5).

Statistical analysis of the data for cokes from the base blend and cokes made with mineral additions shows no significant differences in their means for ASTM stability, hardness, or size. Apparent specific gravity (ASG) values for cokes containing minerals are slightly higher than for the base blend.

Thermal rheology and coke textures

Figure 1 shows that adding 1% minerals decreases fluidity and dilatation properties of the blend. Sulphur and minerals containing iron had the most detrimental effect. Adding iron bearing minerals - hematite; siderite; pyrite; and also sulphur and MgO altered the microscopic textures of cokes during carbonization. Textures from isotropic to fine mosaic were increased as high as 48% when minerals were added compared with 28-32% for cokes from the base blend. Figure 2 shows that the change in textures for iron-bearing minerals is related to the iron oxide contents in the coal ash. Generally, the minerals that affected the dilatation and Gieseler fluidity properties of the coal also affected coke textures. A significant (but weak) linear correlation was observed.

X-ray diffraction studies

Selected cokes were ashed at low temperatures and analyzed by XRD to determine their mineralogy. Quantitative analysis of two coke ashes showed that only about one third of the ash is crystalline and can be identified by this technique. The remaining ash is amorphous. Consequently, conclusions derived for the mineralogical reactions that occur during coking are tentative. However, based on qualitative analysis of the crystalline products identified, it would appear that minerals used in this program can be categorized as those that remain relatively inert during carbonization, e.g., quartz, feldspars, apatite, and gypsum; those that decompose into other mineral forms; e.g., kaolinite to mullite and quartz; and those that react with carbon or other minerals during carbonization, e.g. many of the iron bearing minerals and oxides of calcium.

CSR

CSR of cokes with mineral additions is significantly lower (and CRI significantly higher) as a whole from the results for the base blend. Mineral additives can be divided into those that have maintained or improved CSR and CRI and those that significantly lowered CSR. Minerals or chemicals (1%) that have maintained (or improved) CSR within 2 standard deviations from the mean of the base blend include apatite, plagioclase, orthoclase, muscovite, aluminum oxide, kaolin, and quartz. Kaolin and rutile (at 0.5%) may have improved CSR properties slightly. Additives that diminished CSR and CRI properties of the coke to varying degrees include: pyrite, siderite, hematite, bauxite, calcite, gypsum, lime, and magnesium oxide. Most of these additives contain the basic oxides of Fe, Mg, and Ca.

The CSR for the cokes largely agree with a relationship derived previously between MBI and CSR as shown in Fig. 3 (6). More detailed analysis of these data shows that the nature in which the the basic oxides are contained is important. Hematite, for example, seems to be more detrimental to coke quality than other iron containing minerals. The forms in which calcium is contained also affect CSR (and CRI) as shown in Fig. 4.

Properties of cokes heat treated to 1500°C

Twenty cokes were heated at 5.5 °C/min to 1500°C and soaked for 2 h. Treatments were done on three cokes made from the base blends and seventeen cokes made with 1% minerals (or chemicals). After treatment the cokes were compared with the starting cokes by weighing, analyzing by chemical and textural analysis.

Figure 5 shows the relative order of weight loss caused by heat treating. The cokes containing minerals had larger weight losses than those made from the base blend. Cokes containing calcium or magnesium had the largest weight losses. Figure 6 shows a relationship between the concentration ratio of the elements (Ca +Mg+K+Na) to aluminum in the coke and the total weight loss caused by heating samples to 1500°C.

A mass balance based on chemical analysis shows that the total weight loss is attributable mainly to loss of carbon through devolatilization and gasification reactions of carbon with the oxide minerals in the ash. Carbon was found in the ashes as silicon carbide. The mass of ash was also less after heat treatment and is attributable mainly to the loss of silicon and oxygen.

Textural analysis showed the elongated fine flow textures were consistently higher (with one exception) and mosaic textures lower for 1500 °C cokes than for cokes not heat treated. Increased amounts of fine elongated flow textures in the heat treated cokes could be caused by erosion of the coarse and medium elongated flow by being relatively more reactive with mineral matter than the fine (mosaic and elongated flow) textures.

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Table 1. Variation in properties of base blend when carbonized at different times during program

Blend number	1	3	5	7	9	11	12	14	mean
Time (days from receipt)	10	24	47	75	94	108	115	207	
Coal Properties									
Melting Range	87	86	80	81	78	80	77	77	80.8
Gieseler ddpm	2250	2100	1810	1620	1600	1130	1090	1010	1576
dilatation (c+d)	180	166	155	141	147	132	137	126	148
FSI	8	8	7.5	8	8	8	8 5	8	8
Coke Properties									
Mean Size	53.6	55.5	53.8	53.9	54.4	54.9	53.07	52.1	53.9
Stability	62.0	62.6	60.2	62.5	64.4	64.3	60.2	60.5	62.1
Hardness	71.2	71.6	69.6	72.1	71.0	71.5	69.9	71.3	71.0
ASG	0.932	0.914	0.918	0.938	0.930	0.945	0.913	.929	.927
CRI	21.0	23.6	24.8	23.9	25.1	26.0	26.9	27.9	24.9
CSR	62.8	63.2	62.2	64.1	60.9	60.4	63.1	61.5	62.3
Fine mosaic textures	30.8	-	29.0	-	30.9	31.3	-	31.0	-

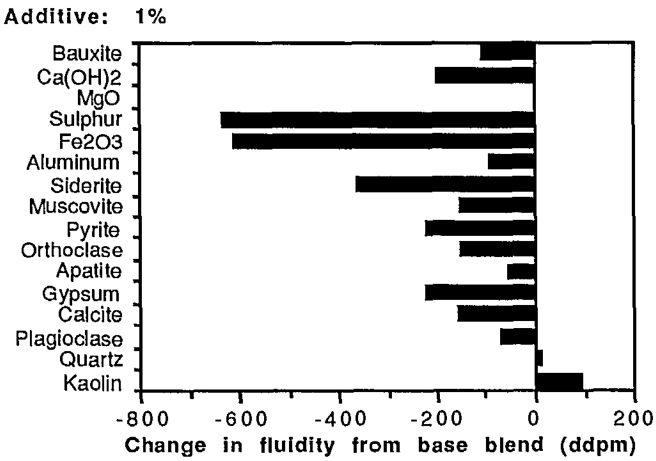

Fig. 1- Change in fluidity of blend when 1% minerals added

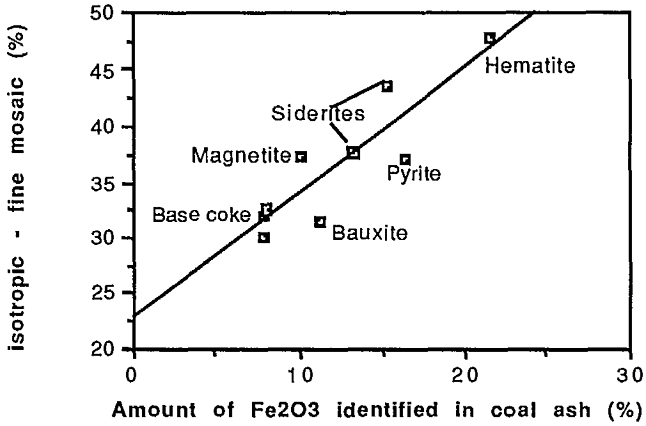

Fig. 2- Effect of Fe2O3 in ash on amounts of isotropic to fine mosaic textures

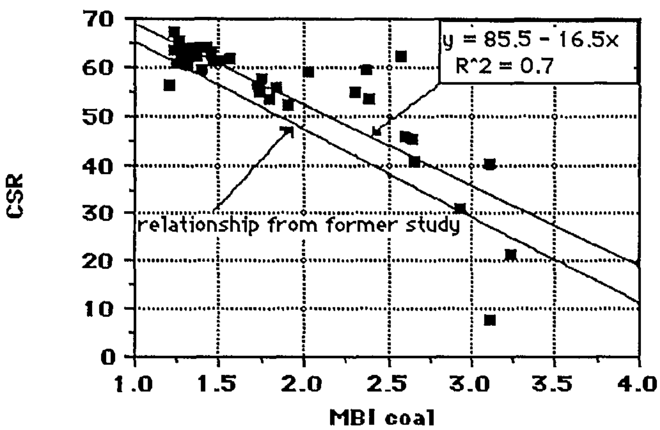

Fig. 3- CSR vs MBI of coal blends containing minerals

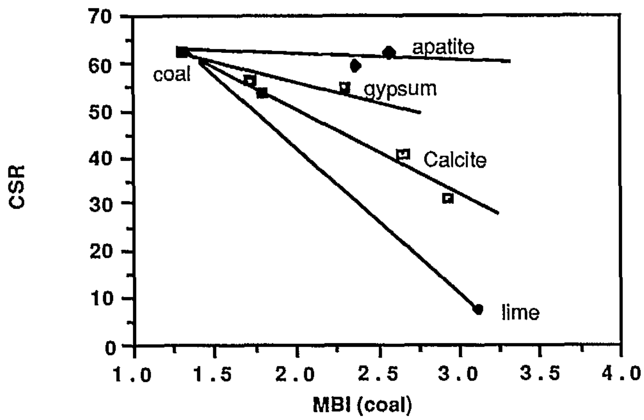

Fig. 4- Effect of calcium minerals and MBI on CSR

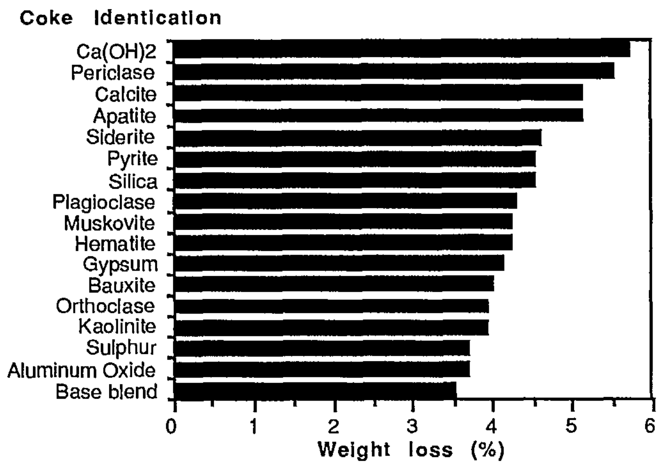

Fig. 5- Effect of 1% additives on weight loss of samples heated to 1500°C

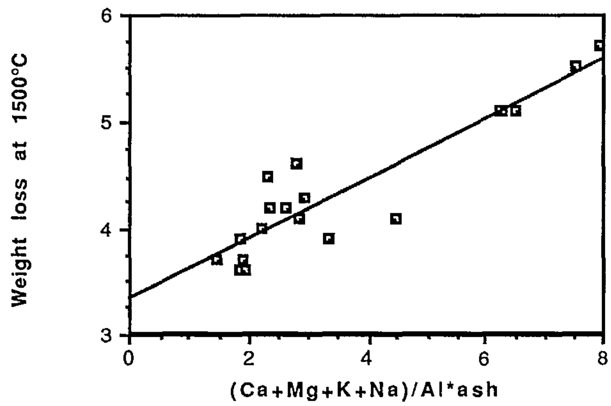

Fig. 6- Effect of basic elements to aluminum ratio on weight loss of coke at 1500°C