

COMPOSITIONS AND MICROSTRUCTURES OF FURNACE-BOTTOM DEPOSITS PRODUCED FROM BENEFICIATED WESTERN CANADIAN BITUMINOUS COALS

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ABSTRACT

Studies of furnace-bottom deposits produced in a pilot-scale research boiler by the burning of fifteen beneficiated western Canadian coals show that the higher the tenor in volatile elements, the higher also is the basicity determined in analyses of coal-ash and furnace-bottom deposits, as well as the degree of ash-slugging in the boiler. The microstructure observed in a furnace-bottom deposit is a function of the basicity of this deposit.

Keywords: coal, ash, chemical composition, microstructures.

SOMMAIRE

L'étude des dépôts de la sole de four produits dans une chaudière expérimentale, à échelle pilote, par quinze charbons bitumineux enrichis de l'Ouest canadien, montre que plus forte est la teneur en matières volatiles examinées, plus grande est la basicité décelée par l'analyse du cendres-charbon et des dépôts de la sole, et plus grande aussi est la formation de scories cendreuse dans la chaudière. La microstructure d'un dépôt de la sole de four est fonction de la basicité de ce dépôt.

Mots-clés: charbon, cendre, laitier, composition chimique, microstructures.

INTRODUCTION

Slagging and fouling of the heat-transfer surface can be serious problems for utility boilers. The effects include: retardation of heat transfer due to ash deposition on the heat-absorbing surface, increased shut-down of the operation caused by rapid deposition of ash and formation of hard-bonded deposits on the convection surface, and corrosion of boilers due to deposition of alkali sulfate, chlorides, etc. Studies of the chemical and physical characteristics of the furnace ash and slag deposits are of primary importance for the understanding of coal-ash fouling and slagging in boilers and, consequently, are important for the design of boilers. Substantial work has been done on ash-fusion temperatures, ash compositions and viscosity (Winegartner 1974, Winegartner & Rhodes 1975, Bryers & Taylor 1976, Huffman *et al.* 1981, Huggins *et al.* 1981, Raask 1982, Streeter *et al.* 1983). The compositions and microstructures of fly ash from coal-burning power plants have been studied extensively (Hulett & Weinberger 1980,

Hulett *et al.* 1980). However, relatively less work has been done on the composition and microstructures of the furnace-bottom deposits (Kiss *et al.* 1972, Fessler *et al.* 1980, Bengtsson 1984), and each study deals with a specific aspect of coal-ash slagging. The study of Hazard (1980) gives a detailed description of the composition and microstructures of the furnace-ash deposits, which consist mainly of coalesced glassy, globular particles. The current study was undertaken as part of CANMET efforts to evaluate the coal-ash slagging process in utility boilers burning low-grade coals and to correlate viscosity measurements, composition and microstructures of furnace-bottom deposits with coal-ash slagging. Viscosity measurements of the slag deposits from these low-grade coals have been reported elsewhere (Quon *et al.* 1984, 1985). This paper is concerned with the microstructures and composition of furnace-bottom (slag) deposits produced by melting of the ash of western Canadian coals.

EXPERIMENTAL

The furnace-bottom deposits were provided by the Canadian Combustion Research Laboratory of CANMET, and were produced by a research boiler under conditions simulating those of utility boilers during evaluation of combustion performance of coals.

The research boiler has been described by Friedrich *et al.* (1972): the boiler is a pilot-scale, pulverized-coal-fired boiler that incorporates two tangentially opposed burners. The furnace is of membrane-wall construction and operates at a pressure of up to 2.5 kPa. At the full-load firing rate of 2500 MJ/h (0.7 MW), the boiler generates 730 kg/h of steam at 690 kPa (6.8 atm.), which is dissipated in an air condenser. Crushed coal is supplied from a 5-ton hopper through a variable-speed worm feeder to a ring-and-roller type of pulverizer, which is normally swept and pressurized by air at any temperature up to 230°C. The pulverizer contains a motor-driven classifier for controlling coal fineness, and a splitter at the pulverizer outlet proportions the coal to each burner. Secondary air can be supplied to the burners at any temperature up to 260°C. Combustion gases leave the furnace between 900° and 1100°C and then pass through a transition section, a test-air heater

and a conventional three-pass air heater before entering the stack. A forced-draft fan supplies air to the air heater at 7 kPa. On leaving the heater, the air is divided into three streams: primary air to the pulverizer, secondary air to the burner, and cooling air to the test-air heater. The last stream, after leaving the test-air heater, can be either exhausted to the atmosphere or blended with the primary air-supply to the pulverizer.

The combustion tests were carried out at full load. Although operating conditions in the boiler had been adjusted slightly to fit the properties of each coal, in general, they simulated those of utility boilers. The operating procedures were maintained the same for all the tests: the boiler was preheated, excess air adjusted, and the boiler was allowed to stabilize at full steaming rate and pressure prior to feeding the pulverized coal to the boiler. The feed rate, coal fineness, and excess-air level were maintained stable during the 7-hour testing period. Upon completion, the boiler was shut down, and the furnace was allowed to cool overnight prior to the collection of the furnace-bottom deposit. The exact sample positions in the furnace are not known; however, in general, the samples are representative of the products of these combustion tests.

The coals have been beneficiated and blended by commercial testing laboratories prior to combustion tests. The beneficiated coals have ranks ranging from high-volatile to low-volatile bituminous, and contain approximately 3 to 19% ash (dry), 18 to 37% volatile matter (dry), 2 to 13% moisture, and have calorific values from 24 to 35 MJ/kg. Partial compositions of these beneficiated coals using the ASTM standard method are given in Table 1. Standard ASTM methods and terminology (ASTM 1983), with conversion to metric units where possible, are used throughout this study.

With the exception of sample No. 15, the coal ashes have a base/acid ratio between 0.07 and 0.26 (base: $\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}$; acid: $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$ in wt.%; Winegartner 1974), base contents from 6 to 19%, alumina from 16 to 30%, silica from 55 to 63%, alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) less than 3%, SO_3 less than 6%, and a $(\text{CaO} + \text{MgO})/\text{Fe}_2\text{O}_3$ ratio from 0.4 to 2.3 (Table 2). Except for samples 2, 6, 9 and 15, all the ash samples are of western type (*i.e.*, have $\text{CaO} + \text{MgO} > \text{Fe}_2\text{O}_3$). The potential slagging-temperatures (Gray & Moore 1974) were calculated from the ash-fusion parameters (ASTM 1983) using the expression $(4I_{\text{Red}} + H_{\text{Ox}})/5$, where I_{Red} is the initial ash-deformation temperature in a reducing atmosphere, and H_{Ox} is the hemispherical temperature in an oxidizing atmosphere. The potential slagging-temperatures have values ranging from 1151 to above 1480°C, and show the familiar relationship that they increase with decreasing base contents and values of the base/acid ratio of the ash. Table 1 gives the ranks and volatile contents of the beneficiated coals and a characteristic grouping according to the potential slagging-temperatures.

In general, the slagged furnace-bottom deposits contain from 6 to 25% of base, a base/acid ratio varying from 0.07 to 0.35, alumina from 18 to 30%, silica from 44 to 68%, Fe_2O_3 from 1 to 21%, CaO from 1 to 7%, a $(\text{CaO} + \text{MgO})/\text{Fe}_2\text{O}_3$ ratio from 0.1 to 1.7, alkali $< 3\%$ and $\text{SO}_3 \leq 0.2\%$ (Table 3). An increase of potential slagging-temperature of the coals with decreasing base content or base/acid ratio in furnace-bottom deposit is apparent in Tables 2 and 3. Microstructural and compositional variations in these samples were studied using an optical microscope, scanning-electron microscope equipped with energy-dispersion X-ray analyzer, electron microprobe and X-ray powder diffractometer.

TABLE 1. CHEMICAL COMPOSITION OF BENEFICIATED COALS

Sample No.	ASTM Classification* Beneficiated coal	Proximate, wt%, dry		Ultimate, wt%, dry				Calorific values, MJ/kg	Ash slagging observed in pilot-scale boiler	Megascopic characteristics of furnace-bottom deposit
		Volatile	Ash	C	H	S	N			
1	LVB	18.0	10.9	79.9	4.0	0.4	0.9	31.8	Low	Friable, sintered-like
2	LVB	20.2	19.0	69.1	3.4	0.2	0.7	27.1	Low	powdery, friable
3	LVB	18.2	16.3	74.5	3.8	0.4	0.9	29.6	Low	Friable, powdery to sintered-like
4	MVB	25.6	14.0	73.1	3.7	0.3	0.9	28.9	Low to Moderate	Glassy, porous to sintered-like
5	MVB	27.5	14.1	71.3	3.7	0.3	0.8	28.1	Moderate	Glassy, porous
6	MVB	25.8	13.5	74.6	4.2	0.5	1.1	30.4	Moderate	Glassy, porous
7	MVB	25.2	13.9	73.5	4.2	0.3	0.7	29.6	Moderate	Glassy, porous
8	MVB	23.7	9.3	78.5	3.7	0.3	0.8	30.1	Moderate	Glassy, porous
9	MVB	24.2	12.6	77.0	4.0	0.3	1.3	30.7	Moderate	Glassy to metallic-like, porous
10	HVBB	34.3	9.9	70.6	4.4	0.3	1.1	28.5	Moderate	Glassy, porous
11	HVBB	34.8	10.9	68.3	4.4	0.2	0.7	27.0	Moderate to high	Glassy, porous
12	HVCB	34.8	17.1	60.8	3.6	0.5	1.5	24.0	High	Glassy, porous
13	HVBB	36.0	10.5	69.9	4.4	0.2	1.3	27.4	High	Glassy to clay-like, porous
14	HVBB	37.1	10.9	70.4	4.2	0.2	1.1	27.8	High	Glassy to clay-like, porous
15	HVAB	36.9	2.8	83.5	5.3	1.2	1.8	34.9	High	Porous, clay to metallic-like

*LVB low-volatile bituminous; MVB medium-volatile bituminous; HVBB high-volatile B bituminous; HVCB high-volatile C bituminous; HVAB high-volatile A bituminous.

TABLE 2. COMPOSITIONS OF ASH

No.	PST***	B/A*	Base*	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
1	1480**	0.07	6.4	30.2	55.2	1.9	2.1	1.4	3.1	0.4	2.0	0.2	0.8
2	1480**	0.07	6.4	29.6	61.1	2.8	1.5	0.4	1.3	0.7	0.4	0.2	1.4
3	1393	0.08	7.7	29.5	56.5	3.0	1.9	0.8	2.8	0.7	2.1	0.1	1.1
4	1317	0.13	11.1	26.1	57.7	4.0	1.5	0.6	4.9	0.8	3.5	0.4	0.9
5	1311	0.15	12.8	25.0	56.9	5.0	1.5	0.6	5.7	0.8	4.0	0.4	0.9
6	1304	0.13	10.2	25.0	57.2	5.7	1.2	1.8	2.5	<0.1	1.2	<0.1	2.0
7	1300	0.14	11.3	24.4	57.7	3.0	1.2	0.6	4.7	1.4	2.5	0.9	1.3
8	1292	0.14	11.5	23.1	57.9	4.4	1.2	0.7	4.4	1.2	3.5	0.4	1.1
9	1291	0.14	12.0	20.1	62.5	8.0	1.2	1.3	2.2	0.8	2.6	0.5	0.5
10	1261	0.16	12.7	20.0	61.5	4.3	0.9	0.4	6.0	1.2	3.7	0.3	0.9
11	1236	0.23	17.8	17.7	55.6	6.1	0.7	0.2	8.9	1.3	3.6	0.4	0.8
12	1229	0.19	14.8	20.1	57.9	3.8	0.5	0.6	6.4	1.3	4.0	2.3	1.0
13	1198	0.25	18.7	17.4	57.5	6.8	0.6	0.1	8.9	1.2	4.0	1.1	0.7
14	1178	0.26	18.8	16.7	55.8	5.1	0.6	0.3	10.6	1.4	6.4	0.9	0.8
15	1151	0.97	47.6	18.4	29.8	42.6	0.9	0.2	1.9	1.2	2.3	0.7	1.2

Results of X-ray fluorescence analyses, in wt. %

* Base = Fe₂O₃ + CaO + MgO + K₂O + Na₂O; Acid = SiO₂ + Al₂O₃ + TiO₂, in wt. %

** Over 1480°C

***Potential slagging-temperature, (4I_{Red} + 1H_{Ox})/5 in °C.

TABLE 3. CHEMICAL COMPOSITIONS OF FURNACE-BOTTOM DEPOSITS*

No.	B/A**	Base**	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	SO ₃	TiO ₂	Na ₂ O	K ₂ O
1	0.08	7.1	30.0	59.4	2.4	2.9	0.8	<0.1	1.4	0.1	1.0
2†	0.07-0.09	6.2-8.5	27.0	61.8-63.7	3.0-3.9	1.3-2.3	0.6-0.8	0.1	0.9-1.2	0.4-0.7	0.8-0.9
3	0.07-0.08	6.6-7.6	28.7-29.4	58.3-58.8	1.5	2.5-2.7	0.6-0.7	0-0.3	1.5	0.1	1.0-1.3
4	0.11	9.9	25.8	61.2	4.2	4.0	0.6	<0.1	1.2	0.2	1.0
5	0.14	12.0	24.8	62.1	5.2	4.7	0.9	<0.1	1.0	0.2	1.0
6	0.13-0.14	11.5-12.4	23.1-23.5	61.6-62.7	5.9-6.6	1.7-2.1	1.1-1.2	0-0.2	0.5-1.0	0.1	2.5-2.7
7	0.11-0.12	8.8-9.6	20.6-23.3	52.2-61.8	2.9-3.0	3.0-3.3	1.0-1.3	0-0.1	0.9-1.0	0.7	1.2-1.4
8	0.10-0.11	9.0-9.5	21.1-22.1	67.6-68.0	3.9-4.6	2.5-2.6	0.9	0.1	0.7	1.1-1.3	0.3
9	0.12-0.15	10.6-13.0	17.8-18.1	64.8-67.2	7.0-8.8	1.8-2.0	0.8-1.1	<0.1	1.2	0.5-0.6	0.4-0.6
10	0.12-0.13	11.0-11.6	20.3-20.5	66.4-66.9	4.5-4.8	4.3-4.6	0.9-1.0	<0.1	0.5	0.2-0.3	0.9
11	0.17	14.8	19.1	63.2	5.8	6.6	1.0	<0.1	0.7	0.8	0.6
12	0.17-0.18	14.0-15.0	19.7-20.4	63.2-64.1	4.6	5.4-6.2	0.9-1.1	0.1	0.3-0.4	1.9-2.1	1.1
13†	0.31	22.0	25.8	44.7	10.8	5.9	4.3	0.2	0.6	0.5	0.5
14	0.20	15.9	22.3	56.3	5.6	8.3	1.1	1.6	0.9	0.3	0.6
15†	0.35	25.3	19.4	52.0	20.6	2.3	0.9	0.2	0.8	1.1	0.4

*The compositions of furnace-bottom deposits produced by different combustion trials from the same coal are given in ranges; results of X-ray fluorescence analyses, in wt. %

† Deposit contaminated by furnace lining due to severe ash-slagging

‡ Blend with high-volatile bituminous coal

**Base = Fe₂O₃ + CaO + MgO + K₂O + Na₂O; acid = SiO₂ + Al₂O₃ + TiO₂, in wt. %

MICROSTRUCTURES

The extent of ash-slagging observed in the pilot-scale boiler, the physical properties of the furnace-bottom deposits (Table 1) and the chemical composition of the coal-ash and slag deposits (Tables 2 and 3) indicate that the furnace-bottom deposits studied can be divided into three groups according to their basicity (base content or base/acid ratio). The analytical results of each group are given in Tables 1-3.

Base < 9%, base/acid ratio < 0.1 (mainly produced from beneficiated low-volatile bituminous coals)

Megascopically, the furnace-bottom deposits of

this group (Nos. 1-3) are friable, powdery or sintered-like (Fig. 1); in detail, they consist of loosely bonded globules of fused or semifused mineral grains (Fig. 2). The deposits have an alumina content greater than 26%. They consist of cristobalite, recrystallized mullite, quartz (residual grains), and minor to trace amounts of iron oxides, (Fe,Al)₃O₄ spinel and Al-Ca silicate bonded by aluminosilicate glass. A typical texture, shown in Figure 3, consists of anhedral quartz grains rimmed by mullite, aggregates of acicular mullite crystals, fine irregular cristobalite blebs, and subspherical aggregates of anhedral iron oxide blebs dispersed randomly in the matrix of aluminosilicate glass. Local concentrations of iron oxides, mullite, TiO₂ and Al-Ca-Fe silicate appear commonly in the matrix phase.

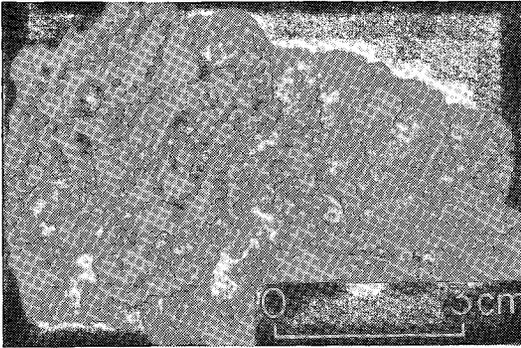


FIG. 1. Optical photograph of furnace-bottom deposit of blended low-volatile bituminous coal (No. 2), showing friable, powdery texture.

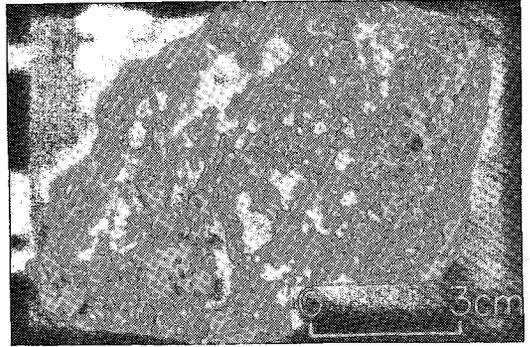


FIG. 4. Optical photograph of furnace-bottom deposit No. 10, showing porous, glassy texture, typical of furnace-bottom deposits from medium-volatile bituminous coals.

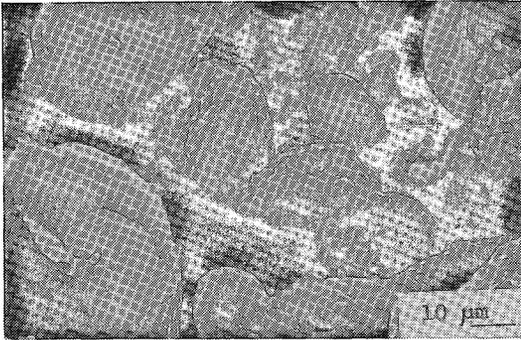


FIG. 2. SEM micrograph of furnace-bottom deposit No. 3, showing bonded globular slag resulting from coalescence of globular molten mineral matter.



FIG. 5. BSE image of the inner portion (near boiler wall) of slag sample No. 7, showing the typical vesicular texture developed in aluminosilicate glass for the furnace-bottom deposits of medium-volatile bituminous coals.

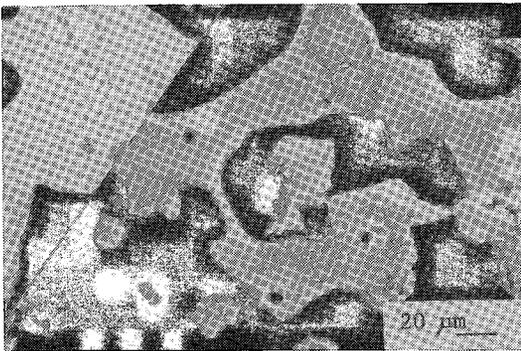


FIG. 3. BSE (backscattered electron) image (composite photo) showing the general texture of furnace-bottom deposit No. 3 from low-volatile bituminous coal. The average composition of the glass matrix, determined by electron-microprobe analysis, is: Al_2O_3 27.4, SiO_2 60.4, FeO 2.7, MgO 1.0, BaO 0.7, TiO_2 1.6, P_2O_5 0.7, K_2O 2.4, CaO 2.9%. The grey inclusions are quartz rimmed by mullite, the bright blebs are Fe oxide, and the dark acicular clusters are mullite.

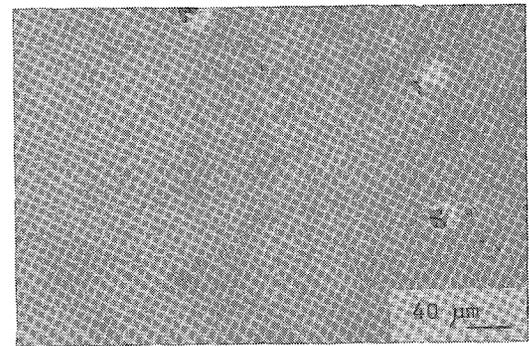


FIG. 6. BSE image of furnace-bottom deposit No. 6, showing irregular variation in glass composition, a typical texture developed from medium-volatile bituminous coals. The darker areas contain more alumina.

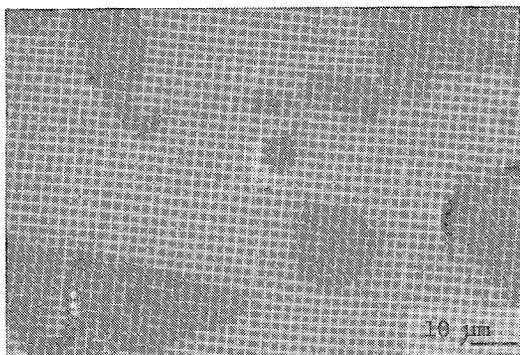


FIG. 7. Subangular quartz (grey) grains rimmed by mullite (dark) in a matrix of aluminosilicate glass, with quartz grains showing fractures; common textures for furnace-bottom deposits of medium- and high-volatile bituminous coals. BSE image, sample No. 10.

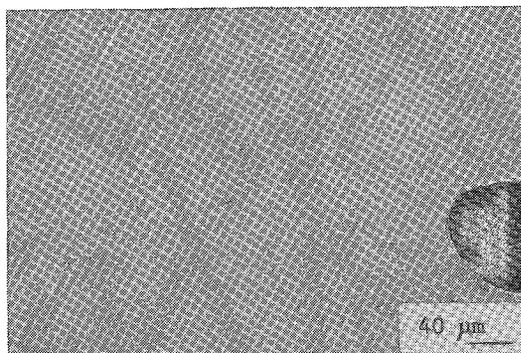


FIG. 10. Furnace-bottom deposit of high-volatile bituminous coal, No. 12, portion near boiler wall, showing recrystallized lath-like anorthite and dendritic Fe oxide (bright) in aluminosilicate glass matrix. BSE image.

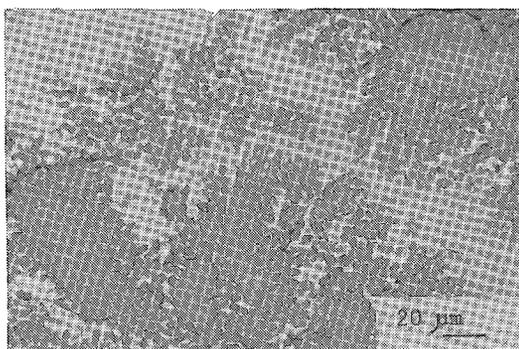


FIG. 8. Furnace-bottom deposit No. 9 (containing more Fe than Ca and Mg), showing mullite (dark) as rims and as leaf-like clusters closely associated with SiO₂ (fractures, dark grey) grains, dendritic and irregular structures of Fe spinel surrounding mullite. BSE image.

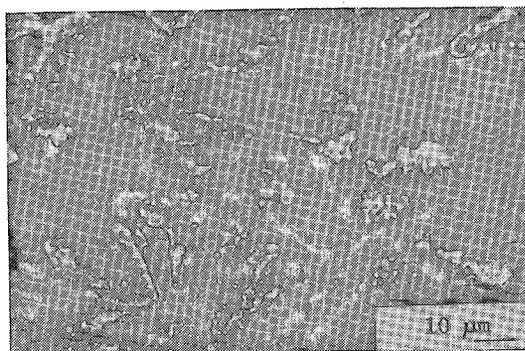


FIG. 11. BSE image of furnace-bottom deposit No. 13, portion near boiler wall, showing recrystallized anorthite crystals (lath), Fe oxide (bright) and cristobalite (dark) in a matrix of aluminosilicate glass.



FIG. 9. Furnace-bottom deposit of high-volatile bituminous coal, No. 11, showing moderate porosity; a typical texture of the deposit from high-volatile bituminous coals. Bright areas Fe oxide, dark areas quartz with mullite rim. BSE image.

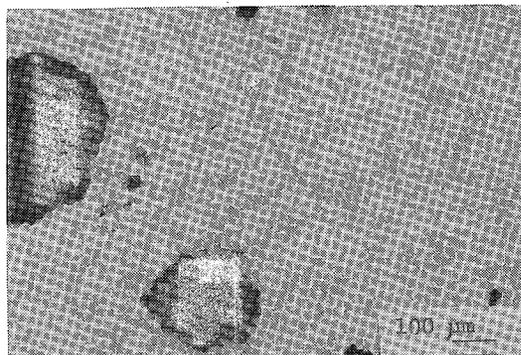


FIG. 12. BSE image of furnace-bottom deposit No. 15, of eastern type, containing 20.6% Fe₂O₃. (Fe,Al)₃O₄ is dendritic and bright, mullite is euhedral and grey.

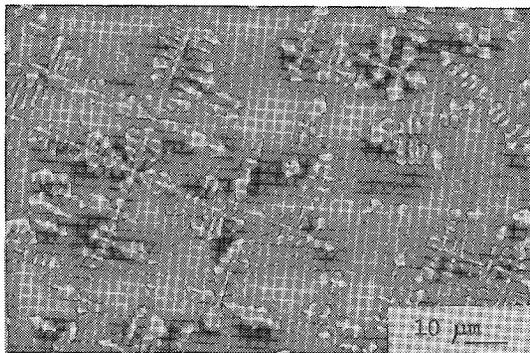


FIG. 13. SEM micrograph of furnace-bottom deposit No. 15, showing $(\text{Fe,Al})_3\text{O}_4$ spinel (bright, dendritic) and euhedral mullite crystals (grey).

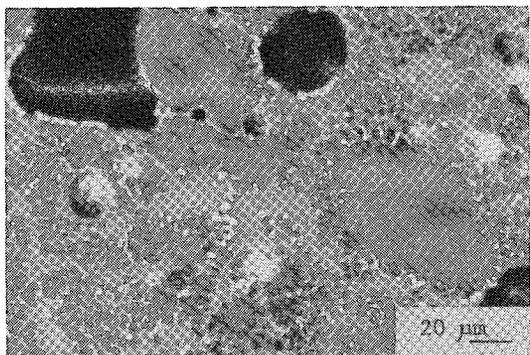


FIG. 14. BSE image of furnace-bottom deposit No. 15, showing SiO_2 (dark), iron oxide (bright), and the coarser-grained iron oxide in vesicles.

Base 9 to 14%, base/acid ratio 0.1-0.17 (mainly produced from beneficiated medium-volatile bituminous coals)

The furnace-bottom deposits of this group (Nos. 4-10; No. 10 from high-volatile bituminous coal) are glassy and porous (Figs. 4,5). The alumina-rich deposits (Nos. 4,5) are more sintered in appearance, whereas the iron-rich deposit (No. 9) is less vesicular and more metallic in appearance. Generally, the near-surface portion (*i.e.*, away from the boiler wall) of the slag is less porous than the inner portion (*i.e.*, near boiler wall), possibly as a consequence of the surface tension of the liquid during cooling. The alumina contents range from 18 to 26%, and Fe_2O_3 contents range from 4 to 9%. The slags consist of aluminosilicate glass with minor to trace amounts of residual quartz, recrystallized cristobalite, mullite, and local trace amounts of anorthite and iron oxide. The glass is composed mainly of Si, Al, minor Ca, Fe, K, Na and traces of P, Ti, Mg and Ba. Local-

ized variations in silica and alumina are present (Fig. 6). No systematic variation in the glass composition can be established from the inner to the outer portion of the slag deposit apart from an irregular increase of alumina, compensated by a decrease of silica, and a gradual decrease of K_2O content toward the slag surface (found in three of the four samples examined). These results are similar to those reported by Quon *et al.* (1984). Quartz occurs as subangular grains and is commonly rimmed by mullite, which apparently has crystallized from the silicate melt and deposited on the surfaces of the grains of residual quartz (Fig. 7). Fractures commonly occur in the quartz grains and along the interface between quartz and the aluminosilicate glass matrix, possibly resulting from the volume changes in quartz and glass matrix on cooling in the furnace. Spherical fly-ash particles comprised of iron oxide, mullite and SiO_2 are present on the slag surface.

In contrast to low-iron slag (No. 4-8,10) the high-iron slag (No. 9; $\text{CaO} + \text{MgO} < \text{Fe}_2\text{O}_3$, or eastern type) contains major amounts of cristobalite, mullite and $(\text{Fe,Al})_3\text{O}_4$ clusters dispersed randomly in the glass matrix (Fig. 8). A trace amount of quartz occurs as cores rimmed with mullite, or as grains surrounded by leaf-like clusters of mullite. Cristobalite occurs as fine blebs associated with mullite. Fine-grained $(\text{Fe,Al})_3\text{O}_4$ is present either as irregular structures or as dendrites surrounding mullite. Fractures are also observed in association with quartz grains.

Base >14%, base/acid ratio >0.17 (mainly produced from beneficiated high-volatile bituminous coals)

The furnace-bottom deposits of this group (Nos. 11-15) are usually dark and moderately porous (Fig. 9), and vary from glassy to somewhat metallic or clay-like owing to increased Fe and Ca contents. Most deposits have Fe_2O_3 and CaO greater than 5%, and have variable alumina and silica contents.

The microstructures of these furnace-bottom deposits vary widely with their chemical compositions. The high-silica type (Nos. 11,12) is glassy, porous, and consists mainly of aluminosilicate glass with minor amounts of quartz, cristobalite and mullite, variable amounts of anorthite, and trace amounts of iron oxide and $(\text{Fe,Al})_3\text{O}_4$ spinel uniformly dispersed in the glass (Fig. 9). Quartz occurs as subrounded grains rimmed with mullite; iron oxide and spinel occur as blebs and dendrites. Localized occurrences of lath-shaped anorthite were observed; its amount increases toward the boiler wall (Fig. 10).

Megascopically, the highly basic (>20%), medium- to high-Fe slag (No. 13) is porous, glassy near the slag surface but becomes somewhat clay-like in appearance near the boiler wall. Near the slag

surface it consists mainly of aluminosilicate glass with trace amounts of subspherical quartz grains and iron oxide aggregates, and grades into predominantly lath-like anorthite, fine-grained cristobalite and iron oxide clusters in the portion near the boiler wall (Fig. 11). The variation in texture is primarily the result of differential rate of cooling.

The texture of the high-Fe slag (No. 15; eastern type) is porous and metallic (Fig. 12). The microstructures vary within the same sample, from predominately dendritic $(\text{Fe},\text{Al})_3\text{O}_4$ spinel and euhedral mullite in a matrix of aluminosilicate glass (Fig. 13) to predominantly anhedral silica (mostly cristobalite) grains and iron oxide in a matrix of aluminosilicate glass (Fig. 14). Trace amounts of anorthite and Fe-Al silicate occur locally. Iron oxide crystallizes either as dendritic spinel or as oxide blebs in the slag, but also occurs as coarse acicular or irregular Fe_2O_3 on the surface of the slag and vesicles.

DISCUSSION

The composition of slagged furnace-bottom deposits is inherited from the mineral matter of the parent coals and influenced by many factors, such as thermal history of combustion, cooling condition after slag deposition, and operating conditions in the boiler. In the present study, the beneficiated coals are mainly of western type, with a base content less than 25%. The beneficiated high-volatile bituminous coals have coal-ash compositions and furnace-bottom deposits with higher contents of base and values of the base/acid ratio than the beneficiated low-volatile bituminous coals; the beneficiated low-volatile bituminous coals have higher alumina content in coal-ash compositions and furnace-bottom deposits than the high-volatile bituminous coals (Tables 2, 3). The potential slagging-temperatures decrease with increasing contents of base (<25%); thus, the beneficiated high-volatile bituminous coals show higher extent of ash-slugging in the pilot-scale boiler than the low-volatile bituminous coals (Table 1). The results are consistent with those reported by Winegartner (1974), that the higher the basicity of coal ash, the higher is the extent of boiler slagging. The effect of sulfur on ash-slugging is not observed, possibly because of its low concentration in the ash. Since there is some overlap in compositions of both ashes and furnace-bottom deposits of different groups of coals (e.g., No. 10), the compositional ranges used to divide the groups, such as base content and base/acid ratio, are only symbolic.

There has been much discussion on the transformation of angular mineral grains to spherical particles in fly ash and slag (Raask 1982). In general, the mineral matter is fused or semi-fused, and particles become spherical owing to surface tension of the

liquid, then coalesce to form sintered or vitreous (slagged) deposits. At constant temperature, the rate of coalescence (or deposit buildup) is proportional to the surface tension and inversely proportional to the viscosity of the aluminosilicate melt and the particle size of fused ash landing on the boiler wall. The development of slag in the boiler can also be perceived from the microstructures displayed by the furnace-bottom deposits. The powdery or sintered texture (Figs. 1,2) represents the smallest extent of coalescence of globular, molten (or semi-molten) mineral matter due to the high liquidus-temperature of the base-poor ash, the high viscosity of the aluminosilicate melt and the longer time required for bulk flow to develop under gravity. As the basicity of the ash increases, the liquidus temperature and viscosity of the liquid decrease, and the time required for bulk flow under gravity decreases, resulting in the formation of extensive deposits of slag (Figs. 4,5,9). Where coalescence of molten aluminosilicates takes place rapidly, some of the gas becomes entrapped but eventually escapes from the melt. The lower the viscosity (*i.e.*, the higher the basicity) of the liquid, the faster the gas escapes. Thus, high-porosity slag deposits result from base-poor compositions (Figs. 5,9). Consequently, the furnace-bottom slags of medium basicity, mainly produced from medium-volatile bituminous coals, are more porous than those of high basicity mainly produced from high-volatile bituminous coals.

The compositions and microstructures of the furnace-bottom deposits and precursor ashes are summarized according to their parent coals as follows: the beneficiated western Canadian low-volatile bituminous coals containing less than 22% volatile matter, in general, have ash compositions with an alumina content greater than 29%, a base/acid ratio less than 0.1, a base content less than 9%, and a potential slagging-temperature in excess of 1393°C. The furnace-bottom deposits generally have high alumina and low base content and are usually lightweight and light in color; they are either powdery or sintered in appearance, and consist of loosely bonded globules of fused mineral-matter. The deposits contain large amounts of quartz, cristobalite, mullite, and minor to trace amounts of iron oxide and Al-Ca-Fe silicate, bonded by an aluminosilicate glass. A very low degree of ash-slugging was encountered in the present pilot-scale boiler.

The beneficiated western Canadian medium-volatile bituminous coals, containing between 22 to 31% volatile matter, usually have ash compositions with an alumina content between 20 and 27%, a base content between 9 and 14% and a base/acid ratio from 0.1 to 0.2. The furnace-bottom deposits are glassy and very porous, and contain medium amounts of base and alumina. Characteristically, the deposits are solidified aluminosilicate melts, with

minor to trace amounts of quartz, cristobalite and mullite as crystalline phases. A moderate degree of ash-slugging took place in the present pilot-scale boiler with these coals.

The beneficiated high-volatile bituminous coals, containing more than 31% volatile matter, usually have ash compositions with a base content greater than 14%, a base/acid ratio greater than 0.2, an alumina content less than 20%, and a potential slugging-temperature less than 1260°C. The furnace-bottom deposits usually contain a high percentage of base and relatively low alumina, are usually dense, dark in color, and moderately porous. They vary from glassy to somewhat metallic in appearance. The constituents of the furnace-bottom deposits vary widely with chemical composition, but generally consist of an aluminosilicate glass matrix with major amounts of anorthite or iron oxide or iron spinel, cristobalite and mullite crystallizing from the aluminosilicate melt. Of the five samples studied, the western-type (Ca-rich) furnace-bottom deposits are rich in anorthite, whereas the eastern-type deposits are rich in iron spinel. Since the cooling rate of the aluminosilicate melt affects the degree of crystallization, the constituents and microstructures vary also with cooling rate. High to severe ash-slugging took place in the present pilot-scale boiler.

It is worth noting that the only residual mineral observed in these furnace-bottom deposits is quartz; all the other phases crystallized from the silicate melts after boiler shutdown.

CONCLUSIONS

The results (Table 1) appear to indicate that under similar conditions of combustion, the extent of ash-slugging in the pilot-scale boiler may be correlated with the rank of coals. However, it should be noted that: 1) the coals studied came from different areas, *i.e.*, they did not necessarily originate from the same depositional environment, 2) the combustion tests that produced these slag deposits were conducted for the purpose of evaluating the feasibility of coal as boiler fuel, not for the purpose of comparing the ash-slugging extent among different ranks of coal, *i.e.*, no preselection of coal sources had been done to ensure that proper coal samples were chosen to represent the coal ranks, 3) the mineral constituents in the beneficiated coals are affected by the methods of beneficiation, because different methods tend to remove different mineral impurities from the raw coals, and 4) the industrial utility-boilers are generally designed to accommodate the slugging problem of a specific coal; consequently, the extent of ash-slugging may change with the design of the boiler. However, the apparent correlation between coal rank and extent of ash-slugging observed in this study should also not be overlooked, because as the coal

gradually changes from low rank to high rank, some trace-element constituents and mineral species that are initially stable in the low-rank environment may become unstable and either disappear or change to other compounds in the new environment. This will change the mineralogy of the mineral matter and affect the extent of ash-slugging. Further studies are needed to look into this correlation. Moreover, it has been commonly accepted that during coal combustion, each individual mineral particle in the pulverized coal is fused in isolation without interaction with other mineral particles (Hazard 1980). This implies that the greater the amount of the low-melting minerals in the coal, the more severe is the extent of ash-slugging in the boiler. Further studies should be carried out to explore this possibility.

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