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BEHAVIOR OF COAL ASH
IN GASIFICATION BEDS
OF IGNIFLUID BOILERS

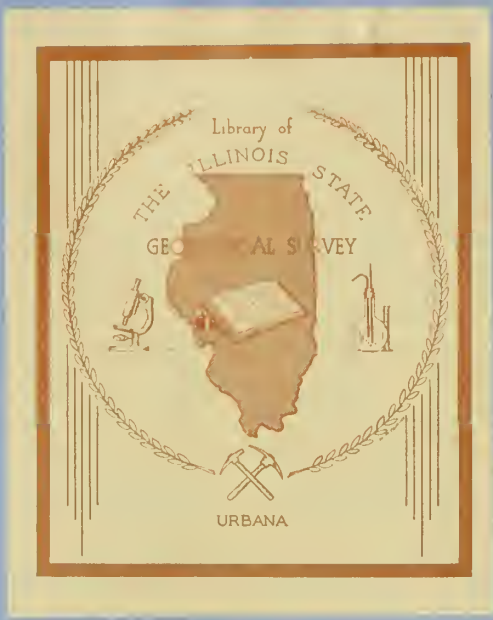*Richard D. Harvey, John M. Masters, and Joseph Yerushalmi*

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BEHAVIOR OF COAL ASH IN GASIFICATION BEDS OF IGNIFLUID BOILERS

Richard D. Harvey, John M. Masters, and Joseph Yerushalmi *

ABSTRACT

The extraction of mineral or ash matter without undue loss of carbon is a major problem in processes designed for the gasification of coal. A unique solution is provided by the Ignifluid process, which has been used for electrical power generation in a few foreign installations for several years.

The Ignifluid process gasifies crushed coal in a bed that rests on an inclined moving grate; the bed is fluidized by air. The resulting fuel gas is burned to raise steam. The gasification takes place between about 1200° and 1400° C. Loose ash agglomerates, low in carbon, form and remain interspersed with the coal throughout the fluidized bed. The agglomerates ultimately reach the grate and are discharged as clinkers.

Because the Ignifluid process has attracted some interest in the electrical power industry, and as it could be applied in gasification of Illinois coals, we procured samples of feed coal, coke from the fluidized bed, ash agglomerates, and discharged clinkers from three commercial Ignifluid plants. We subjected them to microscope and chemical studies to determine the petrographic properties of the ash agglomerates and the mechanism of their formation and to compare the coals used abroad with Illinois coals, especially with regard to their mineral matter.

Two of the plants sampled were fueled by similar types of anthracite coals. Both coals contained about 20 percent mineral matter, which consists of siltstone, quartz sand, pyrite, and clay minerals. In the fluidized beds these constituents form agglomerates that measure 6 to 12 mm in diameter. The third plant was fueled by a bituminous coal that contained 7 percent mineral matter, similar in mineralogy to that of the anthracite coals, and the agglomerates average only about 4 mm in diameter.

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The structure of the agglomerates from the three Ignifluid plants is vesicular and fragmental. The fragments are commonly quartz sand, glass, and coal char, all embedded in a glassy matrix. Crystallites of hercynite and mullite were formed from elements within the glassy matrix. Small globules consisting of pyrrhotite and metallic iron and some particles of quartz were also formed from ash constituents during the gasification process.

The first stage in the formation of ash agglomerates is the appearance of micron-sized beads of molten ash derived from flakes of clay minerals on the surfaces of the coke and coal char particles. Some beads are formed from molten ash from within the particles, especially in particles of coal char, by migration of the molten ash along microlaminations from the inside to the surface of the particles—a kind of sweating process. The beads grow by coalescence and separate from the coke as the coke is consumed and continue to grow by assimilation when they collide with one another in the fluidized bed.

As the bituminous coal studied has mineral-matter characteristics similar to those of many of the bituminous coals in the Illinois Basin, it is likely that the mineral matter in bituminous coals from the basin and elsewhere in the United States would behave in a similar and satisfactory manner if they were used to fuel Ignifluid gasifiers.

INTRODUCTION

Ignifluid gasifiers have operated commercially for many years at several plants in Europe, North Africa, and Asia to generate electric power (Svoboda, 1970). The potential application of the process to the gasification of coal makes it of particular interest in the United States, because conversion of coal to gas is one of the most promising ways of meeting the demand for energy.

The Ignifluid process uses an integrated, two-stage combustion device. In the first stage—the gasifier—crushed coal is gasified in the presence of the primary air (fig. 1) to produce a low-Btu gas primarily composed of carbon monoxide (from the coal) and nitrogen (from the air). The second stage—the boiler—is situated just above the gasifier, and in it the fuel gas burns in the presence of secondary air to raise steam.

Crushed coal is introduced into the Ignifluid gasifier (fig. 1), where the particles are heated and transformed to coke. Strong up-drafts of air (primary) cause the particles to behave like a fluid and promote gasification of the coke. This fluidized bed "rests" upon an inclined, travel-
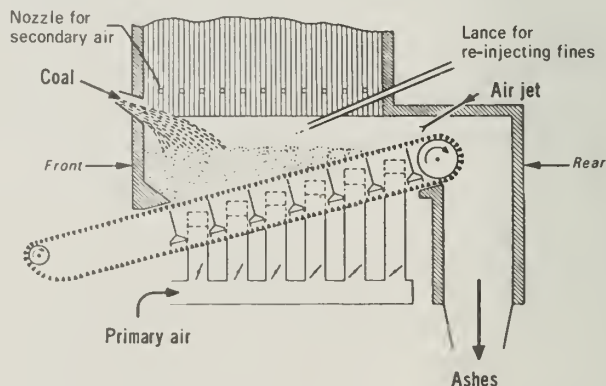

Fig. 1 - Diagram of the Ignifluid process (copyright 1975 by the American Association for the Advancement of Science).

ing grate. The primary air amounts to about 60 percent of that necessary for complete combustion of the coal. The coal is accordingly gasified to yield a low-Btu fuel gas, which is subsequently burned in the boiler above. In the future, the gas could be passed through a cleaning process to remove the H_2S and then piped to other places for consumption.

The most remarkable feature of the Ignifluid process is the manner in which the ash is removed from the fluid-bed gasifier. At the temperatures of about 1200° to 1400° C at which the coal is gasified, the ash of most if not all coals is sticky, and one might expect that a catastrophically massive clinker would form. But that does not happen. Albert A. Godel, the inventor of the Ignifluid process, discovered that small ash agglomerates form throughout the bed and remain fluidized, scattered among the particles of coke (Squires, 1970). The agglomerates grow at a controlled rate. The high-velocity fluidizing air apparently stirs up the bed much as would the continuous action of a poker. The ash agglomerates typically constitute 10 to 20 percent of the weight of the material on the bed, and their carbon content is low. The turbulent motion of the fluidized bed causes the ash agglomerates to hit and be captured by a sticky pad of ash matter resting on the grate. As the grate moves, the ash is discharged into the ash pit as clinker. The agglomerating behavior of the ash in the Ignifluid process is the Godel Phenomenon. It has been described briefly in a recent report (Yerushalmi et al., 1975). In this report we provide more details of the phenomenon and further information regarding the behavior and properties of coal ash in the gasification beds of three commercial Ignifluid boilers so that, if the Ignifluid process is applied in the future to gasification of bituminous coals from Illinois and elsewhere in the United States, the process of agglomeration will be better understood and be used to the best advantage.

Samples

A team from the City College of New York, accompanied by Robert Lundberg of Commonwealth Edison Company, Chicago, Illinois, collected samples (table 1) for this study from Ignifluid boilers at Casablanca, Morocco, at La Taupe, France, and at the Solvay plant, Dombasle, France. Samples were taken from the fluid bed in the gasification chamber with a steel cup, 4 inches in diameter and 8 inches deep, that was welded to a long rod. The filled cup was immediately

TABLE 1—SAMPLE IDENTIFICATION

Sample no.	Location and type of sample
	SOLVAY-DOMBASLE PLANT
S- 1	Coal feed
S- 2	Clinker discharge from grate
S- 3	Ash agglomerates, front, 10:40 a.m.
S- 8	Ash agglomerates, rear, 12:40 p.m.
S- 9	Coke, middle, 10:55 a.m.
S-10	Reinjected fines, cyclone 1
S-11	Reinjected fines, cyclone 2
S-12	Coke from the inclined banks of coke along the sides of the grate
	LA TAUPE PLANT
LT-1	Coal feed
LT-2	Clinker discharge from grate
LT-3	Ash agglomerates, front, 11:00 a.m.
LT-4	Ash agglomerates, front, 12:15 p.m.
LT-5	Ash agglomerates, middle, 11:30 a.m.
LT-6	Ash agglomerates, middle, 12:30 p.m.
LT-7	Ash agglomerates, rear, 12:00 m.
LT-8	Ash agglomerates, rear, 1:00 p.m.
LT-9	Coke, middle, 12:30 p.m.
	CASABLANCA PLANT
C-1	Coal from feeder belts
C-2	Clinker discharged from grate
C-3	Ash agglomerates, front, ½-hour after bed established
C-4	Ash agglomerates, front, 4 hours after bed established
C-5	Ash agglomerates, middle, 1 hour after bed established
C-6	Ash agglomerates, rear, 5½ hours after bed established
C-7	Coke, middle

covered with a brick to shut out air and was quickly cooled. Samples were taken
from the front, middle, and rear of the fluid bed at each plant (fig. 1) at dif-
ferent times so that possible changes in the nature of the ash agglomerates could
be noted as the operation proceeded. The coal feed and the discharged clinker
also were sampled at each plant.

Methods of Study

The samples were examined with a microscope to determine their exter-
nal and internal characteristics. The coal samples were analyzed to determine
their maceral contents and other petrographic characteristics. The mineral mat-
ter in the coals was investigated by X-ray diffraction and microscope studies.
A low-temperature asher (Gluskoter, 1965) was used to separate the mineral mat-
ter from the combustible part of the coal. The asher is a commercial electronic
device that uses a radio-frequency field to produce a ring discharge in a stream
of oxygen. The oxygen is activated by the radio-frequency field and oxidizes
the organic matter in the coal but leaves the ash material essentially as it was
in the coal. The ashing temperature is less than 150° C.

The samples taken from the fluid bed were mixtures of coke and ash ag-
glomerates, which were separated by hand for detailed analyses. The ash agglom-
erates were cast into epoxy molds and thin sections were prepared. These sections
were examined for their petrographic and mineralogic characteristics. Specific
features found in the agglomerates and coals were further studied with a scan-
ning electron microscope equipped with an energy-dispersive X-ray analyzer. The
index of refraction of the glassy matrix in certain samples was determined by
the oil-immersion method. Chemical analyses of samples of coal, coke char, and
selected ash agglomerates were made following the appropriate ASTM standards.

Acknowledgments

RESULTS OF ANALYSES

The results of petrographic analyses of the coals are given in table 2,
chemical analyses of the coals and other selected samples in table 3, and petro-
graphic analyses of the ash agglomerates and clinkers in table 4.

Two terms in this report—coke and coal char—need some clarification
of their usage. Both are used to describe the high-temperature decomposed or
carbonized particles of coal. The term "coke" is used to describe the very porous
and vesicular particles of carbonized coal in which the original structure of the
coal has been obliterated. The term "coal char" is used to describe the car-

TABLE 2—PETROGRAPHY OF COAL SAMPLES

Sample no. and type of coal	Coal macerals (volume %)		Mineral matter (volume %)			LTA*	Porosity	Reflectance[†] (%)
	Major	Minor	Major	Minor	Trace			
S-1, bituminous	Vitrinite (75)	Liptinite (8.7) Inertinite (7.5)	Quartz	Pyrite	Breunnerite Siderite Illite Kaolinite Ankerite	7.2	Low	0.71
LT-1, anthracite[†]	Vitrinite (80)	Fusinite (1)	Quartz[‡] Illite[‡]	Kaolinite[‡] Pyrite (1-2)	Ankerite[‡] Siderite[‡] Mixed-layer clay[‡]	21.9	Medium	5.7
C-1, anthracite	Vitrinite (80.2)	Fusinite & semi-fusinite (5) Inertinite (2-3)	Quartz[‡] Illite[‡] Kaolinite[‡]	Pyrite (1-2)	Ankerite[‡] Mixed-layer clay[‡] Siderite (?)[‡]	19.2	Low	5.1

* Low-temperature ash. Essentially equal to the total amount of mineral matter in weight percent.
† Average maximum reflectance of vitrinite measured under oil.
‡ Traces of lignite occur as contaminants.
‡ Occurs in siltstone fragments in the coals.

bonized particles that are relatively nonporous and laminated. The laminated structure of the coal is preserved in coal char particles.

Coal and Coke

Solvay-Dombasle Coal and Coke

The coal used at the Solvay-Dombasle plant, mined at Lorraine, France (Svoboda, 1970), is a high-volatile bituminous coal that consists of vitrinite and smaller amounts of liptinite, inertinite, and mineral matter; the reflectance of the vitrinite averages 0.71 percent (sample S-1, table 2). The mineral matter (LTA, table 2) is 7.2 percent of the coal and it is mainly quartz and pyrite (table 2). Quartz occurs as discrete grains, about 15 to 20 microns across, and it is associated with the other mineral matter in the coal, especially the clay and pyrite. Pyrite occurs as large single grains (pl. 1A) and as large aggregates (framboids) in vitrinite and fusinite grains. The mineral matter occurs in some particles of coal along microscopic bedding planes. The sulfur content is 0.83 percent (table 3).

The decomposed coal from the combustion chamber at Solvay-Dombasle (sample S-9) consists mainly of particles of coke and a few particles of coal char. In sample S-9 the macerals of inertinite in the coal do not form the vesicular coke particles but become coal char. The coke particles in sample S-9 have undergone considerable swelling and softening during the gasification process. Most particles have a large central cavity and one or two outer layers of coke material. The mean size of the pores, examined on polished surfaces, is approximately 20 μm. Most pores are an irregular, tear-drop shape. At very high magnification the surfaces of the coke appear to be very smooth.
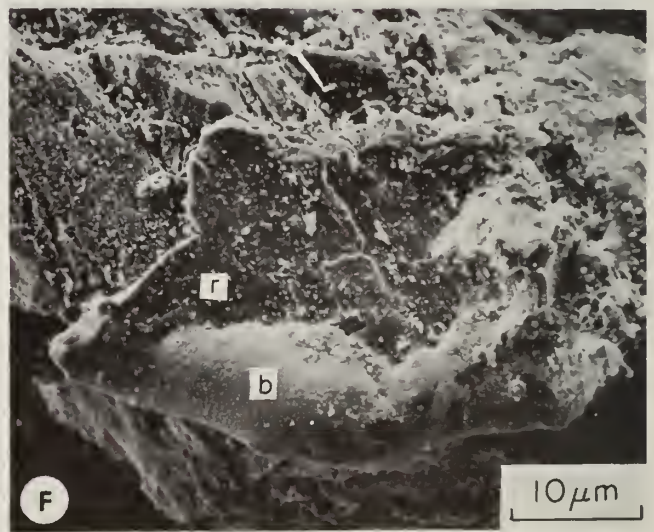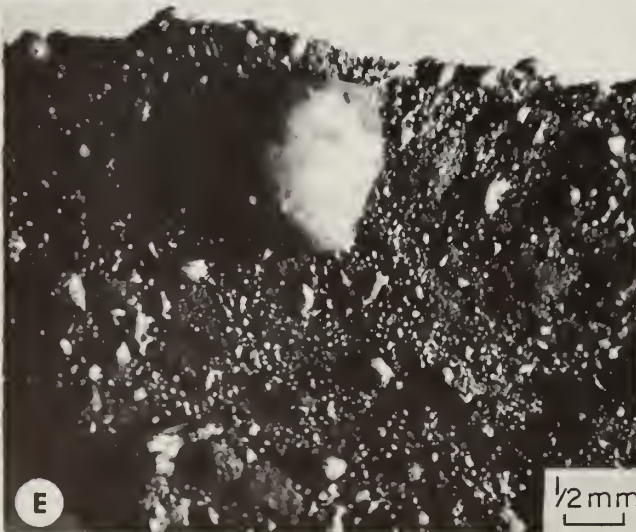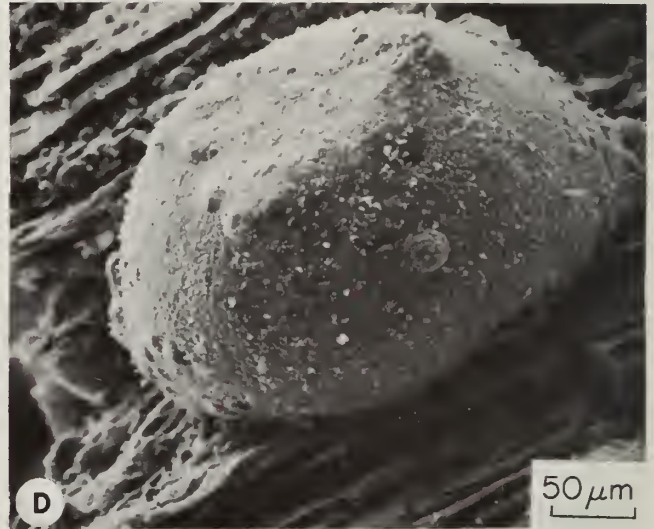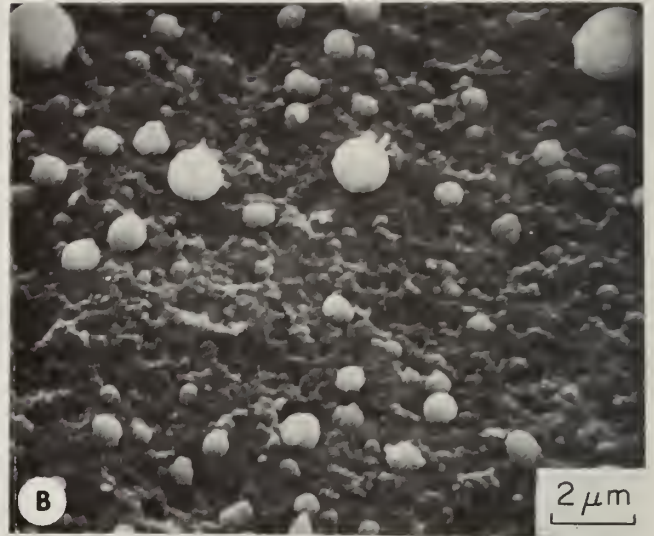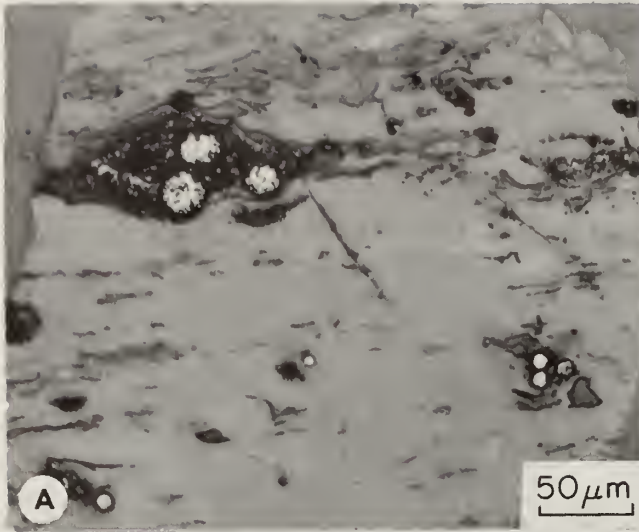
Plate 1

As the coal devolatilizes to coke, the mineral matter decomposes and fuses into glassy beads that range in size from about 0.5 to 1000 μm (pl. 1B). Scanning electron microscope and energy-dispersive X-ray analyses (SEMX) showed the beads are mainly aluminum and silicon, but some contain appreciable amounts of iron. An example of the type of data furnished by the SEMX is shown in figure 2. The samples of reinjected fines from the cyclone collector (S-10 and S-11, table 1) are identical in texture and structure to the coke from the middle of the chamber (S-9), and the sample of coke taken from the sides of the grate (S-12) does not differ significantly from S-9.

La Taupe Coal and Coal Char

The coal used at the La Taupe plant is the middlings from a mine at Auvergne, France, and is anthracite, composed mainly of vitrinite, a minor amount of fusinite (or semifusinite), and a relatively large amount of mineral matter. Some organic particles are composites of broken grains of vitrinite; the average maximum reflectance of the organic matter is 5.7 percent (sample

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Plate 1 - Mineral Matter in Coal and Characteristics of Ash
Material Associated with Coke and Coal Char*

A. Occurrence of mineral matter in bituminous coal. Several granules of pyrite (highlighted grains) are partly surrounded by clay minerals (dark gray). These minerals occur along microlaminations within the coal particles. Polished section, vertical reflected light, sample S-1, magnified X230.

B. Spherulites, one-half to 4 μm in diameter, of glassy ash material, which is composed mainly of Al and Si, are shown on surface of coke particle. They were formed when clay minerals melted. Scanning electron micrograph, sample S-9, magnified X5650.

C. Coal char surface showing detail of laminations and smooth spherulites of ash that appear to have emerged from within the particle. Spherulites are composed of the elements Si, Al, Ca, K, listed in decreasing order of abundance. Scanning electron micrograph, sample LT-9, magnified X550.

D. Ash bead on surface of a coal char particle. The surface of the bead consists of closely packed granules, 3 to 4 μm in diameter, rich in iron (possibly iron oxide). Scanning electron micrograph, sample LT-9, magnified X225.

E. Coal char particle with numerous small beads of ash of various sizes on its surface. Photomicrograph, sample S-9, magnified X17.

F. Fracture surface of coal char particle along one lamination, showing emergence of an elongated bead (b) on the original outer surface of the particle and the feeder veinlet or root (r) attached to the bead. The root is terminated by an irregular fracture shown across the photograph near center. Scanning electron micrograph, sample LT-8, magnified X1720.

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* Micrographs B through F are from Yerushalmi et al., 1975; copyright 1975 by American Association for the Advancement of Science.

TABLE 3—CHEMICAL ANALYSES OF SELECTED SAMPLES
(Weight percent)*

Sample	Type	Volatile matter	Ash (750° C)	C (ultimate)	S	SiO₂	Al₂O₃	Fe₂O₃
S-1	Coal	35.8	6.4	77.44	0.83	—	—	—
S-9	Coke	—†	11.4	86.71	0.59	—	—	—
S-3	Ash agglomerate	—	96.8	4.65	0.23	39.21	27.63	13.64
S-8	Ash agglomerate	—	95.22	4.78	0.20	41.89	29.95	13.70
S-2	Clinker	—	98.5	3.33	0.18	—	—	—
LT-1	Coal	7	20.1	74.68	1.06	—	—	—
LT-9	Coal char	—	9.8	88.74	0.65	—	—	—
LT-6	Ash agglomerate	—	96.4	5.14	1.07	46.1	21.68	14.16
LT-2	Clinker	—	97.9	3.96	0.57	—	—	—
C-1	Coal	7.7	18.0	75.05	1.89	—	—	—
C-7	Coal char	—	6.0	92.28	1.06	—	—	—
C-5	Ash agglomerate	—	96.5	4.74	0.70	52.0	24.25	11.07
C-2	Clinker	—	96.2	6.23	0.26	—	—	—

* Moisture-free values. ASTM procedures used for coal and coke samples.
† A dash indicates no determination was made.

LT-1, table 2). The coal macerals are relatively porous. The mineral matter forms 21.9 percent of the coal and it consists mainly of quartz, illite and kaolinite clays, and pyrite (table 2). The quartz, some of the pyrite, and the ankerite and siderite trace minerals occur as discrete grains of up to about 0.25 mm across. Rare and minute veins in the coal contain the ankerite and siderite grains or crystallites. Numerous grains of quartz are associated with the clay minerals in large siltstone particles. Some of the pyrite occurs with fusinite. The total pyrite petrographically represents 1 to 2 percent by volume of the coal, which is essentially all the sulfur determined in the sample (table 3).

The sample of carbonized anthracite from the La Taupe plant (LT-9) consists of particles of coal char. Coal char has the microlaminated structure of the original anthracite. While nearly all the volatile matter has been removed during carbonization, little or no increase in porosity occurs, and only slight changes in physical structure take place during the transformation of a particle of this coal to char. About 10 percent of this coal char is ash material (table 3), and it consists of glassy material (rich in aluminum and silicon) and pyrrhotite. The char particles are strongly laminated by fractures and are slightly porous. The pores are much as they were in the coal particles. The glassy ash constituents are smooth spherulites
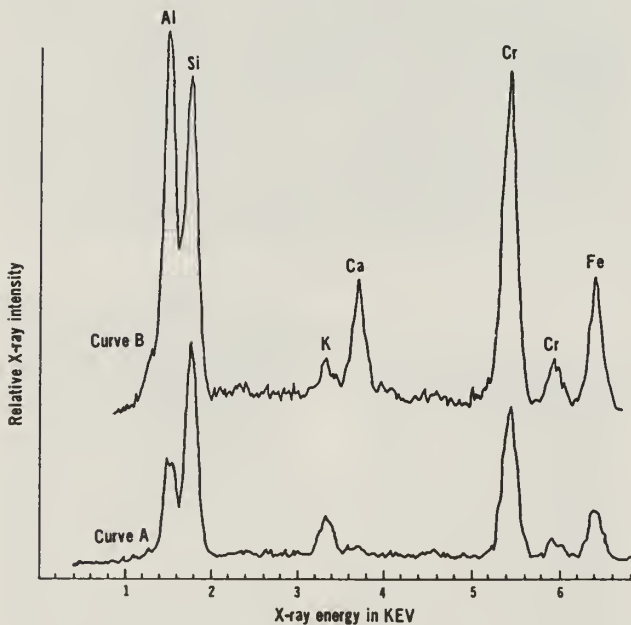

Fig. 2 - SEMX analysis of chromium-coated (Cr) specimens in the scanning electron microscope. A. Fragment of gray vesicular glass in sample LT-2. B. Dark brownish gray glassy matrix in sample LT-3.

1 to 50 μm in diameter that are composed of aluminum, silicon, potassium, and
calcium. They occur within the char particles (pl. 1C) but are most abundant
on outer surfaces of many char particles (pls. 1D, E). Some spherulites, es-
pecially the larger ones, are granular and predominantly iron, but they also
contain traces of sulfur in addition to those elements present in smooth ones.
The larger spherulites are the product of assimilation of many smaller ones
(pl. 1D). Some of the glassy material from within the char particles appears
to have migrated a short distance along laminations to the particle surface
(pl. 1F).

Casablanca Coal and Coal Char

The coal used in the Ignifluid boiler at Casablanca also is an anthra-
cite and was mined at Djerado, Morocco. Two types of coal occur in the sample
(C-1, table 2)—black with vitreous luster and dark gray with finely speckled,
silky luster. Some particles are interlaminated mixtures. The coal is mainly
vitrinite, with minor amounts of fusinite and semifusinite, traces of inerti-
nite, and mineral matter (table 2). It has a high mineral matter content, mainly
quartz and clay minerals, with smaller amounts of pyrite and traces of the car-
bonates ankerite and siderite (table 2). These constituents occur together as
siltstone and shale particles in the sample and, to a lesser extent, along micro-
bedding planes within many coal particles.

The char (sample C-7) derived from the coal used at Casablanca is both
massive and laminated in structure and shows little or no visible swelling or
softening. Microscope study indicates the pores that formed during char forma-
tion are less than 4 μm wide, most of them less than 1 μm in cross section.
Most of the ash in the char is in the form of glass beads that are mainly sil-
icon, aluminum, and iron and have diameters up to 0.2 mm (similar to those shown
in plates 1C, D, E); some of the beads enclose grains of quartz. The ash beads
occur mainly on the outer surfaces of a relatively few particles. The Casablanca
char also contains pyrrhotite granules derived from the pyrite in the coal.

Ash Agglomerates

The ash agglomerate samples from the three plants are similar in com-
position, texture, and structure. However, these properties do vary among the
samples, especially in the type and abundance of constituents that occur within
the agglomerates. The identity of the matrix and inclusions, estimates of their
abundance based on visual examination of section specimens, and an estimate of
the void fractions of the samples appear in table 4. Chemical analyses of se-
lected samples of agglomerates are given in table 3. Samples S-3, LT-3, and C-3
are from the front of the combustion chamber and represent ash material that was
exposed to high temperatures for the shortest period of time. Samples from the
rear of the chamber, numbered S-8, LT-8, and C-6, were exposed for an intermedi-
ate period, and the clinkers, S-2, LT-2, and C-2, are from the point of discharge
from the fluid beds and were exposed for the longest period. The temperature
of the gasification bed at the three plants at the time of sampling was judged to
be about 1200° C in the front of the chamber. The rear temperature was about
1300° C at La Taupe and Solvay and about 1400° C at Casablanca.

TABLE 4—PETROGRAPHY OF ASH AGGLOMERATE AND CLINKER SAMPLES
(Estimates based on visual examination of 2 to 8 specimens in each sample)

| Sample no. | Matrix | | | Fragmental inclusions (%)* | | | | Voids† (%) |
| | Glass (%)* | Mineral inclusions (%) | | Coal char | Glass | Quartz | Pyrrhotitic globules | |
		Hercynite	Mullite					
				ASH AGGLOMERATES				
S-3	36	30	tr†	27	3	4	tr	33
S-8	50	40	tr	12	4	2	tr	26
LT-3	62	tr	tr	15	15	8	tr	35
LT-4	36	tr	tr	11	36	14	3	30
LT-5	50	tr	tr	20	16	9	5	20
LT-6	36	tr	7	11	36	7	3	30
LT-7	50	tr	1	25	15	6	3	20
LT-8	36	tr	1	17	36	7	3	30
C-3	30	nd**	nd	10	40	16	4	50
C-4	47	3	tr	17	19	13	1	30
C-5	36	tr	nd	14	29	19	3	30
C-6	80	nd	nd	3	10	3	4	50
				CLINKERS				
S-2	43	7	tr	29	7	12	1	30
LT-2	44	tr	tr	13	27	13	3	25
C-2	39	tr	tr	11	28	22	2	35

* Volumetric percentage of the solid components, excluding voids.
† Volumetric percentage of void space in the agglomerates.
‡ Trace amount.
** None detected.

Plate 2 - Textural and Mineralogical Features of Ash Agglomerates from the Solvay-Dombasle Plant

A. Ash agglomerates composed of a glassy matrix and coal char fragments.
Photograph, sample S-3, magnified X3.8.

B. A small, multiglobular ash agglomerate consisting of coal char fragments
(dark) embedded in small blobs of glass (gray). The light gray circular
areas are vesicles in the glassy ash material. Thin section, transmitted
light, sample S-3, magnified X11.

C. Detail of a coal char particle showing ash constituents, siliceous and iron-
and sulfur-bearing spherulites occurring along a prominent lamination within
the particle. Photomicrograph, oblique light, sample S-3, magnified X87.

D. Hercynite; octahedral crystallites in glass matrix. Thin section, trans-
mitted light, sample C-4, magnified X585. Insert shows detail of one
crystal, magnified X4010. Scanning electron micrograph.

E. Fracture surface of coal char fragment that was attached to the outer sur-
face of an agglomerate. The occurrence of partly assimilated beads is
shown within the vesicular glassy ash material. Scanning electron micro-
graph, sample S-3, magnified X790.

F. Iron-rich spherulitic sublimates on cavity wall in a glassy matrix. Sul-
fur, silicon, and aluminum are also present. Scanning electron micrograph,
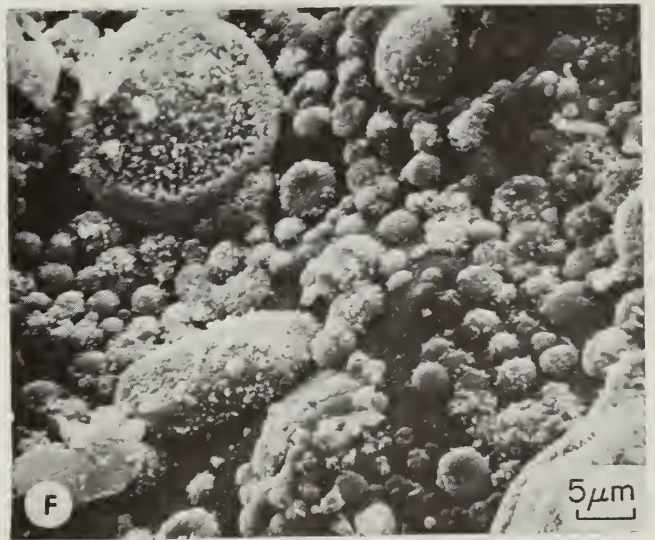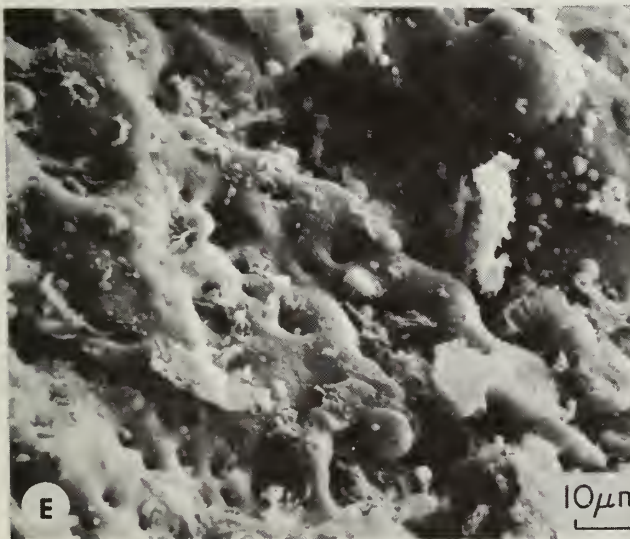sample S-3, magnified X1555.

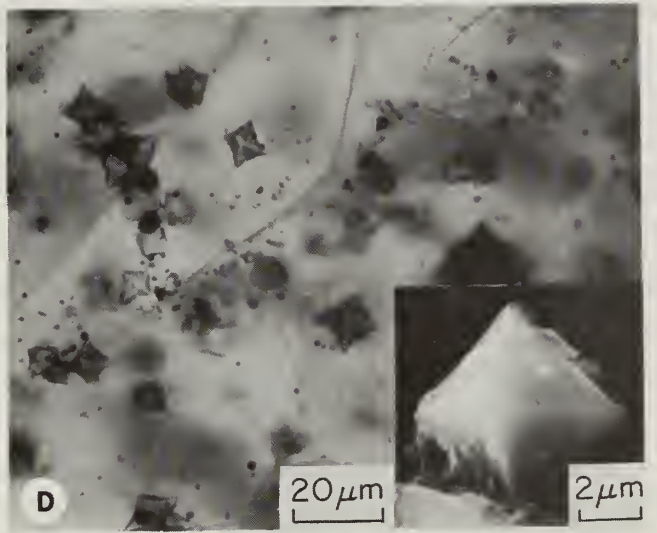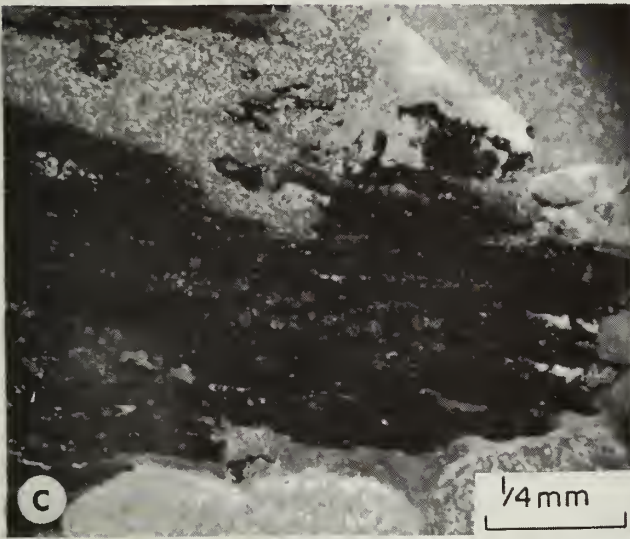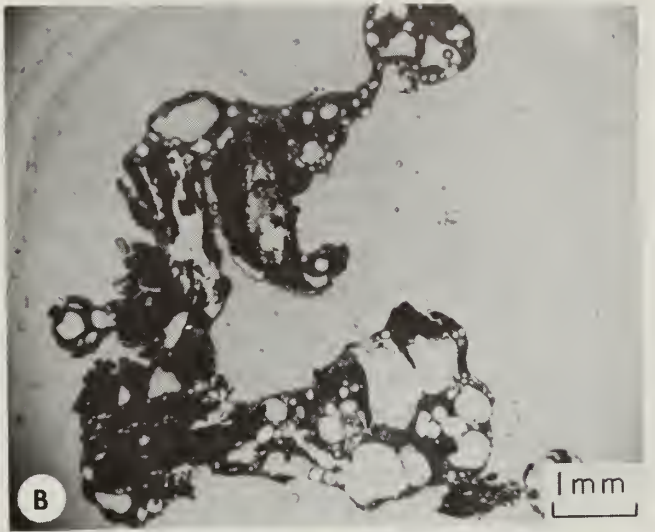A

B

5mm

1mm

C

D

1/4mm
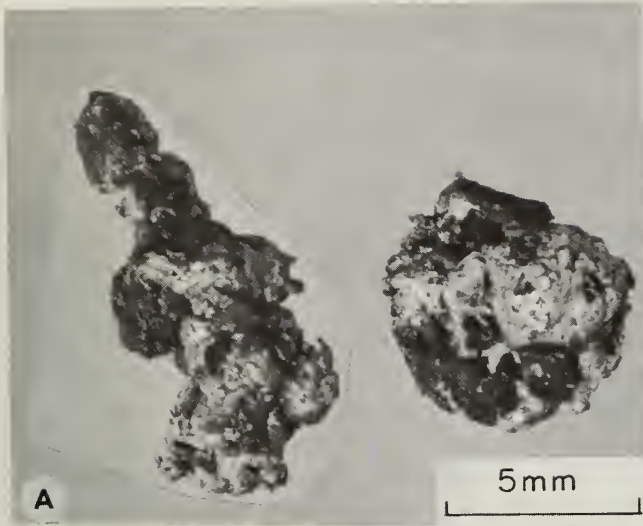
20μm

2μm

E

F

10μm

5μm

Plate 2

Solvay-Dombasle Plant Agglomerates

Ash agglomerates taken from the Solvay-Dombasle boiler are typically 3 to 12 mm across, some are nearly spherical, and others are distinctly multi-globular (pl. 2A). They are steel gray or brownish gray and are mottled by dull black patches. The agglomerates are vesicular and somewhat fragmental in structure, and they have a glassy matrix (pl. 2B). The fragments occur within the globules. The average diameter of the globules within multiglobular specimens is 2.5 mm, and the maximum diameter observed was 8.4 mm. The globules are more than twice the size of the particles of coke from the same part of the fluidized bed.

The major chemical constituents of samples S-3 and S-8 are given in table 3. The constituents listed for each total only about 90 percent, but SEMX analyses indicate the remaining constituents are mainly calcium, potassium, and magnesium. Traces of titanium also were detected in the samples.

The typical vesicular and fragmental character of the agglomerates from the Solvay plant is shown by the specimen in plate 2B. Fragments embedded in the glassy matrix of the agglomerates are predominantly coal char (black fragments, pl. 2C), but a minor fraction is glass and quartz. Only a few globules of pyrrhotite occur in the Solvay agglomerates, which are characterized by an abundance of hercynite (pl. 2D), a double oxide of aluminum and iron ($FeAl_2O_4$), and a mineral of the spinel group. Hercynite in the samples crystallizes in individual octahedrons 1 to 10 μm across. The abundance of these octahedrons in S-3 is normally greater than is apparent on plate 2D. The hercynite crystals occur as inclusions in the dark greenish brown glassy matrix that cements the various fragments together. The glass occurs as more or less isolated beads and as small patches along laminations in coal char fragments. It is more concentrated along laminations near the edges of the fragment (pl. 2E), where it takes on a vesicular structure, but many small beads retain their identities within the mass of the glass. The glassy matrix of the agglomerates is mainly composed of aluminum and silicon with various (but smaller) amounts of calcium, potassium, iron, and magnesium. It has a mean index of refraction of 1.58. In addition to hercynite, trace amounts of mullite have grown within the glassy matrix. Mullite is an aluminum silicate ($Al_6Si_2O_{13}$) and its crystals are fibrous. Traces of iron-rich ellipsoids, about 2 to 20 μm across (pl. 2F), occur on the walls of cavities in the glassy matrix.

Coal char fragments are the most abundant of the fragments (table 4, S-3, S-8). The quartz fragments are randomly scattered in the specimens and are rounded, irregular in shape, and about 30 μm across. Some quartz grains, most 10 to 15 μm across, occur within fragments of dark gray glass. These fragments remain distinct from the matrix glass by being dark gray, by containing the small grains of quartz, and by having a distinct boundary. A few steel gray magnetic globules of pyrrhotite, about 50 μm in diameter, also occur in these agglomerates.

La Taupe Plant Agglomerates

The agglomerates from the front and middle of the La Taupe Ignifluid beds are 3 to 20 mm across and are roughly spherical (pl. 3A). Some of them from the rear of the bed are multiglobular. The color, reddish gray to steel

gray, remains about the same throughout the bed. The agglomerates have a vit-
reous luster stemming from their glassy constituents. Their structure is ve-
sicular and fragmental, as shown in plate 3A through D. Chemical analyses (LT-6,
table 3) show intermediate amounts of silica, somewhat less alumina, and more
iron and sulfur than is found in agglomerates from the other plants. SEMX anal-
ysis shows calcium, potassium, and magnesium also are present in La Taupe ash
agglomerate samples.

Most agglomerates from the front of the combustion bed have one or two
prominent central cavities, whereas those from the rear have several small cav-
ities. Fragments of coal char, bits of dark gray to colorless vesicular glass,
and large particles of quartz are embedded in brownish to greenish gray glassy
matrix. The distribution of the various fragments within the agglomerates is
random. Most of the coal char fragments seem to adhere to the outer surface,
but some are embedded within the interior of the agglomerate. On the other hand,
the glassy and other fragments are most commonly covered by a thin skin of glas-
sy matrix, rarely being exposed as the char fragments are.

The large quartz particles are 100 to 500 μm across and about half of
them have a special form characteristic of recrystallized silica—elongate but
very irregular in shape, with abundant parallel to subparallel fractures and
strain lamellae that are oriented normal to the elongation (pl. 3C). Agglomer-
ates from the front, middle, and rear of the gasification bed contain some frag-
ments of quartz that show these properties. About half of the quartz particles
are well rounded (normal detrital) grains derived from the coal.

The dark gray fragments of glass are the most abundant fragmental in-
clusions in three of the ash agglomerate samples from La Taupe (table 4). A
typical glassy fragment is shown prominently in plate 3A. They are highly ve-
sicular, and subrounded quartz grains of various sizes are always scattered
throughout the glass. Some of the fragments are lighter shades of gray and
others are colorless, mainly because of differences in their iron composition.
The dark gray ones are dominantly iron and smaller amounts of silicon and alu-
minum, and the colorless ones are dominantly silicon and aluminum. Other ele-
ments commonly detected in the glassy fragments are potassium, calcium, and, in
smaller amounts, magnesium. A plot of the SEMX data of a specimen of this type
of glass is shown in figure 2, curve A.

Pyrrhotitic globules, 40 to 600 μm in diameter, are scattered within
the agglomerates. They are rounded, steel gray, and magnetic. They occur from
trace amounts to as much as 5 percent in the La Taupe agglomerates (table 4).
In cross section they have a granular mosaic texture and little or no pore space
(pl. 3F). These globules are mixtures of about one-third metallic iron and two-
thirds pyrrhotite, a sulfide of iron. The grains of metallic iron have a more
rounded grain form than the pyrrhotite grains. SEMX data from a chromium coated
specimen are shown in figure 3.

The glassy matrix, which represents about 36 to 62 percent of the ag-
glomerate matter (table 4), surrounds the various fragments and, like the glassy
fragments, contains a wide range of pore sizes. An important characteristic of
the matrix glass is the degree of flow structure developed in the glass, evident
in the pattern of distribution of tiny vesicles and inclusions. The pattern,

typically a swirl, is hardly detected in samples from the front of the bed, is moderately well developed in agglomerates from the middle and rear of the bed (pl. 3D), and is best developed in the final clinker. The composition of the matrix is dominantly silicon, iron, and aluminum in various amounts, plus minor amounts of calcium, potassium, and magnesium. A typical SEMX record of the glassy matrix is shown in figure 2, curve B.

The matrix contains two mineral components, mullite and hercynite, which crystallized from the elements contained in the glass. Traces of mullite occur in the matrix of each of the agglomerates examined from the La Taupe plant.

Plate 3 - Textural and Mineralogical Features of Ash Agglomerates from the La Taupe Plant*

A. Ash agglomerate in cross section, showing a roughly spherical shape, two large irregularly shaped voids, several large vesicular glassy inclusions, and many other smaller inclusions embedded in dark matrix glass. Photograph, sample LT-4, magnified X4.5.

B. Ash agglomerate showing fragmental nature of the agglomerate and a moderately well developed flow structure in the matrix glass. Very small inclusions have been concentrated in a swirl pattern by the flow of the matrix glass. The dark fragment at the lower left is a gray glassy fragment. The large circular objects are vesicles in the matrix, and spherulites occur on the inner walls of the cavities, as shown in E (below). Thin section, transmitted light, sample LT-7, magnified X25.

C. Quartz with numerous lamellae (alternating light and dark) within the grain, typical of quartz grains in the agglomerates and clinkers. Inclusions of coal char fragments in the grain are shown in the lower part. Thin section, transmitted light, sample LT-8, magnified X87.

D. Ash agglomerate showing flow structure and also part of a dark gray glassy fragment at the right and part of a vesicle with its wall coated with spherulites at the lower edge (E). In the upper left is part of a coal char fragment. Thin section, transmitted light, sample LT-7, magnified X125.

E. Pyrrhotite spherulites, 1 to 3 μm in diameter, on a wall of a vesicle in the matrix glass. Indentations occur on the wall where certain spherulites have been dislodged, and, in the center of these indentations, the core of the spherulites remains attached. Scanning electron micrograph, sample LT-3, magnified X1020.

F. Fracture surface of a metallic globule, 2 mm in diameter. The large rounded grains are iron (curve B, fig. 2) and the matrix material is pyrrhotite (curve A, fig. 2). Scanning electron micrograph, sample LT-5, magnified X470.

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* Micrograph A is from Yerushalmi et al., 1975; copyright 1975 by American Association for the Advancement of Science.
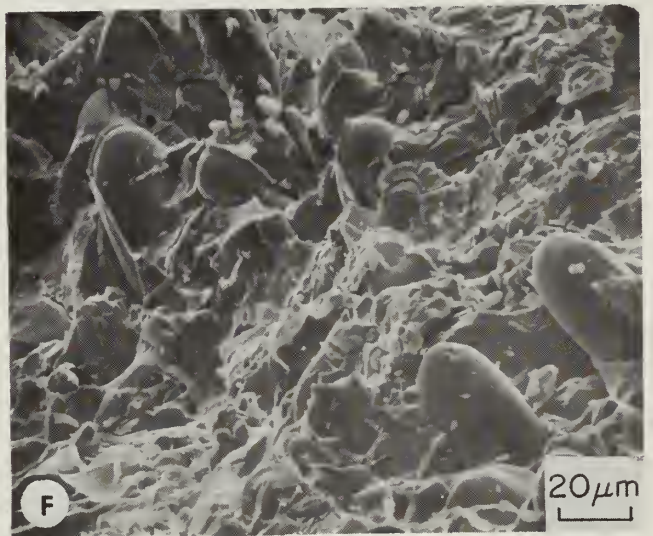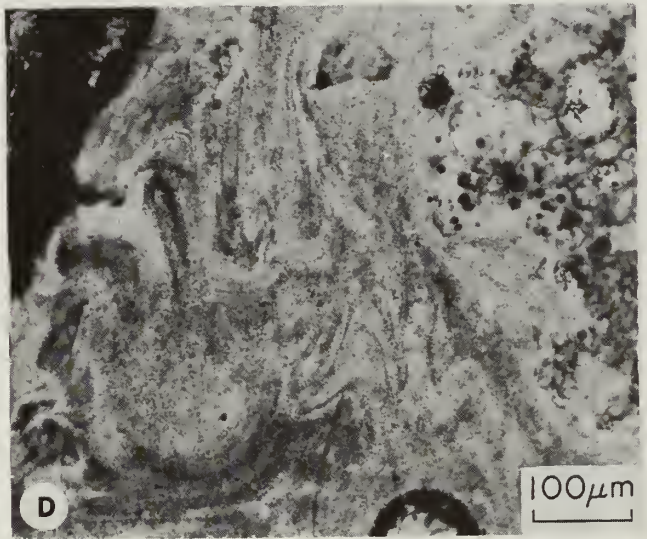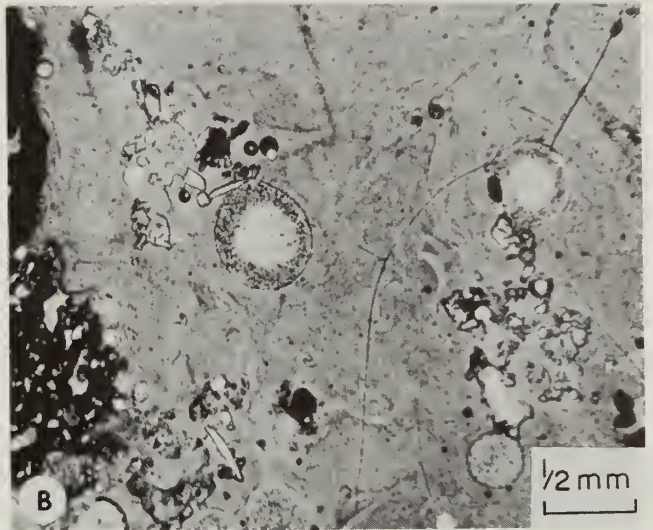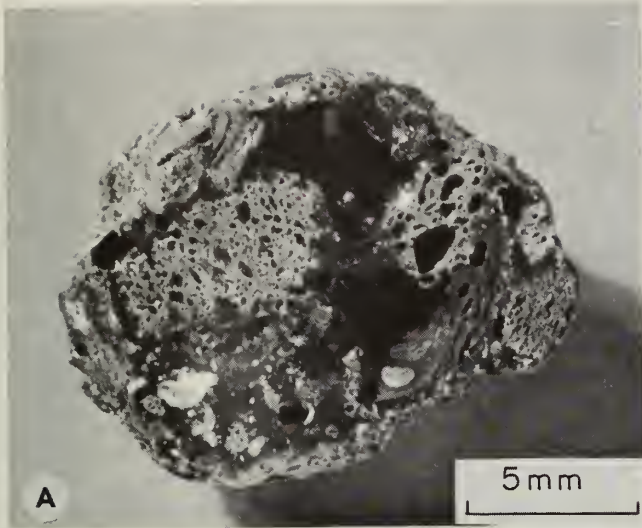
Plate 3

Individual crystallites of mullite are fibrous, and they occur as aggregates on one of two forms—closely packed parallel fibers varying in length from about 100 to 500 µm, or, more commonly, a loosely matted network of fibers oriented in all directions (see a similar occurrence in pl. 4E, F). Hercynite octahedrons are identical in form and composition to those in the Solvay samples, although they are much less abundant in the La Taupe samples.

An iron and sulfur compound, probably pyrrhotite, crystallizes as ellipsoids 1 to 3 µm across on the surface of many cavities within the glassy agglomerates (pl. 3E). These must have sublimated and grown while the glass was still partly molten, because indentations in the glass can be seen in the places where they have been knocked off (note these indentations in plate 3E). A small nucleus of the ellipsoid appears to be retained in the center of the indentations, suggesting that the nucleus was surrounded by an outer layer more easily detached from the cavity wall.
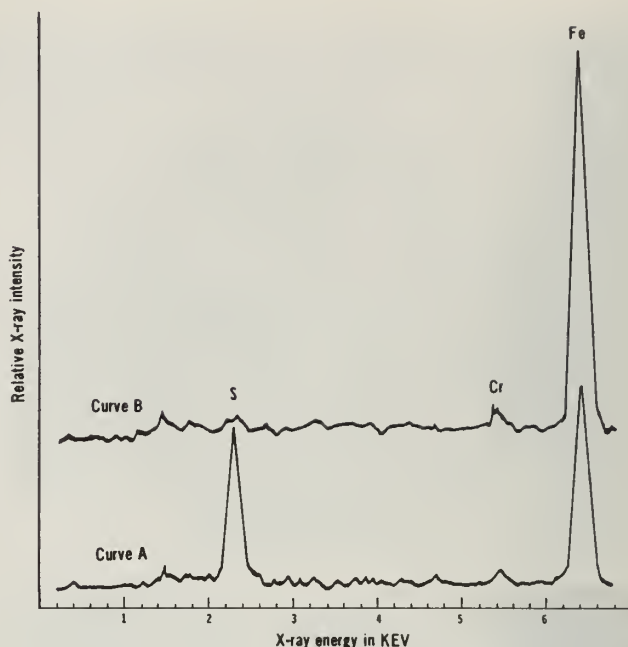

Fig. 3 - SEMX analysis of the metallic globule illustrated in plate 3F. Curve A, the matrix material, which consists of iron and sulfur in the form of pyrrhotite grains. Curve B, grains of iron distributed throughout the globule. The specimen was coated with a thin film of chromium (Cr).

The total amount of sulfur in the ash agglomerates at La Taupe (table 3) is practically identical to that in the coal feed, in contrast to the reduced amount of sulfur in the agglomerates at the other two plants.

Casablanca Plant Agglomerates

The ash agglomerates obtained from the Casablanca plant were by far the largest in size, typically 15 mm and ranging up to nearly 50 mm. The large size can be attributed to the operating temperature at Casablanca, which was higher than that at the other plants. Most of the Casablanca agglomerates are roughly spherical (pl. 4A) but many are multiglobular (pl. 4B), including samples from the front section of the bed. The color is similar to that of samples from La Taupe, but their surface texture is commonly somewhat ropy (poorly shown in plate 4A but more apparent in plate 5B). The ropy texture is indicative of a somewhat higher viscosity of the molten glass at the high temperature. Differences in the relative amounts of silica in molten silicates cause different degrees of viscosity. The silica content of the ash agglomerate in C-5 is the highest of all the agglomerates examined (table 3) because of the presence of a great abundance of quartz particles, many of which are elongate and laminated patches of recrystallized quartz. The iron content of the Casablanca agglomerate is low in comparison with agglomerates from the other plants, and the abundance

of the pyrrhotitic globules scattered in the Casablanca agglomerates varies more from sample to sample (1 to 4 percent, table 4). These globules are identical in size, structure, and composition to those in the previously described agglomerates.

Agglomerates in C-3 and C-6 generally have a prominent central cavity; however, one specimen from C-3, shown in plate 4C, has two very large cavities as well as numerous smaller cavities or vesicles. The distinct textural differences of the material on the right from that on the left of the photograph clearly show that two small ash agglomerates joined to form a large one while at high temperature in the fluidized bed. Other samples are composed of larger agglomerates that generally have numerous small cavities dispersed between fragmental inclusions and the vesicular glassy matrix, typically illustrated in plate 4D.

The matrix glass has many of the same physical and chemical characteristics described for the glass of the La Taupe agglomerates, but the degree of development of the flow structure in the matrix glass does not so clearly increase from the front to the rear sections of the bed. Mullite and hercynite were not detected in C-3, but about 3 percent hercynite and a trace of mullite occur in C-4, which was taken from the same front location in the fluid bed as C-3 but three hours later. The crystalline form of the mullite is shown in plates 4E and 4F. We found no mullite in C-5 (middle bed), but traces of hercynite do occur in the glassy matrix of that sample. In the sample from the rear of the bed (C-6) no traces of either mineral were detected. The decreased abundance of hercynite and mullite, compared with that at the other plants, may be related to the higher temperature of the gasification bed at Casablanca. The percentage of glassy matrix increases in the fluidized bed from front to rear at the Casablanca plant (table 4).

Clinkers

Samples of the pad of ash that forms on the Ignifluid grate also were studied. Samples, in the form of broken pieces of clinker, were obtained by capturing a portion of the pad as it was being discharged from the top of the grate. The clinkers had been exposed to the high temperature of the boiler longer than the other types of samples. Results of studies of the samples (S-2, LT-2, and C-2) are listed in tables 3 and 4. The shape, surface texture, and structure of the clinker samples are very much the same for all three plants (pl. 5A). However, the Casablanca clinker, as was true of the Casablanca agglomerates, has a distinctive ropy texture, visible on its outer surface (pl. 5B). This sample also had a weakly developed flow structure in its glassy matrix, whereas the clinkers from the La Taupe and Solvay plants have a well to very well developed flow structure within their matrices (pl. 5C).

The microscopic structure of the clinkers is identical in most respects to that of the multiglobular ash agglomerates in that it is vesicular and contains fragments of coal char, gray vesicular glass, and quartz. Many of the latter fragments are elongate and laminated. Pyrrhotitic globules also occur. All of the various types of fragments are randomly embedded within a glassy matrix. The fragments and the glassy matrix are similar in size, structure, and composition to their counterparts in the agglomerates. However, the
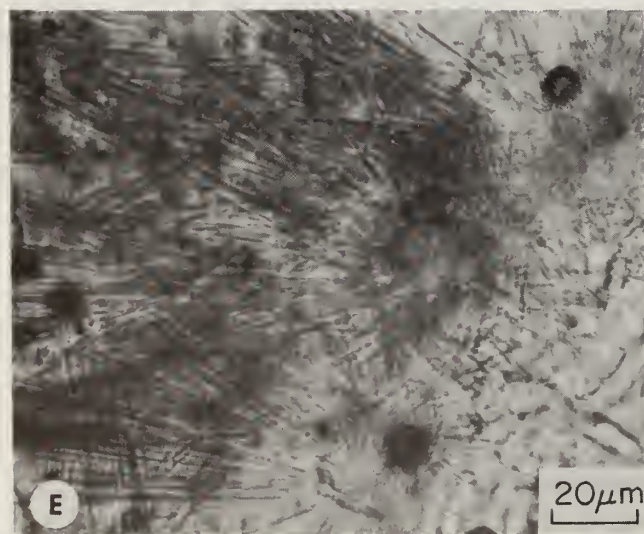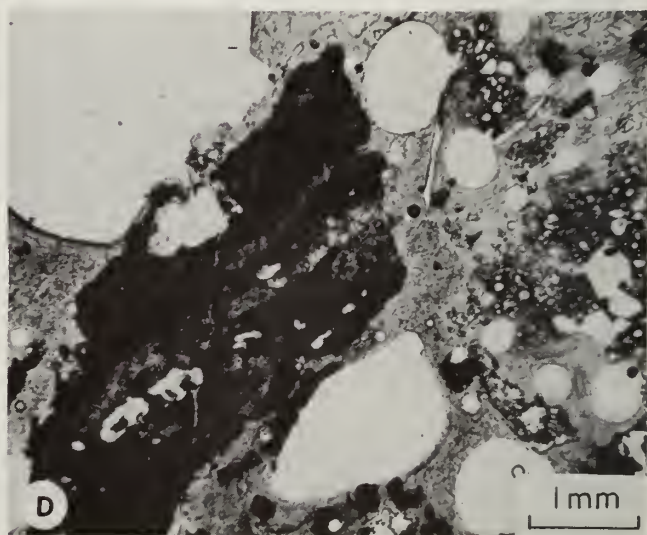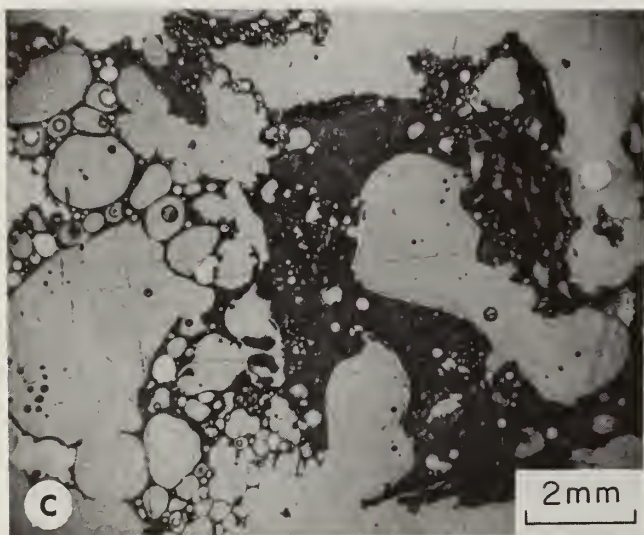
Plate 4

hercynite content of the Solvay clinker is decidedly lower than that in the Solvay agglomerate. The La Taupe and Casablanca clinkers, like the agglomerates from those plants, showed traces of hercynite and mullite. Coal char was the most abundant type of fragment in both the clinkers and agglomerates of the Solvay samples.

The clinkers from the Solvay plant contain only one type of quartz particle—large rounded and partly fractured grains—whereas the clinkers from the La Taupe and Casablanca plants contain three types of quartz. The three types are also present in the La Taupe and Casablanca agglomerates—large rounded and fractured grains, small equant and subrounded grains derived from siltstone impurities in the coals, and elongated but irregular particles of recrystallized quartz, some of which contain abundant inclusions (pl. 5D).

Aluminum and iron concentrated in submicron spherulites were observed only on some outer surfaces of the clinkers, especially on coal char particles

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Plate 4 - Textural and Mineralogical Features of Ash Agglomerates from the Casablanca Plant*

A. Ash agglomerates, all nearly spherical and having the glassy luster that is characteristic of most agglomerates in the sample. Photograph, sample C-6, magnified X4.3.

B. Ash agglomerate exhibiting the multiglobular form typical of the larger agglomerates in the sample. This type results from the fusion of the forms shown in A. The degree of fusion varies from weak adherence to complete assimilation. Photograph, sample C-5, magnified X1.7.

C. Ash agglomerate illustrating the fusion of two smaller forms, each characterized by a different texture. The very vesicular one on the left lost some of its wall material between vesicles during the sample preparation. The cavities, or vesicles, are light; ash matter is dark in this photograph. Thin section, transmitted light, sample C-3, magnified X7.

D. Ash agglomerate showing fragments of coal char (large black fragment) and of dark gray glass with quartz (light) inclusions scattered in a vesicular glassy matrix (dusty gray). The large circular and highlighted areas are vesicles in the sample. Thin section, transmitted light, sample C-4, magnified X15.

E. Mullite fibers that have crystallized within the glassy matrix in random orientation. Thin section, transmitted light, sample C-4, magnified X570.

F. Mullite fibers in random orientation. Fibers of mullite occur in parallel and in radiating orientations in other areas of the sample. Specimen etched in HF. Scanning electron micrograph, sample C-4, magnified X4460.

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* Micrographs A and B are from Yerushalmi et al., 1975; copyright 1975 by American Association for the Advancement of Science.

A   10mm

B   10mm

C   1mm

D   100μm

E   1μm

F   2μm

Plate 5
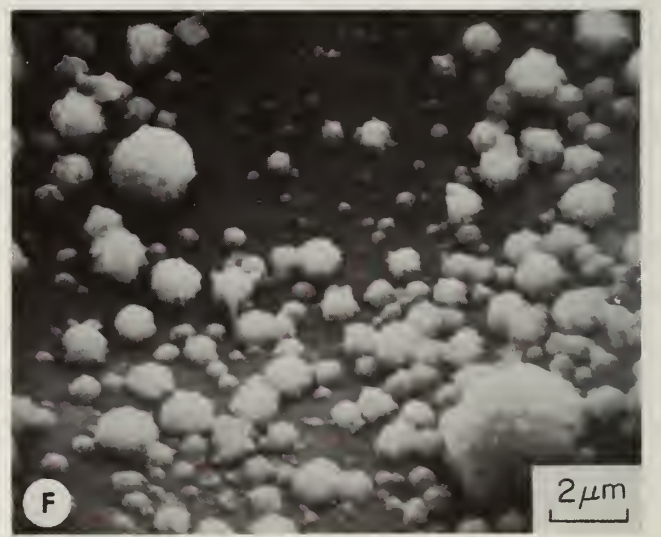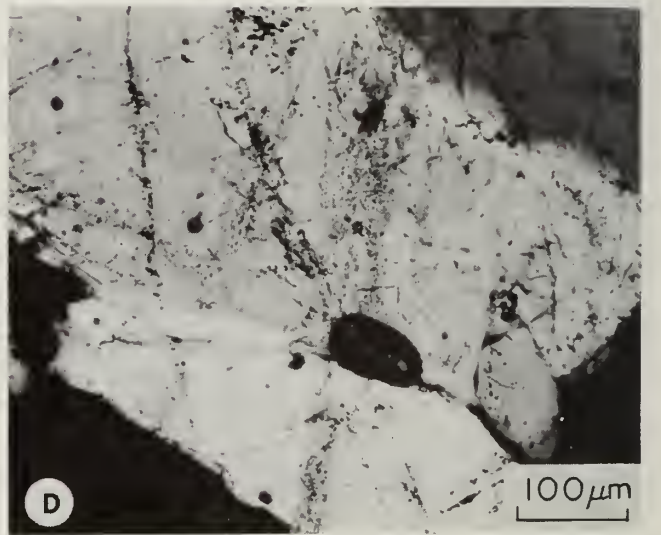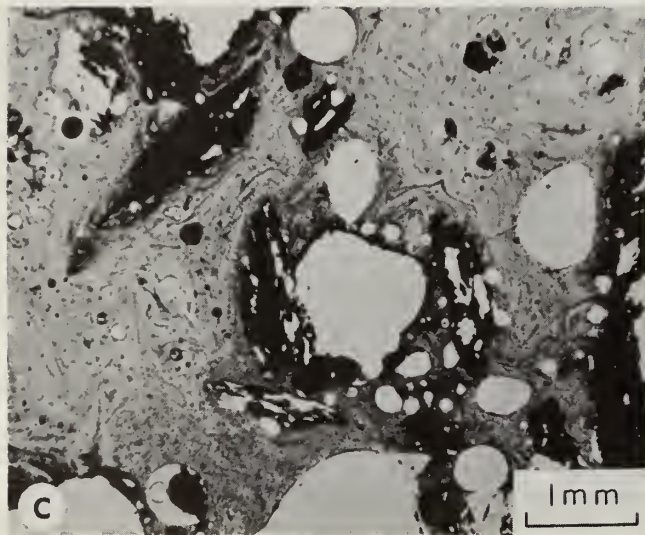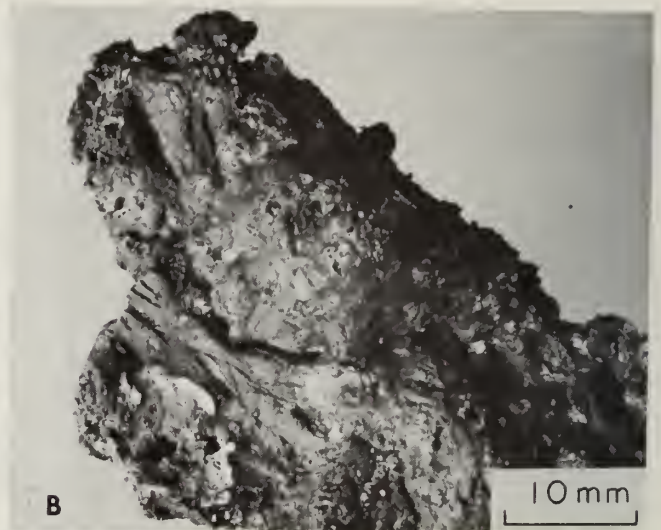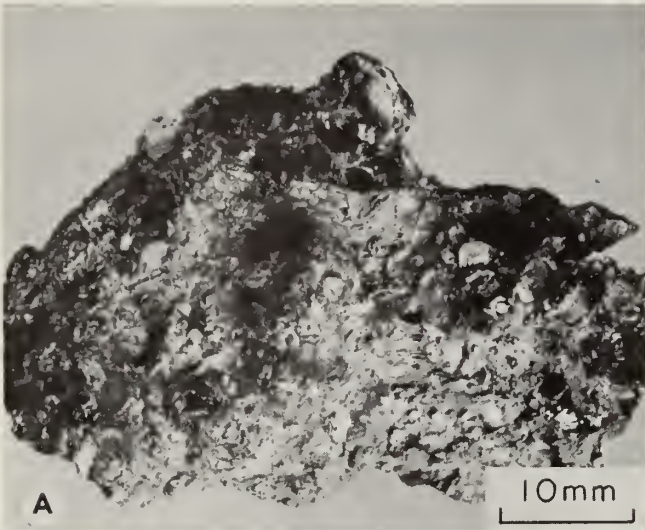
from the Casablanca clinker (pl. 5E). Iron-rich spherulites, possibly iron oxide free of sulfur, also were observed on cavity walls in both the La Taupe (pl. 5F) and Solvay clinkers. The spherulites in the latter also contained minor amounts of aluminum and silicon. Traces of titanium were detected in the light gray glassy fragments in the La Taupe and Casablanca clinkers.

The index of refraction of the glassy matrix was measured on agglomerate samples (S-3, LT-3, C-3) from the front sections of the gasification bed and on clinker samples in an attempt to detect changes in composition, if any, in the glass fraction. The results are as follows:

Index of Refraction of Glassy Matrix

	Agglomerate		Clinker	
	Range	Mean	Range	Mean
Solvay	1.548-1.580	1.564	1.566-1.570	1.568
La Taupe	1.573-1.576	1.574	1.588-1.604	1.596
Casablanca	1.575-1.582	1.576	1.575-1.577	1.576

The mean index remains essentially the same in the Solvay and Casablanca samples but increases in clinkers from the La Taupe plant. The increase suggests that a progressive change in chemical composition of the matrix glass occurs in the La

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Plate 5 - Textural and Mineralogical Features of Clinkers

A. Clinker showing rough and mottled surface and multiglobular shape only partly preserved because the assimilation of the several nearly spherical ash agglomerates is almost complete. Photograph, sample LT-2, magnified X1.7.

B. Clinker showing rough, mottled, and ropy surface with multiglobular shape. Original ash agglomerates only faintly preserved. Photograph, sample C-2, magnified X1.7.

C. Glassy matrix of clinker showing very well developed flow structure, embedded fragments of coal char (dark), and vesicles (light). Thin section, transmitted light, sample S-2, magnified X14.

D. Recrystallized polygranular quartz with linear pattern of inclusions that trend in six different directions within the grain. Thin section, crossed polarized and transmitted light, sample LT-2, magnified X145.

E. Spherulites, rich in Al and Fe, occurring in recesses between micro-laminations of a coal char fragment in a clinker. Scanning electron micrograph, sample C-2, magnified X8210.

F. Spherulites, rich in Fe, probably iron oxide, occurring on vesicle walls in a light gray fragment of glass in a clinker. Scanning electron micrograph, sample LT-2, magnified X4550.

Taupe agglomerates as they pass through the fluid bed and onto the grate where the clinkers are formed. The specific changes in composition are speculative, but it is reasonable to conclude that alumina, silica, and iron are progressively mobilized and added to the matrix glass by fusion of more and more ash material from the coke particles as they move through the fluidized bed. These elements also are probably added to the matrix glass by fusion of mullite, formed earlier, with hercynite crystals in the rear section of the fluidized bed, where the highest temperature occurs.

DISCUSSION AND CONCLUSIONS

The hercynite crystals formed in the front part of the fluidized bed at each plant. They crystallized and started to grow, probably at about 900° C, from molten clay minerals, just as the hercynite-like spinels in the Bradley and Grim (1951) experiments formed from illite and similar clay minerals heated to 900° C. Their work also showed mullite formed at the expense of spinel (hercynite) when the temperature was raised further to 1100° C and that the mullite melted near 1300° C. Therefore, the large decrease in the amount of hercynite between ash agglomerate and clinker from the Solvay plant could be due to the resorption of hercynite crystals into the glassy matrix at temperatures above 1100° C. Also, experiments by Glass (1954) showed that heating kaolinite to 1250° C produced mullite plus crystobalite, a high-temperature form of silica. The mullite present in the samples, therefore, may have come from hercynite formed earlier but also may have originated from kaolinite. The recrystallized quartz particles in the samples, which have the unusual crystalline form of parallel-strain lamellae oriented normal to the elongation, were probably formed as a by-product of the kaolinite-to-mullite reaction as demonstrated in the report by Glass (1954). The gradual cooling of the clinker would permit crystobalite to invert to quartz. Rapid raising and slower lowering of the temperature through the inversion points of α to β quartz (573° C) and of β quartz to tridymite (850° C) may account for the fractures in many of the quartz grains in the samples.

The amount of unburned carbon in the clinkers should be reasonably low if the coal is efficiently consumed. The percentage of carbon in the Solvay and La Taupe clinkers (S-2 and LT-2, table 3) is slightly lower than that of the agglomerates from the same plants, but at the Casablanca plant the ash agglomerate sample from the front of the fluidized bed had less carbon than the clinker. However, the carbon analysis of the Casablanca clinker (sample C-2) may be erroneously high, because for some unknown reason the total percentage of constituents in sample C-2 is 102.7 percent instead of 100.

A good approximation of the fraction of the total sulfur introduced with the coal that is retained in the clinker can be calculated from the sulfur analyses (coal and clinker) and the percentage of ash in the coal (table 3). The balance of the sulfur was discharged into the air. Data from the Solvay samples indicate 1.4 percent of the sulfur is retained in the clinker, in the La Taupe samples 10.4 percent is retained, and in the Casablanca samples 2.5 percent. These values are similar in magnitude to sulfur fractions retained in ash from a power plant in Illinois described by Rees et al. (1966).

The roots of the glassy beads, observed to extend from some beads on the surface of coal char particles into the interior of the particles, could form by migration of molten ash from the interior of the particle to the surface or by absorption of the ash into cracks by capillary action. We prefer the former explanation. According to Kingery (1956), "...the driving force causing a liquid to flow into joints is directly proportional to the surface tension (of the liquid) times the cosine of the contact angle." The contact angle the molten ash makes with the coal char or coke surfaces (measured through the ash bead) appears to be distinctly greater than 90° (pl. 1B-F). The cosine of angles between 90° and 180° is negative, and thus the force of capillary migration would be negative. In other words, the driving force would tend to move the molten ash to the surface, not into the particle. Furthermore, the well known practice of glassblowers of using graphite blocks or tools for shaping molten glass attests to the fact that graphite, which, like coke and coal char, is rich in carbon, is not wetted by molten and siliceous glasses. This behavior tends to support the conclusion that molten ash was not absorbed by the coal char particles. Finally, Ellefson and Taylor (1938) tend to support the non-wetting character of molten ash on coke. They measured the work of adhesion of molten sodium-silicate on gold, platinium, and carbon (graphite) surfaces in vacuum and determined this property to be 481, 431, and 68 ergs/cm^2 for the three elements, respectively. The low value for carbon indicates it is essentially not wetted by molten glass.

Consideration of the results of this study leads to the following statements regarding the origin and formation of ash agglomerates. It is convenient to consider the agglomerating process, the Godel phenomenon, as occurring in four stages (Yerushalmi et al., 1975).

1) Small glassy beads appear on the surface of a particle undergoing gasification. Some of the beads appear to have oozed through microcracks from at least a short distance inside the particle.

2) The ash beads grow by several mechanisms. As coke is consumed by its gasification, molten ash continues to accumulate on the particle surface and contiguous beads merge. The particle can also capture ash beads from another coke particle when the two particles touch each other in the fluidized bed.

3) The molten beads grow and eventually separate from the coke surface because molten ash does not wet coke. In the turbulent currents of the fluidized bed, a loose bead may be accreted to ash agglomerates or to another bead present in the bed. It may also be captured by ash still attached to a coke surface by molten matter that is rooted into capillary pores of the coke particle.

4) The ash agglomerates themselves coalesce and grow. They may also grow by plucking off ash beads still attached to a coke surface. Some agglomerates are round whereas others (usually the larger agglomerates) exhibit composite structures (multiglobular) that result from coalescence and fusion of smaller agglomerates. The degree of fusion varies from weak adherence to complete assimilation.

Gasification of different particles of coal, containing slightly different assemblages of coal macerals and mineral matter, give rise to particles

of molten ash that vary in composition and vesicularity. The clay minerals contribute aluminum, silicon, potassium, iron, calcium, and magnesium to the molten beads. In some beads, hercynite, mullite, and quartz crystallize. Sand and silt-sized grains of quartz within the coal develop parallel fractures from thermal shock, and some gases and tiny particles of coke become trapped along these fractures.

Pyrite grains in the coal disassociate to sulfur vapor and pyrrhotite at about 740° C. The pyrrhotite remains stable until it reaches about 1000° C, at which temperature it probably disassociates to metallic iron and FeS in the reducing environment that exists in the close vicinity of the coke particles. As the iron and sulfur compounds cool, they form the metallic globules observed in the agglomerates and clinkers. Gaseous sulfur condenses on cavity walls and combines with iron, some of which may be available on the surfaces of the molten glassy matrix, to produce pyrrhotite sublimates. More than 90 percent of the sulfur escapes as sulfur oxides or hydrogen sulfide in the flue gases.

The size distribution of ash agglomerates in the fluidized bed and the percentage of ash agglomerates in the bed are broadly seen to be functions of:

a) the rate of release of ash matter from coke undergoing gasification,

b) the stickiness of the matter at the temperature of the bed, and

c) the eddy diffusivity of ash agglomerates in the bed and the resulting frequency of contact between an ash agglomerate and the sticky pad of clinkers resting on the grate.

The last factor is related to the ratio of the velocity of the fluidizing gas to the minimum velocity of fluidization for a particular bed of coke. As the velocity ratio increases, the turbulence of the bed intensifies, and contact between an ash agglomerate and the sticky pad on the grate becomes more frequent. The percentage of the ash agglomerates in the bed and their size would both be reduced. A low velocity ratio, on the other hand, would reduce the frequency of contact between ash agglomerates and the sticky pad and would thereby permit ash agglomerates to grow larger in the bed. Indeed, there is probably an operating limit of the velocity below which undesirably large ash clinkers would form. This operating limit would of course depend on such factors as temperature and the dimensions of the bed.

The ash agglomerates captured upon the pad of ash at the rear of the fluidized bed lose their separate identities. However, the siliceous and vesicular glassy fragments, the quartz particles, and the metallic globules retain their identities throughout the agglomeration and clinker stages.

Ash agglomerates from the three plants are similar in many ways, even though the type of coal used at the plants was significantly different. The mineral matter in the coals studied, especially that in the bituminous coal from the Solvay plant, is not significantly different from that commonly found in the

bituminous coals of the Illinois Basin. In the basin coals, illite, kaolinite, mixed-layer clay minerals, quartz, calcite, and pyrite are the most common mineral constituents (Rao and Gluskoter, 1973). The principal, but minor, difference between this suite of minerals and those found in the Solvay coal is the absence of calcite and the presence of the iron-bearing carbonates siderite and ankerite in the Solvay coal. It is unlikely that this difference would alter the behavior of the agglomeration sufficiently to foul the Ignifluid process if coals from the Illinois Basin were used.

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