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# INSTITUTE OF GAS TECHNOLOGY

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## INTRODUCTION

The U-GAS Process is being developed by the Institute of Gas Technology to produce a low- to medium-Btu (150 to 300 Btu/SCF) fuel gas from coal. The primary use of the gas is as an industrial fuel replacing natural gas and fuel oil. In the form of synthesis gas, the product may be used as a chemical feedstock for production of hydrogen, ammonia, and methanol.

The U-GAS Process accomplishes four important functions in a single-stage, fluidized-bed gasifier: It decakes coal, devolatilizes coal, gasifies coal, and agglomerates and separates ash from the fluidized bed. Other characteristics of the process are shown in Table 1.

Table 1. U-GAS PROCESS CHARACTERISTICS

- High conversion of coal to gas using the ash agglomeration technique
- Capability to gasify all ranks of coal
- Ability to accept fines in coal feed
- Simple design and safe, reliable operation
- Easy to control and ability to withstand upsets
- Product gas significantly free of tar and oils
- No environmental problems.

In the process, washed coal (1/4 inch X 0) is dried and pnuematically injected into the gasifier through a lockhopper system. Within the fluidized bed, coal reacts with steam and oxygen (air can be substituted for oxygen) at a temperature of 1750° to 1900°F and pressure between 50 and 350 psi to produce a gas mixture of hydrogen, carbon monoxide, carbon dioxide, and a smaller fraction of methane. Because of reducing conditions in the bed, sulfur present in the coal is converted to hydrogen sulfide. Simultaneously with coal gasification, the ash is agglomerated into spherical particles and separated from the bed by utilizing the technique of "ash agglomeration." In this manner, the fluidized bed achieves the same low level of carbon losses in the discharge ash generally associated with the ash-slagging type of gasifiers. Coal fines elutriated from the fluidized bed are returned to the bed where they are gasified, agglomerated with bed ash, and discharged with ash agglomerates. The raw product gas is significantly free of tar and oils, thus simplifying ensuing heat recovery and purification steps.

## PILOT PLANT DEVELOPMENT PROGRAM

Most of the U-GAS Process development work has been accomplished on a large pilot plant. The pilot plant gasifier and peripheral equipment is contained in an enclosed structure about 100 feet high.

The pilot plant (Figure 1) consists of a drying and screening system, feed storage silos, a lockhopper system (weighed) for feeding a dry pulverized material at rates up to 3000 lb/hr, a refractory-lined fluidized-bed reactor with a special agglomerate withdrawal system in its base, a product gas quench system, a cyclone system for removal and recycle of elutriated fines, a product gas scrubber, a product gas incinerator, and all necessary instrumentation and controls. The 3-foot inside diameter by 25-foot high reactor is lined with high alumina and insulating refractory to reduce the wall temperature to acceptable levels with an internal temperature of 1900°F.

The coal is fed to the reactor from the lockhoppers by a screw feeder discharging into a system that injects the feed directly into the gasifier. The product gas leaving the reactor enters the first quencher where it is direct cooled to about 1000°F. Two cyclones located downstream of the first quencher are for dust collection; these are followed by the second quencher, where the product gas is cooled to about 500°F before it is sent to a gas scrubber. The scrubbed gas is then finally burned in an incinerator.

The process development began with the construction of the pilot plant in 1974. The development work can be divided into three separate phases — Phase I, during which the process viability was demonstrated using metallurgical coke and char as feed; Phase II, during which the pilot plant was modified to feed coals and trial tests were made with coal; and Phase III, during which process viability was proved using coal as feed and data were developed for scale-up of the process and design of a demonstration plant.

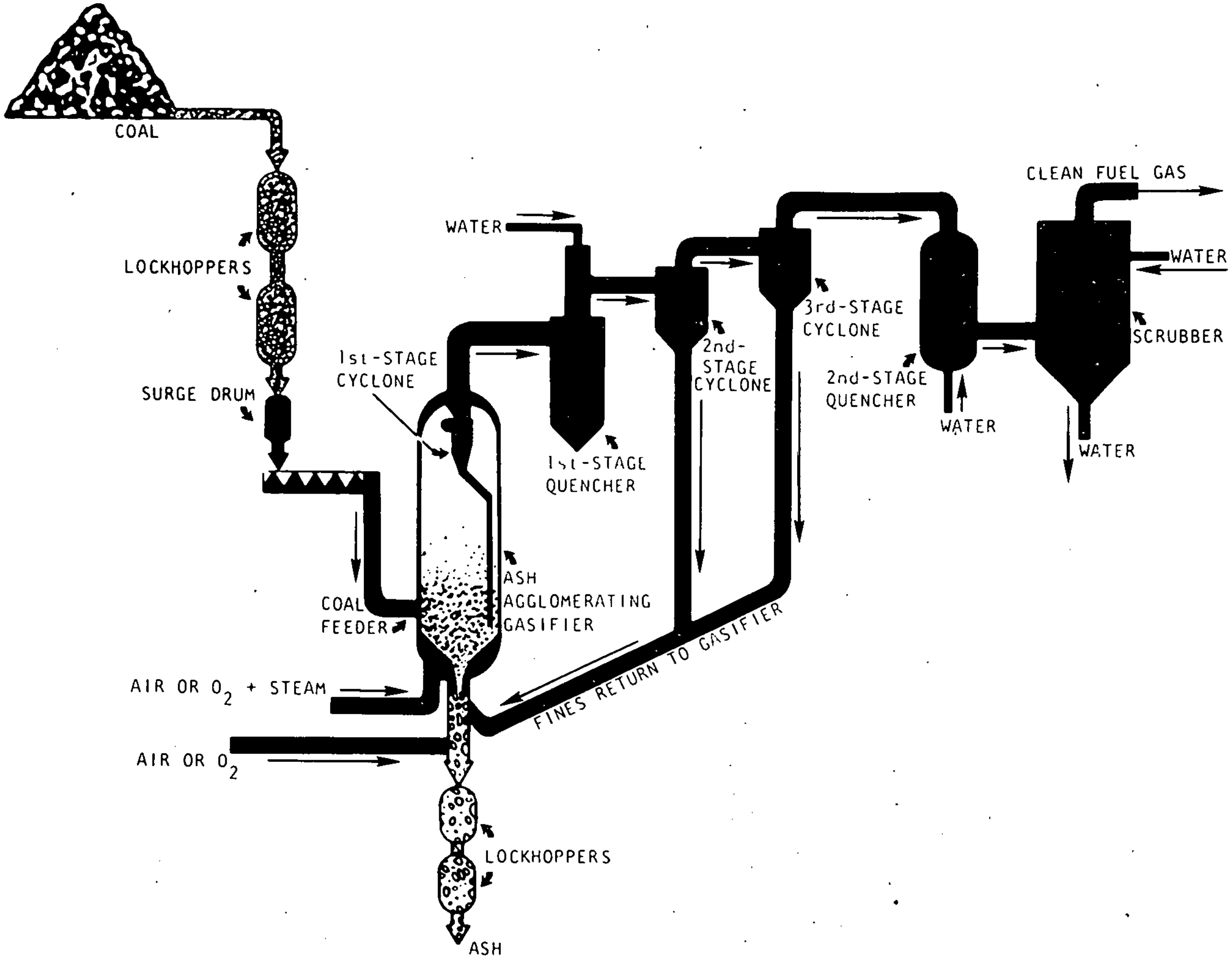

Figure 1. FLOW DIAGRAM FOR ASH-AGGLOMERATING GASIFIER

Various feedstocks have been used in the pilot plant to determine process sensitivity to variables such as ash content, particle size, reactivity, and free-swelling index of caking coals. Table 2 lists the characteristics of these feedstocks.

During the past 5 years of pilot plant operations, a total of over 5600 hours of operating time has been logged, and more than 100 test runs have been completed. Several test runs have lasted for over 2 weeks during which steady-state, continuous operation of 100 to 150 hours have been achieved. A summary of the pilot plant tests is shown in Table 3.

A detailed description of the pilot plant development effort can be found in several publications.[1-3] The ash chemistry work described in this paper was conducted during Phase III of the development period. Therefore, a brief description of the pilot plant effort and some test results are presented before the ash chemistry section.

The U-GAS Process was selected by Memphis Light, Gas and Water Division and the U.S. Department of Energy for design of a demonstration plant to be located in Memphis, Tennessee. The pilot plant began operations in January 1978 in support of this program. The objective was to provide mechanical, operating, and process data for the design of the demonstration plant using Western Kentucky No. 9 coal. A total of 16 test runs were conducted with both coke and run-of-mine and washed Kentucky coal. Most of the tests were conducted at a pressure of 30 psia except the last test with washed Kentucky coal which was at 60 psia. The fluidized-bed operating temperature was in the range of 1815°to 1900°F. A summary of the operating data for tests conducted in this period is shown in Table 4.

In the initial tests (Runs 118 through 122), the objective was to determine the operating conditions necessary for stable gasification and agglomeration of the unwashed Western Kentucky coal. These tests revealed that a superficial velocity in the range of 4 ft/s, higher than used previously, is necessary to maintain stable fluidization conditions in the bed when operating at 1850° to 1900°F with the bituminous coals.

In the next series of tests (Runs 123 through 126), successful stable gasification was obtained. Both steam-air and steam-oxygen gas mixtures were used for gasification. However, during these tests sufficient ash could not be agglomerated and withdrawn from the fluidized bed to maintain an overall

## Table 2. PILOT PLANT FEEDSTOCK CHARACTERISTICS

| | | COED CHAR | | | | W. Kentucky No. 9 Bituminous Coal | |
|---|---|---|---|---|---|---|---|
| | Bethlehem Coke Breeze | Illinois No. 6 Bituminous | W. Kentucky Bituminous | Montana Subbituminous Coal | Illinois No. 6 Bituminous Coal | ROM | Washed |
| Proximate Analysis, wt % | | | | | | | |
| Moisture | 2 - 4 | 1.5 | 2.5 | 19.1 | 3.9 | 1.6 | 3.1 |
| Volatile Matter | 3 | 6 | 8.3 | 26.0 | 33.2 | 34.4 | 35.8 |
| Ash | 11.0 | 19.5 | 12.5 | 8.0 | 10.5 | 19.9 | 12.0 |
| Fixed Carbon | 83.0 | 73.0 | 76.7 | 46.9 | 52.4 | 45.1 | 49.1 |
| Ultimate Analysis, wt % (dry) | | | | | | | |
| Ash | 11.0 | 19.8 | 12.8 | 8.3 | 11.0 | 19.2 | 12.1 |
| Carbon | 86.5 | 74.6 | 78.3 | 66.2 | 71.4 | 64.3 | 72.2 |
| Hydrogen | 0.4 | 0.8 | 1.8 | 4.4 | 4.3 | 4.4 | 4.5 |
| Sulfur | 0.8 | 3.2 | 2.7 | 0.6 | 3.9 | 4.6 | 3.1 |
| Nitrogen | 0.6 | 0.5 | 1.7 | 1.1 | 1.2 | 1.3 | 1.3 |
| Oxygen | 0.7 | 1.1 | 2.7 | 19.4 | 8.2 | 6.2 | 6.8 |
| Bulk Density, lb/ft$^3$ | 52 | 39 | 39 | 53.1 | 53 | 61 | 50.4 |
| Free Swelling | 0 | 0 | 0 | 0 | 3 - 4 | 5 - 6 | 4 - 7 |
| Heating Value, Btu/lb (dry basis) | - | - | - | 11,160 | 12,456 | 11,570 | 12,498 |
| Feed Size | 1/4"X 0 | -20 Mesh | -20 Mesh | 1/2"X 0 | 1/4"X 0 | 1/4"X 0 | 1/4"X 0 |
| Initial Deformation Temperature*, °F | 2020 | 1960 | 2040 | 2050 | 1960 | 1975 | 1995 |

* Under reducing atmosphere

Table 3. SUMMARY OF U-GAS® PILOT PLANT TESTS

| TEST RUN | PERIOD | FEED | FUNCTION |
|---|---|---|---|
| 1 - 9 | 1974 | Metallurgical Coke | Equipment Shakedown |
| 10 - 53 | 1974 | Metallurgical Coke | Process Feasibility |
| 54 - 67 | 1975 | COED Char | Test High Reactive, Small Size Feed |
| 101 - 104 | 1977 | Metallurgical Coke | Shakedown of Modified Pilot Plant |
| 104 - 112 | 1977 | Montana Subbituminous | Test Highly Reactive Feedstock |
| 112 - 117 | 1977 | Illinois No. 6 | Coal Trial Runs |
| 118 - 133 | 1978 - 1979 | W. Kentucky No. 9 | Demonstration Plant Design Data |

## Table 4. OPERATING DATA WITH WESTERN KENTUCKY NO. 9 COAL

| Run No. | 124 | 130 | 131 | 131 | 132 | 133 | 133 | 133 |
|---|---|---|---|---|---|---|---|---|
| Feed Material | Western Kentucky No. 9 | | | | | | | |
| Gasification Mode | Steam-$O_2$ | | | | | | | |
| Run Duration, hr (Coal Feed) | 168 | 106 | 104 | | 74 | 153 | | |
| Pressure, psia | 22.5 | 23.6 | 24.1 | 26.5 | 27.2 | 56.3 | 57.5 | 56.0 |
| Bed Temperature, °F | 1815 | 1870 | 1880 | 1900 | 1880 | 1880 | 1850 | 1850 |
| Solid Feed Rate, lb/hr (Dry) | 1005 | 1894 | 1323 | 1091 | 966 | 1733 | 1510 | 1686 |
| Steam Feed, mol/hr | 69.5 | 70.6 | 80.2 | 76.3 | 86.8 | 160.0 | 160.0 | 188.0 |
| Oxygen, mol/hr | 19.9 | 31.7 | 26.4 | 37.1 | 23.5 | 43.7 | 38.4 | 40.3 |
| Superficial Velocity, ft/s | 4.0 | 4.3 | 4.3 | 4.2 | 4.0 | 3.6 | 3.4 | 3.6 |
| Ash Discharge Rate, lb/hr | 207 | 62 | 117 | 111 | 99 | 163 | 133 | 126 |
| Agglomerate Ash Content, wt % | 65.7 | 76.4 | 83.1 | 78.0 | 89.2 | 95.2 | 91.7 | 88.4 |
| Coal Utilization Efficiency,* % | 81 | 75 | 81 | 94 | 93 | 92-89 | 86 | 86 |
| Product Gas HHV, Btu/SCF | 266 | 281 | 275 | 253 | 260 | 256 | 253 | 250 |
| Product Gas Composition (Dry), % | | | | | | | | |
| CO | 28.6 | 30.5 | 25.5 | 23.7 | 26.8 | 26.0 | 22.6 | 22.8 |
| $CO_2$ | 22.1 | 21.8 | 24.9 | 32.1 | 26.0 | 26.9 | 29.5 | 29.8 |
| $H_2$ | 45.6 | 42.4 | 43.6 | 38.4 | 42.9 | 43.0 | 43.1 | 42.9 |
| $CH_4$ | 2.6 | 4.7 | 4.9 | 5.0 | 3.4 | 3.5 | 4.0 | 3.7 |
| $N_2$ | 1.1 | 0.6 | 1.1 | 0.8 | 0.9 | 0.6 | 0.8 | 0.6 |

* Based on coal input compared to carbon lost in ash discharge and fines.

ash balance. Several attempts to increase the ash agglomeration rate by increasing operation temperature (up to 1950°F) and the bed ash content (up to 70%) were not successful. Therefore, after Run 126, the mechanical design of the ash-agglomerating section was changed to provide more flexibility in introducing oxygen to the system and, at the same time, to remove ash agglomerates from the fluidized bed.

The next series of seven tests (Runs 127 through 133) was highly successful. The changes in configuration and mode of operation completely eliminated the problem of ash sintering or clinkering and, after each of the seven tests, the grid and the fluidized-bed area were free of any ash buildup. Two tests were conducted with metallurgical coke to establish baseline operating conditions of the gasifier, and the next five tests were conducted with a washed Western Kentucky coal. During these tests, repeated stable gasification and ash agglomeration were achieved with both steam-air and steam-oxygen mixtures. The raw product gas heating value was 255 to 285 Btu/SCF. Coal fines from both the first and the second cyclones were recycled, yielding coal gasification efficiency of up to 99% and coal utilization efficiency of about 95%.*

## ASH AGGLOMERATION

The agglomeration of ash is of critical importance in the U-GAS Process. At steady-state conditions, the amount of ash as coal fed to the gasifier must be equal to the amount of ash removed as agglomerates. Therefore, for ash-balanced operations, ash not only has to be agglomerated, but also has to be separated from the fluidized bed and discharged from the reactor at a rate equal to the rate of gasification.

The rate of agglomeration, the size of agglomerates, and the ash content of agglomerates is dependent on the following variables: fluidized bed temperature, bed ash concentration, average feed particle size, superficial velocity, and bed height. The exact mathematical relationships to these variables is not yet known, and the mechanism by which agglomerates form is believed to be quite complex.

Based on the pilot plant program, the following qualitative effects have been observed. There is a minimum temperature for each feedstock below which

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* Coal gasification efficiency accounts for loss of carbon in agglomerates; coal utilization efficiency accounts for loss of carbon in ash discharge and coal fines.

ash agglomerates do not form at an appreciable rate. Operating at a temperature higher than this minimum increases the rate and the size of agglomerates. However, operating at too high a temperature results in sintering and defluidization. There is also a minimum threshold value of bed ash content below which agglomerates do not form, probably because ash concentration determines the sticky surface area that is available for captivation and growth of ash particles. Particle size affects the rate of ash agglomeration because it directly relates to the number of inter-particle collisions required to produce an agglomerate. As the particle size of material in the fluidized bed decreases, a higher temperature is required to maintain a given rate of ash agglomeration. Superficial gas velocity determines the circulation pattern of solids in the bed. A first-order relationship has not been determined between agglomeration and superficial velocity. Too low a velocity, even though beneficial for agglomeration, has a tendency to lead to ash sintering and defluidization. Increasing the bed height increases the gasification rate and also requires an increase in the agglomeration rate. If agglomerates are assumed to be forming throughout the fluidized bed, both of these rates will go hand in hand.

## ASH CHEMISTRY

Difficulties encountered, as described previously, in producing ash agglomerates from bituminous coals and differing agglomerating tendencies of various coals and cokes led to a program involving the study of ash chemistry as it affects ash agglomeration in the U-GAS Process. This study was conducted in support of the pilot plant program and was beneficial in guiding the test work and in subsequent success in agglomerating both run-of-mine and washed Kentucky coal.

## EXPERIMENTAL METHODS

Petrographic samples were mounted, sectioned, and polished according to methods used in coal petrography.[4] Most of the microscopic observations were made with 40X Achromat and 16X Antiflex oil immersion objectives on a Zeiss Universal microscope.

Iron oxides and sulfides can be identified by appearance, especially when more than one species of oxide or sulfide is present. Ferrous sulfide is brilliant, although not as brilliant as pyrite, has a yellowish cast, and is distinctly anisotropic. Ferrous oxide is dead white; magnetite is darker and blue-gray in color. X-ray emission in a scanning electron microscope conducted at the Illinois Institute of Technology Research Institute or at McCrone Associates, was relied upon for initial identification of glass and crystal phases such as ferrous aluminum silicate, ferrous silicate, ferrous aluminate, calcium aluminum silicate, and quartz. These phases can usually be recognized under the optical microscope by reflectance, which varies roughly with the iron content, and morphology. Quartz has a reflectance similar to that of the epoxy resin mounting medium and is only slightly anisotropic; thus, it is not easy to identify under the optical microscope. Its most distinctive characteristic in ash is the presence of fractures from thermal shock.

Ash samples were analyzed by the lithium metaborate fusion method of Boar and Ingram[5] with atomic absorption finish for aluminum, calcium, iron, silicon, and titanium. Sodium and potassium were determined by flame emission.

Sulfide content in chars, coke, and ash agglomerates was determined by refluxing the ground sample with 6N hydrochloric acid, trapping evolved hydrogen sulfide in alkaline cadmium chloride solution, reacting this sulfide with standard iodine solution, and titrating the excess iodine with standard thiosulfate. It was assumed that the sulfide was present as ferrous sulfide, although it is possible that calcium also could form a sulfide. The percentage of the iron present as sulfide was calculated from this determination and from the determinations of ash and total iron in the ash.

The treatment of ash agglomerates with hydrochloric acid dissolved about 90% of the iron and practically all of the calcium; thus, the method appears adequate for the purpose of this program, although small amounts of iron sulfide occluded in sintered clay may not be measured. The treatment does not dissolve the iron that is present as ferrous aluminosilicate glass.

## ANALYSES AND OBSERVATIONS

### Ash From Coke

Previous work on agglomerates from coke and FMC char was reported in a paper presented at the American Chemical Society Fuel Chemistry Division meeting of May-June 1977.[6] Ash agglomerate beads from coke were shown to consist of unmelted ash particles embedded in a matrix believed to be molten in the gasifier. This is shown in the photomicrograph in Figure 2, which was taken with oblique illumination at low magnification. The unmelted, unassimilated particles appear lighter than their background. The beads also contain many vesicles: Some are empty and appear black, others are filled with the mounting medium and thus have the same tone as the outside of the beads.

With vertical illumination, residual coke is highly reflectant. Only a small amount was present in the agglomerates as small particles on the outside surface of the bead or on the inside surface of vesicles in the beads. The low content of the ash agglomerates was confirmed by analysis of a hand-picked sample in which only 1.9% carbon was found.

Under higher magnification, the matrix in most regions of the agglomerates that were obtained in early runs appears as a glass containing small crystals (Figure 3). X-ray emission in the scanning electron microscope indicated that the glass contains iron, aluminum, and silicon; the crystals are ferrous aluminate. The lack of the graininess typical of sintered clay and the presence of well-fromed crystals within the matrix indicated that the matrix had been molten in the gasifier. A few regions are present that also contain small amounts of one or more of other kinds of crystals: iron silicate, ferrous oxide, magnetite, and (probably) calcium aluminum silicate. These regions were observed in greater abundance in agglomerates from some of the later coke runs when the ash had higher calcium content. (See Table 5.) A few small particles of ferrous sulfide are also present in the matrix and unassimilated ash.

## Ash From Kentucky Run-of-Mine Coal

The composition and fusibility of the ash samples of coke and Kentucky coal are shown in Table 5. The average fusibility temperatures of run-of-mine coal are slightly lower than those of coke, but the difference is probably not significant.

A mineralogical analysis of a sample of run-of-mine Kentucky coal was obtained from the Illinois State Geological Survey. The sample yielded 24.09% low-temperature ash (mineral matter) compared with 19.2% high-temperature ash. Results of the analysis are as follows:

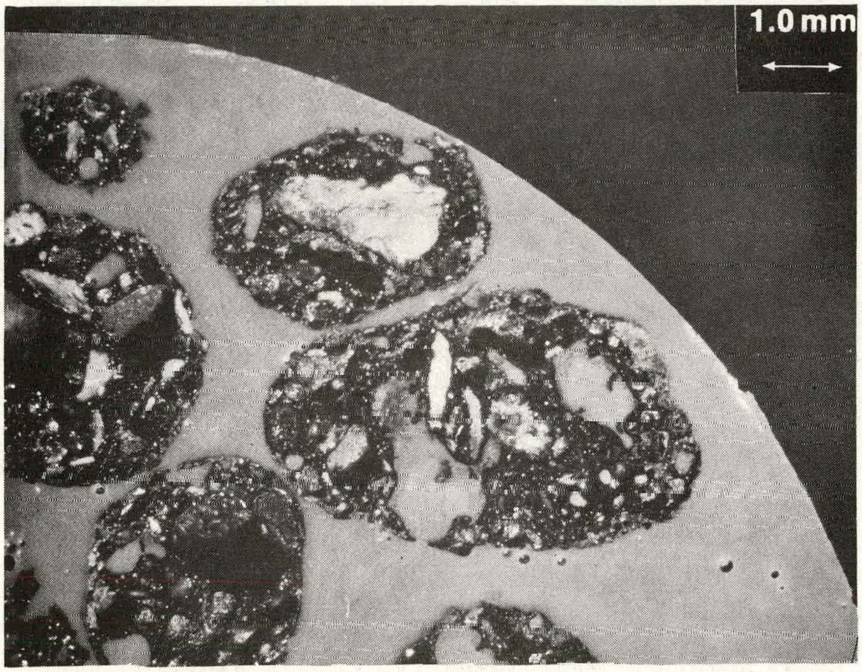

Figure 2. PHOTOMICROGRAPH OF AGGLOMERATES FROM COKE

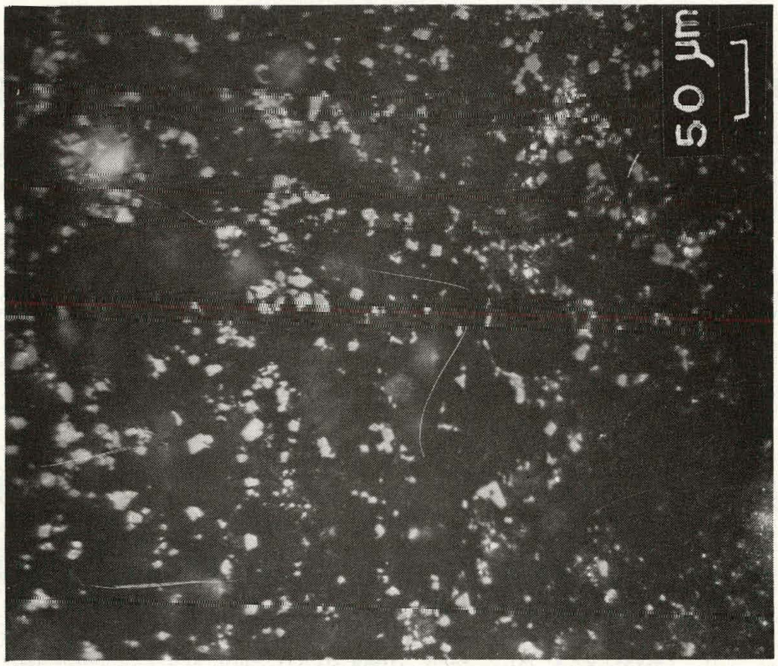

Figure 3. PHOTOMICROGRAPH OF GLASSY SILICATE MATRIX WITH FERROUS ALUMINATE CRYSTALS IN COKE AGGLOMERATES

## Table 5. COMPOSITION AND FUSIBILITY OF ASH OF FEEDS

| | Coke Feed To Early Runs | Coke Feed Runs 111 to 127 | | ROM Kentucky Coal | | Washed Kentucky Coal | |
|---|---|---|---|---|---|---|---|
| | | Avg. | Range | Avg. | Range | Avg. | Range |
| | wt % | | | | | | |
| Ash Composition* | | | | | | | |
| $SiO_2$ | 50.0 | 44.3 | 38.6-47.2 | 46.9 | 43.2-46.9 | 46.5 | 42.1-49.4 |
| $Al_2O_3$ | 22.1 | 20.9 | 16.6-23.4 | 17.2 | 15.9-18.7 | 18.0 | 15.6-19.2 |
| $Fe_2O_3$ | 20.1 | 24.3 | 18.2-30.0 | 24.8 | 21.0-23.5 | 22.7 | 20.5-27.4 |
| $TiO_2$ | 0.86 | 0.95 | 0.8- 1.1 | 0.81 | 0.8-0.84 | 0.99 | 0.93-1.15 |
| CaO | 3.45 | 5.68 | 4.0- 6.9 | 6.14 | 5.3- 6.4 | 7.75 | 4.96-10.8 |
| MgO | 1.07 | 1.69 | 1.5- 1.7 | 1.11 | 0.85-1.16 | 1.08 | 0.94-1.06 |
| $Na_2O$ | 0.57 | 0.53 | 0.1- 0.8 | 0.62 | 0.60-0.72 | 0.61 | 0.41-0.85 |
| $K_2O$ | 1.83 | 1.66 | 1.1- 2.1 | 2.43 | 0.85-2.45 | 2.43 | 2.09-2.62 |
| $SO_3$ | - | - | 1.9- 3.8 | - | | | |
| | °F | | | | | | |
| Ash Fusibility | | | | | | | |
| Reducing Atmosphere | | | | | | | |
| IT | 2085 | 2018 | - | 1975 | - | 1993 | 1960-2040 |
| ST | 2155 | 2173 | - | 2106 | - | 2108 | 2060-2160 |
| HT | 2230 | 2248 | - | 2199 | - | 2166 | 2130-2200 |
| FT | 2440 | 2390 | - | 2329 | - | 2246 | 2170-2340 |
| Oxidizing Atmosphere | | | | | | | |
| IT | - | 2313 | - | - | - | - | - |
| ST | - | 2431 | - | - | - | - | - |
| HT | - | 2491 | - | - | - | - | - |
| FT | - | 2581 | - | - | - | - | - |

| Component | Analysis of Mineral Matter, wt % | |
|---|---|---|
| Pyrite | 24 | |
| Quartz | 12 | |
| Calcite | 8 | |
| Kaolinite | 13 | Ratio determined on —2μm fraction. Coarser particles of clay, present in minor amounts, may differ in composition. |
| Illite Clay | 30 | |
| Expandable (Mixed Layer) Clay | 13 | |
| Total | 100 | |

This distribution is typical of the mineral matter found in Illinois Basin coals, except that illite is higher and expandable clays lower than average.[7]

The form of iron in the feeds was also investigated. Iron is most commonly present in coal as pyrite ($FeS_2$) but also occurs as carbonate and as part of the structure of illite clay. Some pyrite may have been oxidized to iron oxide or sulfate when the coal was dried in the pilot plant. Hydrochloric-acid-soluble iron content varied from 16% to 36% of the total iron and averaged 23.5%.

About a third of the mineral matter of the coal was present in relatively large, dense particles, as shown by a float-sink test on the fraction of the coal coarser than 40-mesh sieve size at a density of 1.6 g/cm$^3$.

Some ash agglomerates were produced in some periods of operation with the Kentucky run-of-mine coal, but balanced operation, with essentially all ash converted to agglomerates that could be removed through the central venturi, was not achieved during the period covered by this paper. During extended periods of operation, ash was periodically removed from the bed through a side discharge in addition to continuous removal through the central venturi.

Samples of the central venturi discharge from Run 122, obtained during periods when run-of-mine Kentucky coal was fed, were examined petrographically. Ferrous sulfide was dispersed throughout most of the particles. About three-quarters of them have an iron-rich, low-melting coating on the outside of an iron-poor, aluminosilicate-rich interior (Figure 4). The uncoated particles and the interior regions of coated particles are similar to each other and to particles of shale in the coal. A few particles of coarse char and particles consisting only of iron sulfide and/or oxide are also present, but

Figure 4. PHOTOMICROGRAPH OF CROSS-SECTION OF A SHALE PARTICLE WITH AN IRON-RICH COATING IN THE VENTURI DISCHARGE FROM RUN 122

very few particles are composed of continuous, iron-rich, low-melting matrix containing small unmelted particles of ash. The iron-rich coating of the particles contains mostly crystals of calcium aluminosilicate, iron silicate, and ferrous sulfide, with lesser amounts of calcium iron silicate and magnetite.

Petrographic examination of a bed discharge sample from this run showed the presence of ash particles with the same type of structure as was found in the central venturi discharge, together with a much greater proportion of char particles. However, few of the larger shale particles were present.

Side-discharge samples from a number of coal-feeding periods of Run 124 were also examined petrographically. Very few of the large shale particles that were present in the Run 122 venturi discharge were found, and only a small amount of silicate matrix phase was observed on the outside of some of the ash particles that were present. Most of the ash particles consist of only partially rounded noncrystalline aluminosilicate (shale) cores surrounded by ferrous sulfide (Figure 5). A layer of ferrous sulfide on an aluminosilicate core has also been noted frequently in samples from operation with FMC char. A layer inside of an iron silicate matrix layer is also not uncommon, as shown in Figure 6. (The outermost layer in this photomicrograph is magnetite.) Thus, it appears that formation of a ferrous sulfide layer is a precursor to formation of some or all of the low-melting matrix phase. It might be formed by oozing of the ferrous sulfide out of porous shale particles to the surface, or by spreading of ferrous sulfide after contact between a shale particle and a ferrous sulfide particle. It is also possible that ferrous sulfide itself can act as an agglutinating agent, as suggested by the morphology of a few particles in the Run 124 samples. These particles consist of distinctly separate shale regions joined by ferrous sulfide, as shown in Figure 7.

Bed discharge samples from most of the steady-state periods of Run 124 on run-of-mine Kentucky coal were chemically analyzed for iron sulfide. Very little discharge through the venturi occurred during these periods; thus, the side discharge was representative not only of the bed but also of the total ash product, if that removed as cyclone dust is neglected. In the first 3 days of the run, operated with steam-air and bed temperatures from 1850° to 1900°F, no conversion of sulfidic iron occurred. During another 3 days, operated at bed temperatures of 1800° to 1850°F, partly with steam-air and partly with steam-oxygen, sulfidic iron in the bed had decreased from the original 67% to between

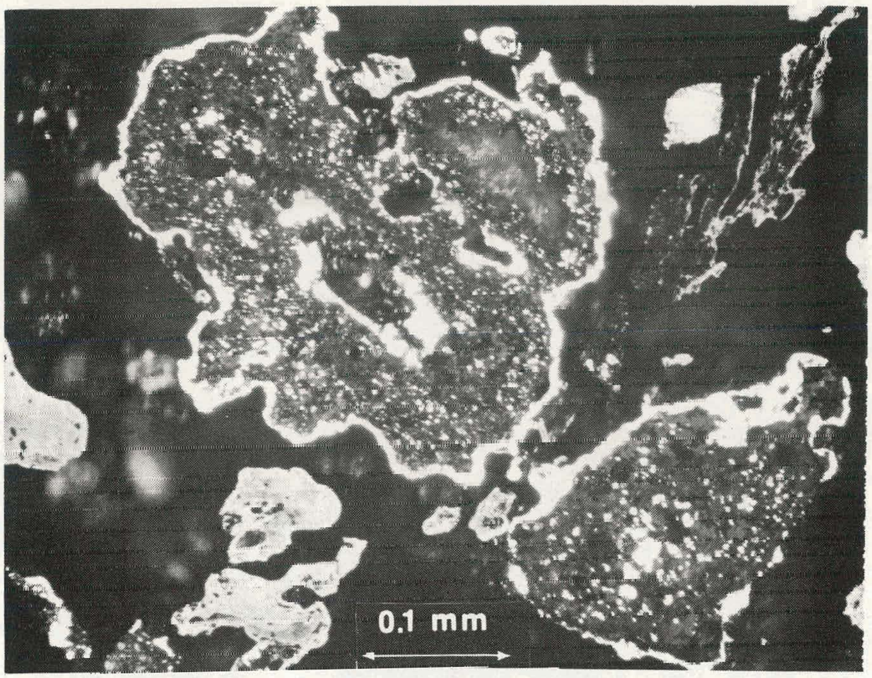

Figure 5. PHOTOMICROGRAPH OF TYPICAL ASH PARTICLES IN SIDE DISCHARGE FROM RUN 124

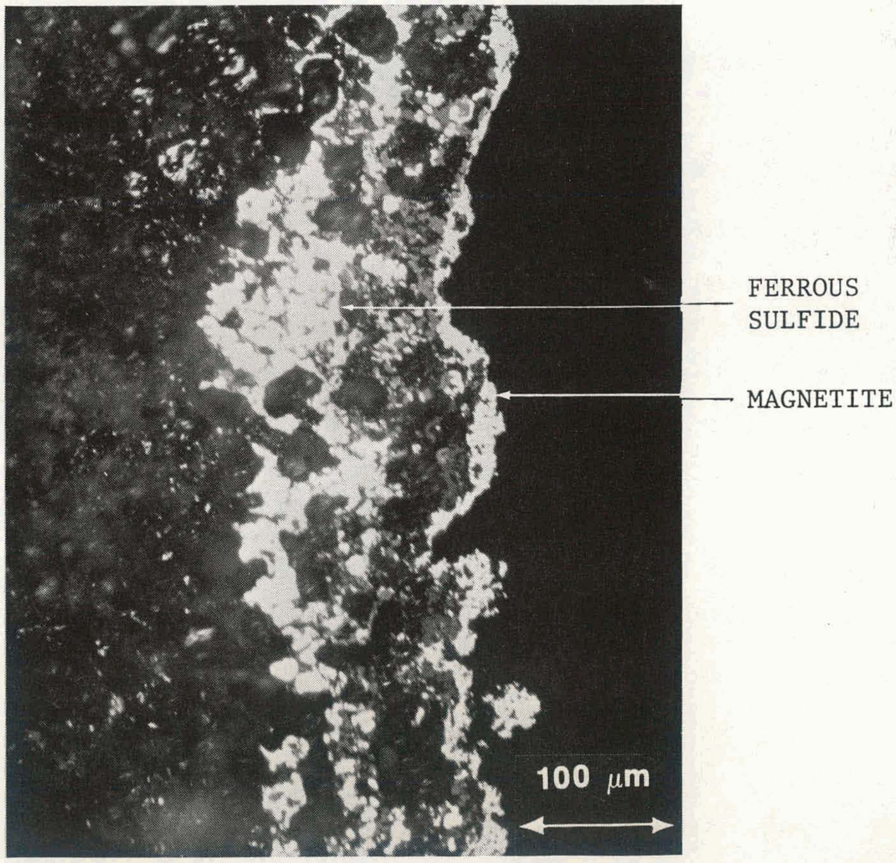

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Figure 6. CRYSTALS IN THE IRON-RICH COATING FOUND ON SOME PARTICLES IN VENTURI DISCHARGE FROM RUN 122

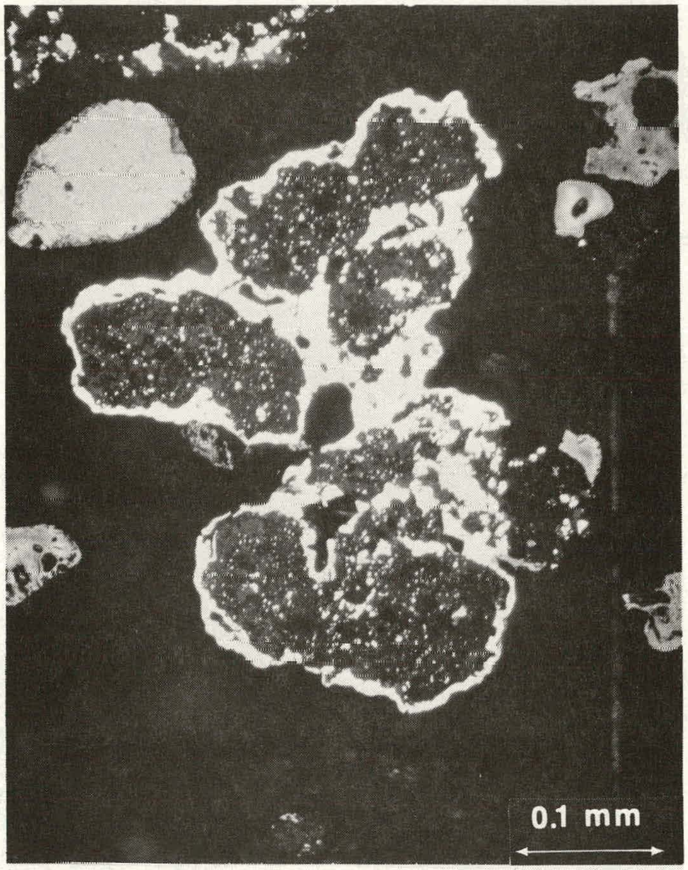

Figure 7. FeS JOINING SHALE PARTICLES IN SIDE DISCHARGE FROM RUN 124

36% and 54%. In the last 2 days of operation with steam-oxygen at the same bed temperature, sulfidic iron in the bed had decreased to 24% to 39%. Very little, if any, production of agglomerates occurred in this run.

## Ash From Washed Kentucky Coal

Data on composition and fusibility of the ash of the washed Kentucky coal are presented in Table 5. They do not differ significantly from those of the unwashed coal and coke.

As a result of changes in operation of the pilot plant unit, principally in the method of introduction of oxygen, agglomerates were produced in sufficient quantity that ash-balanced operation was achieved in several runs on the washed Kentucky coal.

A sample of the venturi discharge from Run 130 on washed Kentucky coal was examined. Agglomerated ash was present in the form of small beads concentrated in the —12+20 mesh sieve fraction. Petrographic examination of the beads confirms the absence of the large shale particles that were present in ash from run-of-mine Kentucky coal. The crystal pattern in the iron-rich silicate regions, as shown in Figure 8, resembles that in the coating on shale particles of the venturi discharge from Run 122 on run-of-mine Kentucky coal. The crystals are composed mainly of ferrous silicate, ferrous calcium silicate, and calcium aluminum silicate; small grains of ferrous sulfide and ferrous oxide are also present. Analysis of the total venturi discharge showed that only about 1% of the iron was present as sulfide; thus, almost all of the iron had been converted to oxide and silicate.

Data on the composition of the ash of feed and products of Run 130 are presented in Table 6. Calcium oxide content varies more than other components, as also shown by other analyses including one on a sample from the coal pile in which only 3.0% was present. Also note that the venturi discharge samples are greatly enriched in calcium oxide while the cyclone dust samples are depleted. We tentatively attribute the latter effect to occurrence of the calcium oxide in the coal as particles of calcite that are large enough to be selectively retained in the bed even after their decomposition to oxide. The variability in the amount of calcium found in the coal can be attributed to the occurrence of calcite as linings of cleat (fracture) surfaces that are unevenly distributed in the coal bed. Segregation of these particles in the coal pile may also occur.

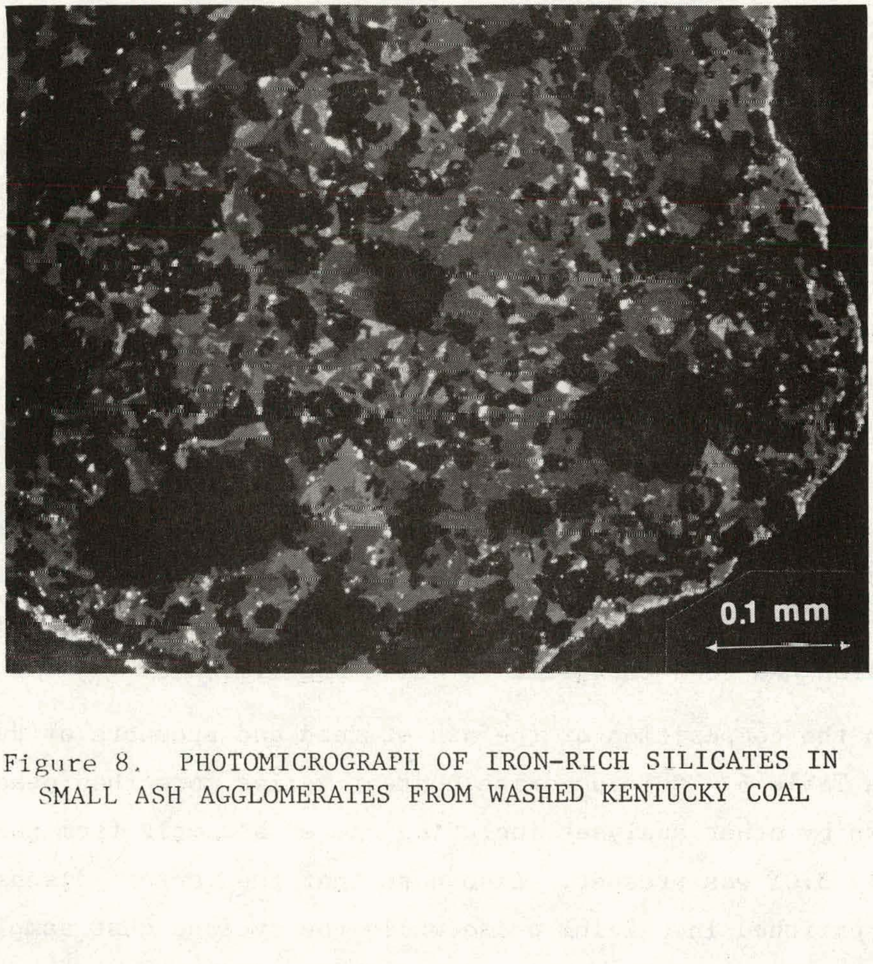

Figure 8. PHOTOMICROGRAPH OF IRON-RICH SILICATES IN SMALL ASH AGGLOMERATES FROM WASHED KENTUCKY COAL

## Table 6. COMPOSITION OF FEED AND PRODUCTS OF RUN 130 ON WASHED KENTUCKY COAL

| | Coal Feed | | | Central Venturi Discharge | | | | Second-Stage Cyclone Dust | |
|---|---|---|---|---|---|---|---|---|---|
| Run and Sample No. | 130-93 | 130-96 | 130-99 | 130-83 | 130-85 | 130-86 | −12+20 Fraction | 130-42 | 130-45 |
| Sample Hour | 2000 | 2400 | 2200 | 1830 | 0200 | 0600 | 1000 | 2200 | 1400 |
| Sample Date | 11/4/78 | 11/5/78 | 11/6/78 | 11/6/78 | 11/7/78 | 11/7/78 | 11/7/78 | 11/6/78 | 11/7/78 |
| | wt % | | | | | | | | |
| Ash Content of Sample | 8.5 | 8.4 | 7.4 | 55.0 | 73.9 | 81.6 | 95.4 | 19.8 | 18.7 |
| Ash Composition | | | | | | | | | |
| $SiO_2$ | 44.0 | 45.4 | 46.9 | 45.0 | 44.2 | 43.2 | 41.3 | 52.3 | 51.4 |
| $Al_2O_3$ | 17.7 | 18.2 | 18.6 | 18.4 | 18.0 | 17.4 | 16.7 | 19.3 | 19.0 |
| $Fe_2O_3$ | 21.7 | 21.0 | 21.6 | 20.8 | 24.1 | 25.4 | 25.8 | 18.7 | 18.8 |
| $TiO_2$ | 0.9 | 0.9 | 0.9 | 0.6 | 0.5 | 0.5 | 0.6 | 1.2 | 1.2 |
| CaO | 7.5 | 6.6 | 4.8 | 13.5 | 12.6 | 14.2 | 14.5 | 3.2 | 3.4 |
| MgO | 0.9 | 0.9 | 1.0 | 1.1 | 1.0 | 0.9 | 0.9 | 0.9 | 0.9 |
| $Ng_2O$ | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 | 0.2 | 0.2 | 0.6 | 0.6 |
| $K_2O$ | 2.3 | 2.4 | 2.5 | 1.1 | 0.9 | 0.7 | 0.5 | 3.1 | 3.2 |
| $SO_3$ | 4.3 | 3.4 | 2.7 | 1.5 | 1.2 | 1.1 | 1.0 | 2.2 | 2.2 |
| Total | 99.7 | 99.2 | 99.4 | 102.3 | 102.8 | 103.6 | 101.5 | 101.5 | 100.7 |
| Nonpyritic Iron | 28.8 | 19.3 | 23.3 | - | - | - | - | - | - |
| Ferrous Sulfide | - | - | - | 11 | 4 | 3 | 1.3* | 22 | 37 |

* On total discharge sample.

The ash analyses also indicated that potassium is depleted in the venturi discharge and is enriched in the cyclone dust. This effect can be attributed to the volatility of potassium oxide.

## Agglomeration Tests

Three samples of ash particles (agglomerates from coke, agglomerates from washed Kentucky coal, and shale particles found in the venturi discharge from Run 122 on run-of-mine Kentucky coal) were subjected to agglomeration tests. In these tests a small (1 to 2 centimeters in diameter) heap of the material in a small alumina or porcelain boat is inserted in a hot furnace and left there for about 10 minutes, which is sufficient time for the test heap to attain furnace temperature but not to sinter appreciably if it does not melt. Tests were run in both a reducing atmosphere (60:40 ratio of carbon monoxide to carbon dioxide) and in air. The agglomeration tests are designed to show the temperatures required for the ash particles or agglomerates to 1) become stuck together and 2) run together and form a rounded agglomerate or bead in the gasifier. The two temperatures are termed "agglomerated" and "fused," respectively, in Table 7, which shows the results of the test.

Table 7. AGGLOMERATION TEMPERATURES OF ASH PARTICLES

| Sample | Reducing Atmosphere (60:40 $CO/CO_2$) | | Air | |
|---|---|---|---|---|
| | Agglomerated | Fused | Agglomerated | Fused |
| | °F | | | |
| Ash Beads From Venturi Discharge, Run 127 (Coke Feed) | 1910 | 1983 | 1910 | 2125 |
| Ash Particles From Venturi Discharge (Run 122 (Run-of-Mine Kentucky Coal) | 1925 | 2160 | 1930* | 2225 |
| Venturi Discharge, –12+20 Mesh, Run 130 (Washed Kentucky Coal) | 1920 | 1980 | 1900 | 2030 |

* Some particles were sticking at temperatures of 1800°F and higher. At 1930°F particles with iron silicate coating stuck to each other and to uncoated particles as well.

Agglomeration (sticking) temperatures in the reducing atmosphere for the three samples are essentially equal at about 1920°F. The temperature for fusion or rounding of beads is higher (about 1980°F) and is also higher than the bed temperature for both coke and coal. Thus it appears that agglomeration can occur in the bed but that the formation of rounded beads can occur only in higher temperature regions of the reactor.

The behavior of the venturi discharge ash particles from Run 122 run-of-mine Kentucky coal in the air atmosphere was surprising. Some dark particles stuck together at temperatures as low as 1800°F. These were probably iron sulfide particles that, on insertion in the furnace, were partly oxidized to yield a liquid mixture of ferrous sulfide and oxide; the phase diagram shows a eutectic between ferrous sulfide and ferrous oxide melting at 1724°F.[8] The fact that the agglomeration temperature of the coal ash agglomerates (Run 130) was slightly lower in air than in the $CO/CO_2$ mixture may be the result of a similar effect of ferrous oxide and ferrous sulfide in a silicate mixture. The eutectic of a mixture of the two compounds with ferrous silicate melts at 1688°F.[9]

## DISCUSSION

### Formation of Low-Melting Silicates

The melting behavior of the ash of Eastern U.S. coals is dominated by the content of the three most abundant oxides — silica, alumina, and iron oxide — and also depends greatly on the oxidation state of the iron. The effect of iron content on initial deformation and softening temperatures from the ASTM ash fusibility tests on ashes of typical U.S. coals is shown in Figure 9 for both reducing and oxidizing atmospheres.[10] In the mildly reducing atmosphere of the test, in which the iron is in ferrous form, the temperatures decrease sharply with increasing iron content. The effect is much less in an oxidizing atmosphere in which the iron is present as ferric oxide or in a strongly reducing atmosphere in which the iron is reduced to metal. The phase diagram for $FeO\text{-}Al_2O_3\text{-}SiO_2$ in Figure 10 shows a quadrilateral low-melting region at about 45% FeO, 13% $Al_2O_3$, and 39% $SiO_2$ by weight.[11] The minimum liquidus temperature at the lower left corner of this quadrilateral is 1900°±90°F. However, the other component of the eutectic, iron cordierite ($2FeO\cdot 2Al_2O_3\cdot 5SiO_2$), tends not to crystallize in the absence of seed crystals, and a metastable eutectic of fayalite, hercynite, and tridymite may form at 1963°+9°F.[12] The diagram presented as Figure 10 applies to the oxides when they are in equilibrium with metallic iron; at 1990°F this is equivalent to a steam-hydrogen mole ratio of 0.8. Note that the system is a pseudoternary one, that is, some ferric iron is present in the liquid even when it is in equilibrium with metallic iron. The eutectic melting temperature decreases with an increase

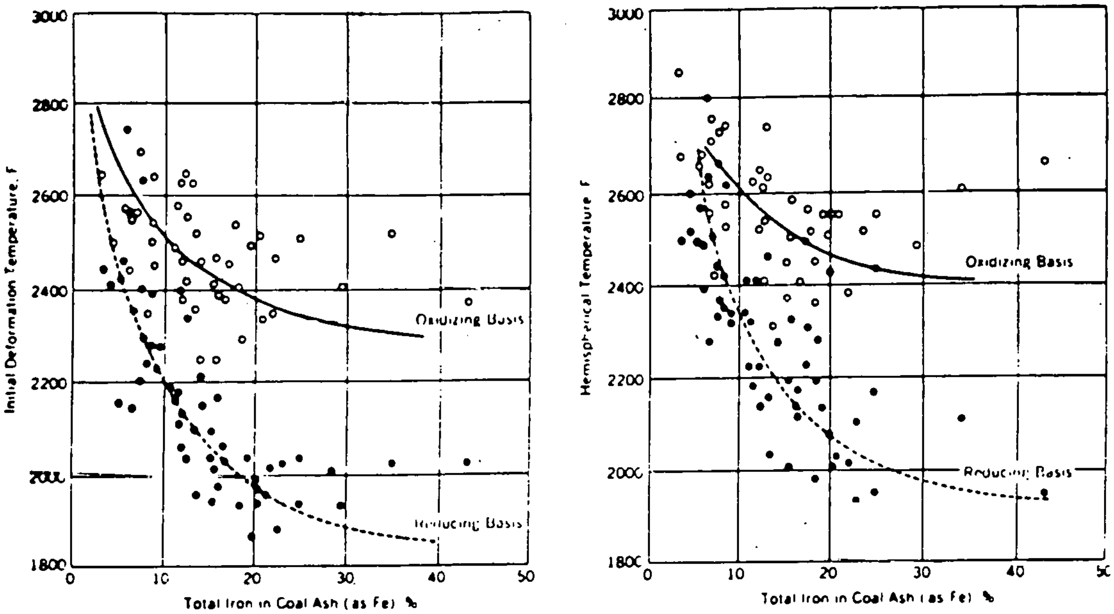

Figure 9. EFFECT OF IRON CONTENT ON FUSIBILITY OF COAL ASH[2]

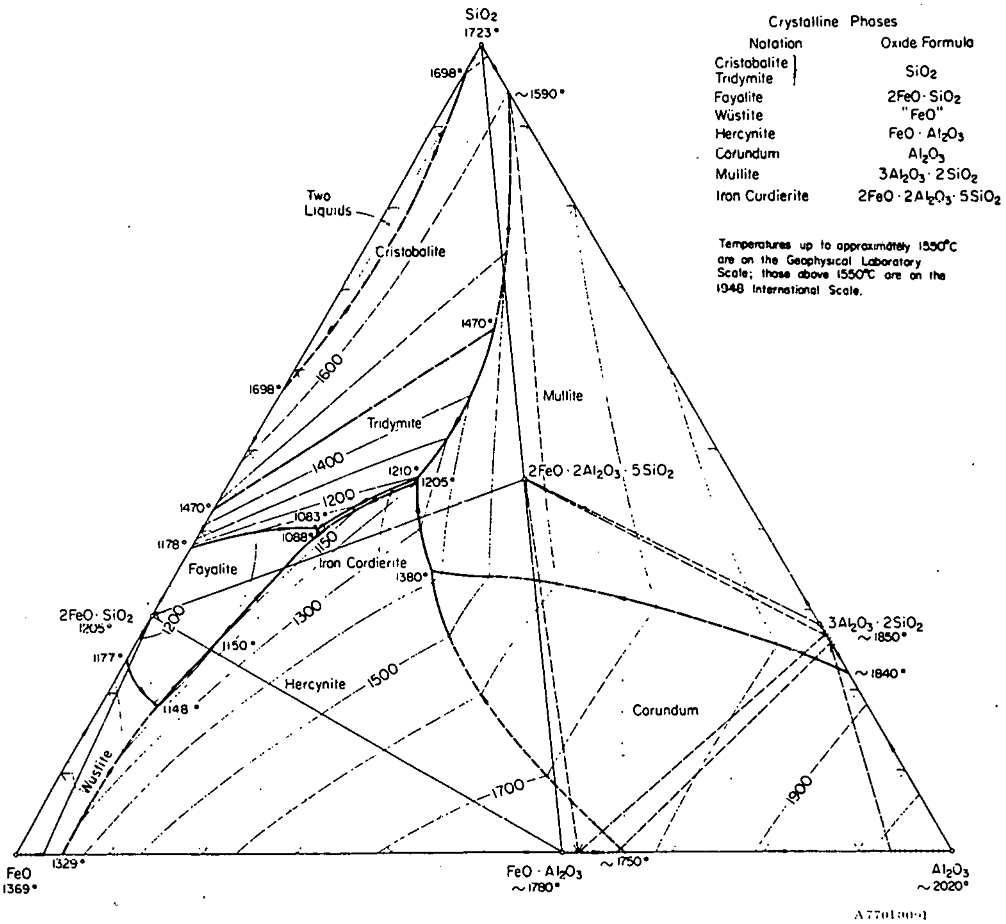

Figure 10. PHASE DIAGRAM OF THE FeO-Al -SiO SYSTEM[9]
(Temperatures in °C and Compositions in wt %)

in oxidizing potential to a minimum of approximately 1920°F at a steam/hydrogen mole ratio of about 25 ($10^{-10}$ atm of oxygen). Of greater importance for ash mixtures is the solubility in the liquid for the minor components of calcium, magnesium, sodium, and potassium oxides and the resulting probable decrease in melting temperature; it is also possible, and indeed very likely according to petrographic observations, that some liquid compositions may supercool.

Formation of a low-melting silicate mixture from coal ash may be envisioned as follows: pyrite ($FeS_2$) in the coal readily decomposes to ferrous sulfide (FeS) when heated to reactor bed temperatures; the ferrous sulfide must then be oxidized to ferrous oxide, wustite ($Fe_{0.947}O$). When a particle of the ferrous oxide comes into contact with a particle of clay, a reaction occurs that yields compositions at the particle junction ranging from pure ferrous oxide on one side to pure clay on the other; on the phase diagram these compositions lie along a line from the left (FeO) corner to a point on the $Al_2O_3$-$SiO_2$ leg of the triangle. The position of the line terminus there depends on the alumina/silica ratio of the clay. This ratio ranges from about 0.3 to 0.9 by weight in different clay minerals; higher ratios are typical of kaolinite, and the lowest are typical of montmorillonite.[13] Those of illite, the most prevelant clay in coals of the Illinois Basin, are intermediate. Thus, the reaction line falls close to or some distance to the right of the quadrilateral, depending on the silica/alumina ration. At ferrous oxide contents above 40 weight percent this places the line in the hercynite (ferrous aluminate) field, thus accounting for the presence of hercynite crystals in the matrix phase of some agglomerates. In the ash of our coal and coke feeds, the ferrous oxide content is about 27% on the silica plus alumina plus ferrous oxide basis. Thus, reaction of the ferrous oxide with all of the clay and quartz in the coal or coke ash would place the product in the mullite field; the eutectic is then at the right end of the quadrilateral, melting at 2200°F. Thus, it appears that reaction of the iron with only a fraction of the aluminosilicates and quartz in the ash is essential for production of a low-melting matrix phase and agglomeration. We think that, at equivalent temperatures, a greater amount of reaction occurs in the ASTM fusibility test than in agglomerate formation because of the slower heating rate and finer particle size (and thus greater surface area) in the ASTM test. This may also account for the "fusion" temperature of 1980°F obtained in IGT's agglomeration tests (Table 7) on agglomerates, compared with the ASTM softening temperature of 2200°F or higher obtained on the coke and coal ash (Table 5).

Silica occurs in coal as quartz ($SiO_2$) as well as in aluminosilicates. A search was made for particles of quartz in agglomerates from Run 127, made with coke feed. A sufficient number were found immersed in the matrix phase to indicate that quartz is much less reactive than the aluminosilicates of the coke or coal ash.

Calcium oxide is the next most abundant oxide in coal ash, especially in coals of the Illinois Basin. It also is a flux for aluminosilicates but, in general, is not as effective as ferrous oxide. For example, the lowest melting eutectic on the $CaO-Al_2O_3-SiO_2$ phase diagram melts at 2138°F.

In Sondreal and Ellman's correlation for ash softening temperature under a reducing atmosphere, the softening temperature rises as large amounts of calcium oxide plus magnesium oxide replace iron oxide.[14] The effect of small amounts of calcium oxide is not readily apparent from the available data. It seems likely that the initial addition of calcium oxide to the three-component eutectic would lower the eutectic melting temperature. However, our agglomeration tests indicate that increase in calcium oxide content up to about 14 weight percent does not affect melting behavior appreciably. According to our petrographic observations, an increase in calcium oxide above about 3% produces a different set of solid compounds on cooling: calcium aluminum silicate (anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$), iron silicate, and calcium iron silicate, instead of ferrous aluminum silicate glass.

Role of Sulfur

Most of the iron in coal occurs as pyrite, which readily decomposes to ferrous sulfide in the reactor bed. Oxidation of the ferrous sulfide by oxidizing gases is therefore a prerequisite for formation of the low-melting silicate mixture and for agglomerate formation.

The stable form of ferrous sulfide at elevated temperatures is pyrrotite. Rosenqvist's phase diagram shows a range of sulfur content above stoichiometric FeS[15]; the equilibrium amount is dependent on the pressure of sulfur vapor or, equivalently, on the hydrogen sulfide/hydrogen mole ratio of the surrounding atmosphere. The maximum melting point of ferrous sulfide is 2174°F, but at lower $H_2S/H_2$ ratios it forms liquid mixtures with metallic iron. The eutectic, at about 30 weight percent sulfur, melts at 1810°F (988°C).

Ferrous oxide also forms liquid mixtures with ferrous sulfide, yielding a eutectic that melts at 1724°F.[8] However, no experimental equilibrium data on their conversion reactions are readily available. With steam the equation is as follows if stoichiometric FeS is assumed:

$$Fe_{0.947}O + 0.947\ H_2S + 0.053\ H_2 \rightarrow 0.945\ FeS + H_2O \qquad (1)$$

The equilibrium relations were estimated by combining Rosenqvist's equilibrium data for the reaction —

$$Fe + H_2S \rightarrow FeS \qquad (2)$$

with Baran and Knacke's thermodynamic data for the formation of ferrous oxide from metallic iron and steam,[16] and solubilities of FeO and FeS read from the FeO-FeS phase diagram. The liquid mixtures were assumed to be ideal solutions.

Results of the calculation are shown in Figures 11 and 12. In the central parts of the figures, the solubility of metallic iron in the sulfide-oxide mixture affects the relations. Thus, the position and shape of the dashed curves are conjectural.

Ratios of $H_2S/H_2$ in the product gases were calculated from the sulfur balance with the assumption that 95% of the difference between sulfur fed and sulfur appearing in solid products was converted to hydrogen sulfide. Points from these and the $H_2O/H_2$ or $CO_2/CO$ ratios report to the solid FeS field of Figures 11 and 12. Thus it appears that ferrous sulfide cannot be oxidized to ferrous oxide in the upper part of the fluidized bed. The hydrogen sulfide/hydrogen ratio is likely to be lower and the oxidizing potential higher, both being more favorable to the oxidation, in the bed below the coal entry level. However, it appears likely that most of the oxidation occurs in the vicinity of the oxygen reaction region.

## CONCLUSIONS

Agglomerated ash in the form of rounded beads was produced in pilot plant tests on coke and washed Kentucky coal.* With both feeds, formation of the agglomerates is dependent on production of an iron-rich, relatively low-melting matrix in which a substantial portion of other ash is embedded. The matrix, which appears to have been molten in the gasifier, consists predominantly of a ferrous aluminosilicate mixture with smaller amounts of other oxides.

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* In subsequent pilot plant tests similar ash agglomerates have also been formed from run-of-mine Kentucky coal.

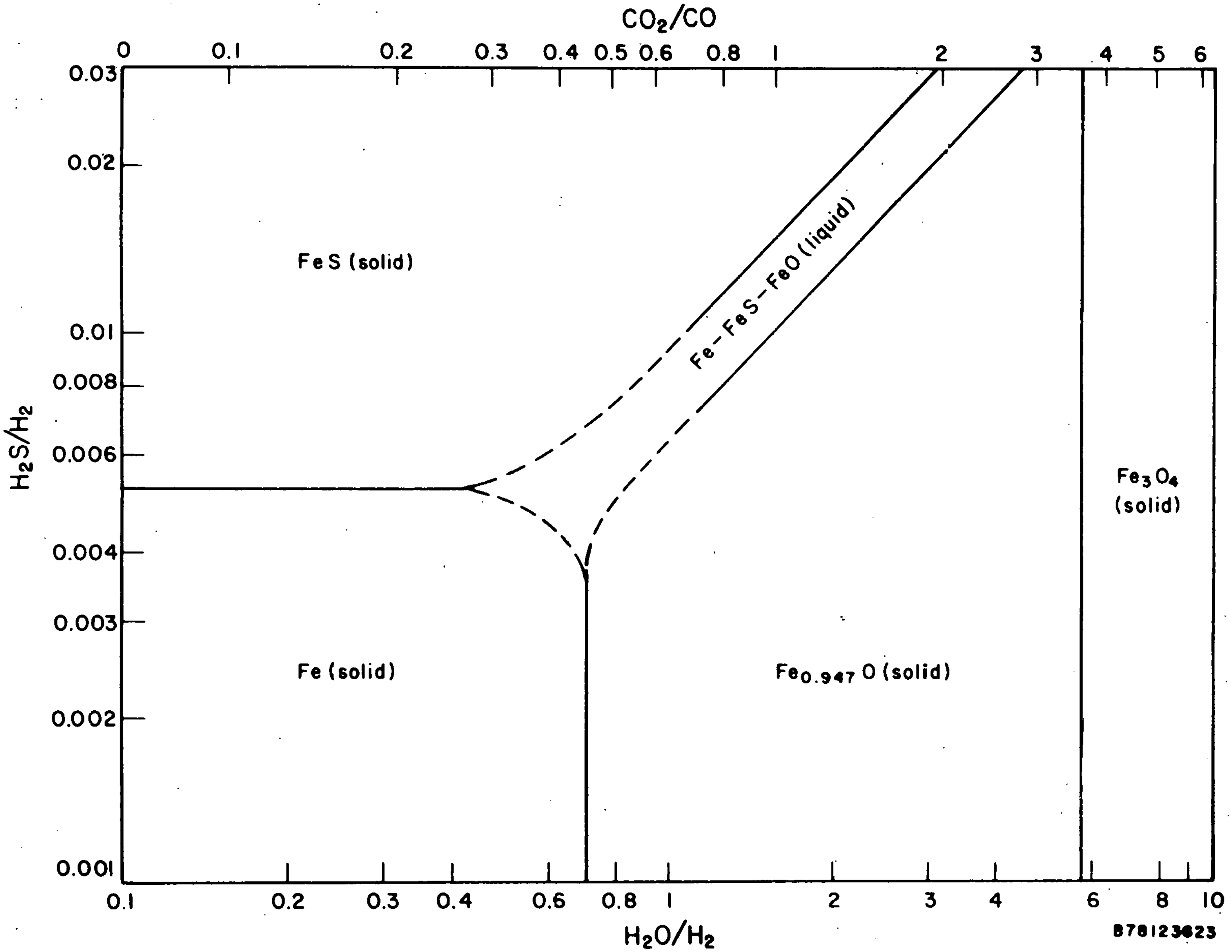

Figure 11. EFFECT OF ATMOSPHERE ON THE Fe-S-O SYSTEM AT 1800°F

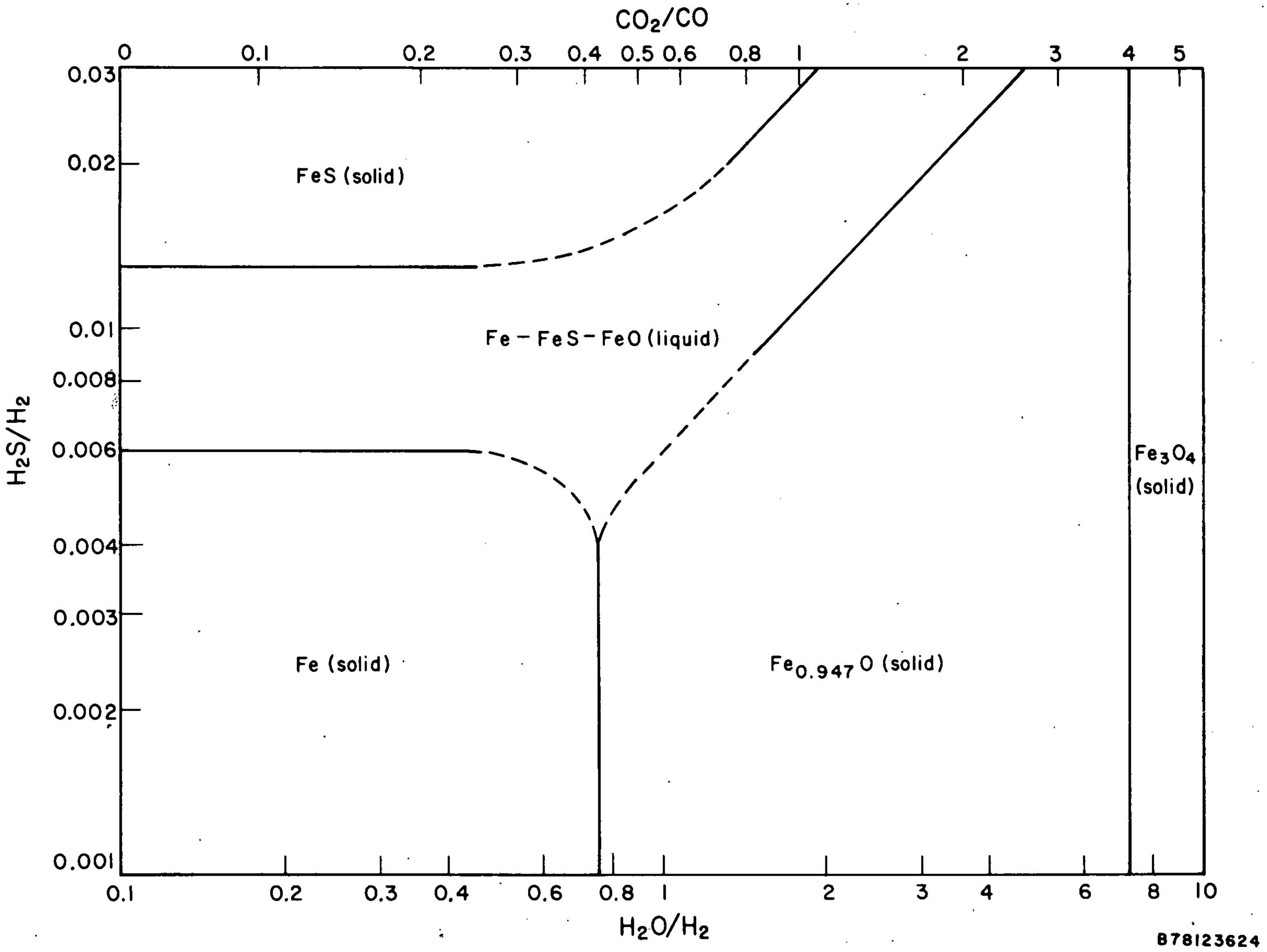

Figure 12. EFFECT OF ATMOSPHERE ON THE Fe-S-O SYSTEM AT 1900°F

The aluminosilicate matrix is produced by reaction of iron oxides with aluminosilicate (clay minerals) in the coal, or in the coal feed to coking in the case of coke. Most of the iron occurs in the Kentucky coal as pyrite, $FeS_2$, with small amounts present in other forms, perhaps as carbonate or as a constituent of the clay minerals. (Some of the pyrite may have been oxidized to oxide or sulfate when the coal was dried at the pilot plant.) Ash of the coke feed to the pilot plant had an equal amount of iron, but very little of it was present as sulfide.

Pyrite readily loses half its sulfur to form ferrous sulfide, FeS, when heated to reactor bed temperature. The ferrous sulfide in the coal char must then be oxidized before the iron can react with the aluminosilicates to form the low-melting matrix material. Thermodynamic data indicate that ferrous sulfide cannot be oxidized to an oxide in the product gas atmosphere of the gasifier. Conditions may be more favorable in the bed below the coal entry level, but it appears likely that most of the oxidation of sulfide occurs in the vicinity of the oxygen reaction region.

Oxidation of ferrous sulfide and formation of the agglomerating matrix material were achieved in runs on washed Kentucky coal but not in some runs on run-of-mine coal. In Run 124 with run-of-mine coal, for example, sulfide iron in the bed discharge ranged from about 70% of the total iron when gasifying with oxygen; petrographic and other tests show that in neither case was there appreciable formation of the low-melting matrix material or agglomeration of the ash. However, it is probable that successful production of agglomerated ash with washed Kentucky coal was more the result of differences in the mode of operation than of the character of the feed.

The temperature at which ash agglomerates from coke or from washed coal stick firmly together was determined to be about 1920°F in a reducing gas atmosphere. The temperature at which the agglomerates run together (presumably that which is required to form rounded beads in the reactor) was about 1980°F in a reducing gas atmosphere. This is higher than bed temperature in both the coal and coke runs, which indicates that formation of agglomerates occurs only in the vicinity of the oxygen reaction region where temperatures are higher than in other regions of the bed.

From phase diagrams and other evidence, it appears that the iron content of the matrix material that is responsible for agglomeration of ash is probably 35 weight percent (calculated as ferric oxide) or more. Fusion temperatures of ash containing 22 to 24 weight percent ferric oxide, the amount present in the coal and coke ash, are substantially higher than those found above. Thus, reaction of the iron with only part of the aluminosilicates in the ash is an essential feature for production of the low-melting material.

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