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The nature of solids accumulated during solvent refining of coal

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Solids accumulated in the reactor of a solvent-refined coal (SRC-1) pilot plant during processing of three coals were studied using optical microscopy and X-ray diffraction. A classification system was devised for each of the two groups of components: organic materials and mineral matter. The various organic components were classified by the extent of change from the original coal macerals, and by optical properties of different semi-cokes and other organic phases. Minerals were divided into four groups: those unchanged from the original coal; minerals which were physically degraded; minerals which were chemically or crystallographically transformed; and those minerals formed during processing of a subbituminous coal. Gold-tube carbonization experiments were performed on SRC to determine the conditions under which retrogressive reactions occur to form mesophase semi-coke. Autoclave experiments were designed to investigate the recrystallization of pyrite as pyrrhotites, and to determine the causes of carbonate-mineral formation in the reactor. Calcium carbonate was found to crystallize from the interaction of ion-exchangeable calcium and carbon dioxide, which are available when low-rank coals are processed.

Solvent-Refined Coal (SRC) processes are currently under development for the production of clean fuels from coal by hydrogenative liquefaction. In these processes powdered coal (90% <75 μm) is mixed with an internally generated solvent in the presence of hydrogen at elevated pressure (7.0 to 21.0 MPa). The reactors operate at temperatures of 673 to 723 K; residence time within this vessel is usually between 1/2 and 1 h. After leaving the reactor, the product stream is cleaned of residual solids.

During operation of the Wilsonville, Alabama SRC-1 pilot plant, not all insoluble solids leave the reaction vessel with the product stream; materials referred to as reactor solids accumulate within the coal-slurry preheater and the main reaction vessel. The amount of solids which accumulates has varied from about 0.2 to 1.9% of the moisture-free weight of the feed coal¹, the larger quantities accumulating during processing of subbituminous Wyodak coal. The nature of these materials is important for several reasons. Rapid or extensive build-up of solids can plug the reactor, a problem which can be alleviated only by time-consuming and costly solids removal. Certain materials can cause abrasion in many parts of the system. One possible benefit of some mineral solids is catalysis of certain liquefaction reactions².

Reactor solids recovered from the SRC pilot plant at Wilsonville can be classified into two principal types of components. These are (a) carbonaceous solids derived from the organic components of the coal slurry, and (b) inorganic materials, minerals either derived from the parent coal or formed during the process. This investigation characterizes these reactor solids in terms of the carbonaceous and inorganic components.

Materials are related to processes and mechanisms of formation when these have been determined.

EXPERIMENTAL

Samples of coal and reactor solids were obtained from the Wilsonville, Alabama SRC pilot plant operated by Catalytic, Inc. These materials were derived from two high-volatile bituminous coals, Illinois No. 6 and a blend of West Kentucky Nos. 9 and 14; and from a subbituminous Wyodak coal.

Samples of reactor solids were centrifuged in an epoxy resin and prepared as pellets³. Polished surfaces of these pellets were examined in reflected plane- and cross-polarized light using oil immersion at magnifications of 250 to 800, which enabled particles larger than 1 μm to be resolved. The microscope was equipped with a rotatable compensation plate.

The classification of carbonaceous substances is based on observed or assumed relations to components of the parent coal and on optical properties such as reflectance, bireflectance, and domain type. Minerals are grouped according to the extent to which they have changed relative to coal minerals (one group had formed in the reactor). Volume percentages of mineral components were estimated visually⁴ for some reactor solids. Polished pellets of samples of feed coals were subjected to maceral and vitrinite-reflectance analyses⁵. Minerals in these coals were identified optically.

In conjunction with the optical microscopic studies, major minerals in reactor solids were also identified by X-ray diffraction techniques. Diffraction patterns were

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obtained by use of nickel-filtered CuK α radiation. The concentration of minerals in most reactor solids was sufficiently large for direct qualitative analysis without special sample preparation such as low-temperature ashing. The amounts of exchangeable calcium ions were determined for samples of the three feed coals, by a method similar to that of Schafer⁶, in which calcium was exchanged with barium acetate at pH 8.3⁷.

RESULTS AND DISCUSSION

Both carbonaceous and inorganic components are present in all of the reactor solids included in this discussion, although one type usually predominates in a specific sample. The two component types are explained separately, even though they are commonly associated physically.

Carbonaceous solids

Carbonaceous materials are present in all reactor solids examined. Unlike minerals they do not have fixed chemical and crystalline properties, so there are no standard definitions or terms for some of the carbonaceous components. However, these studies have shown that they can be categorized by the extent of structural change which has occurred during liquefaction, as indicated by differences in optical appearance. These materials have been divided

into two major groups: those which are formed during the liquefaction process; and those which are relatively unchanged from the feed coal (*Table 1*).

Solids formed during processing. Carbonaceous solids which are formed in the SRC process represent the degree to which retrogressive reactions have occurred during liquefaction. The first stage of liquefaction is the disruption of the coal structure by thermal fragmentation and depolymerization. The products of these reactions can then either form the desired products or they can polymerize to form insoluble carbonaceous solids. For optimum conversion of the coal to SRC, rates of retrogressive reactions must be minimized. Extremely adverse conditions, such as excessive temperature or low hydrogen-donor capacity of the solvent, can cause carbonaceous solids to form in the reactor extremely rapidly and necessitate termination of operations.

Carbonaceous materials formed during liquefaction are optically isotropic or anisotropic solids and are usually of higher reflectance than the vitrinite of the corresponding feed coal. One petrographically distinct isotropic substance in this category is a fairly rare (<1% by volume of most solids) pitch-like homogeneous material with relatively low reflectance (<1.5%)⁷. It was described by Mitchell *et al.*⁸ and designated as 'vitroplast'. They suggested that this material results from decomposition of vitrinite and to a lesser extent other macerals into a plastic phase. Another, somewhat more common material is physically similar to vitroplast but has a much higher reflectance (>3%). These two isotropic materials are possibly related although occurrences with intermediate reflectance values have not been identified definitely. The isotropic material with higher reflectance is designated 'isotropic semi-coke' (*Table 1*). Investigation of the chemical nature of these substances is continuing.

Optical characteristics of the anisotropic semi-cokes found in reactor solids are listed in *Table 2*. The optical characteristics summarized in this Table are generally applicable to solids derived from all three feed coals included in this study. Reflectance values reported for these mate-

Table 1 Carbonaceous components of reactor solids

1. <i>Materials formed during liquefaction</i> Pitch-like solids (vitroplast) and isotropic semi-cokes Anisotropic Semi-cokes (see <i>Table 2</i>)
2. <i>Unreacted macerals</i> Fusinite Semifusinite Vitrinite Mixed-maceral particles

Table 2 Optical characteristics of anisotropic semi-cokes in coal-liquefaction reactor solids

Type	Optical character	Reflectance ^a	Particle size ^b	Associations ^c	Estimated relative abundance
Mesophase-derived	Single- or multiple-domain spheres, coalesced or agglomerated domains	2 to 5%, high bireflectance	Spheres, 2 to 20 μ m, coalesced masses to 200 μ m, agglomerates to 800 μ m	Reactor-formed minerals; traps all other components in agglomerates	Up to 50% of some Wyodak solids, <5% of others
Maceral-derived	Granular optical texture, some maceral structure	0.4 to 2%, lower bireflectance than mesophase	Usually <75 μ m	Can be coated with reactor-formed minerals	>20% of some Wyodak samples, usually <5% of others
	Highly reflecting, structure of fusinite or semifusinite	Usually 4.0 to 6.5%, bireflectance range \leq 1%	60 to 200 μ m for particles of multiple domains	Commonly in same particle with flow-type semi-coke; sharp boundaries	>50% of Ill. No. 6 and W. Ky solids, <20% of Wyodak solids
Unknown origin	Flow anisotropy, multiple domains in each particle	3 to 8%; each reading includes several domains	Usually 60 to 200 μ m	Commonly with highly reflecting maceral-derived semi-coke	>30% of W. Ky and Ill. No. 6, rare in Wyodak solids

^a Based on <100 measurements for each type. Reported as percentages of incident light, in oil, at 546 nm

^b Approximate size ranges (<50 measurements of maximum dimension on polished surface)

^c Other materials seen commonly as part of the same particle

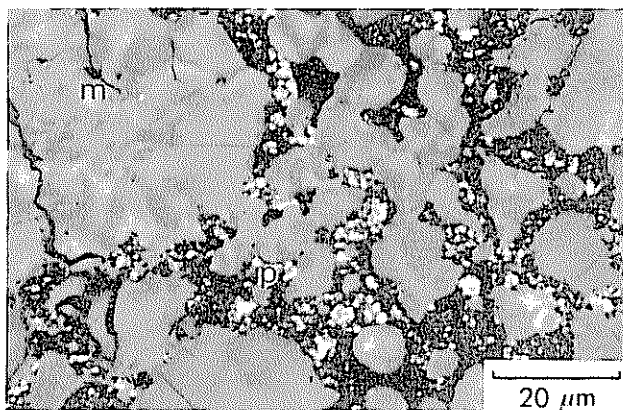


Figure 1 Individual and coalesced spheres of mesophase semi-coke (m) and disseminated pyrrhotite (p). Wyodak reactor solid

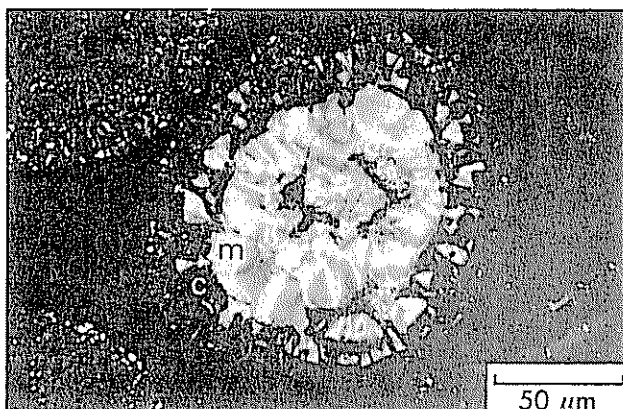


Figure 2 Coalesced domains of mesophase semi-coke (m), forming central area of particle coated with calcium carbonate (c) (see text). Wyodak reactor solid

rials are average values measured on areas covering many domains, oriented differently relative to their optical extinction. These values, then, are neither true maxima nor true minima, but provide an adequate basis for comparison among semi-coke types.

Semi-coke formed via the mesophase mechanism⁹ was identified in reactor solids from the three coals examined, in the form of individual or coalesced spheres of 3 to 20 μm (Figure 1); coalesced domains (Figure 2); or as a matrix of agglomerates (commonly 800 μm or larger) of mineral and carbonaceous particles (Figure 3). Mesophase-derived semi-coke results through molecular alignment of planar organic species into pseudo-nematic liquid crystals. Its presence indicates the occurrence of retrogressive reactions and thermal decomposition to form semi-coke from liquid phases in the reactor. In addition, the adhesive properties of mesophase enable it to coalesce into wall-scale deposits and agglomerates, trapping other particles as shown in Figure 3. The deposits of scale and other large masses thus formed are difficult to remove from the reaction system. Other types of semi-coke, described below, form smaller discrete particles which apparently remain mobile in the reactor and accumulate more slowly and less detrimentally.

Many factors can influence the propensity of liquid components in the liquefaction process to form mesophase, e.g. chemical functionality, molecular weight, aromaticity, temperature, residence time and hydrogen-donor capacity of the solvent. Experimental carbonization of

specification-grade SRCs has shown that these materials form well-developed mesophase semi-coke³. Other factors are currently under investigation.

Other types of anisotropic semi-coke apparently are formed directly from macerals (Table 2): these semi-cokes maintain some physical resemblance to the macerals from which they are derived. One type of maceral-derived semi-coke has fairly low reflectance (Table 2). Under crossed nicols with a compensation plate, it appears as particles with granular optical texture having isochromatic areas of less than 3 μm diameter. There is no evidence of flow in these materials, and particles may maintain a framework related to that of a coal maceral (Figure 4).

Another maceral-derived semi-coke is present in all the reactor solids examined. This type is relatively highly reflecting (reflectance range 4.0 to 6.5%) with domains of 50 to 150 μm diameter (Table 2). Particles of this material display no granularity or other optical texture. The structure it usually displays is similar to that of fusinite or semi-fusinite, but reflectance and bireflectance are far greater for the semi-coke (Figure 5). It is commonly associated with yet another type of semi-coke. This fourth type has the highest reflectance, greatest bireflectance, and largest flow-type domains of all the semi-cokes in these reactor solids (Figure 6). These features and its common association with maceral-derived semi-coke distinguish this substance from the mesophase type. However, both this

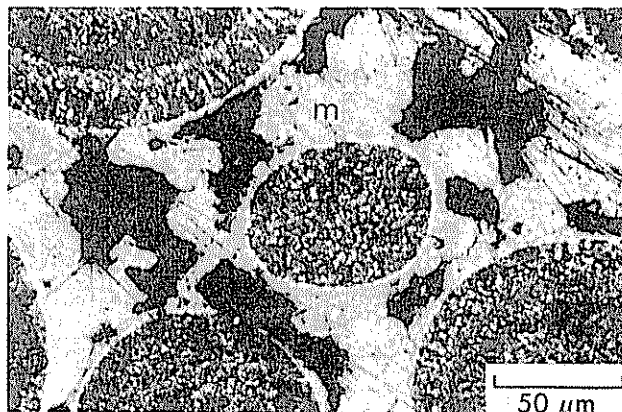


Figure 3 Mesophase semi-coke (m) as matrix of wall-scale, including mineral spheres. Wyodak reactor solid

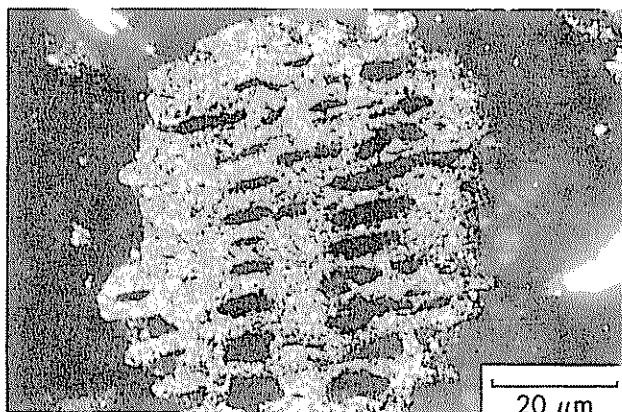


Figure 4 Granular semi-coke with structure related to original coal maceral. Wyodak reactor solid

type and much of the mesophase-derived semi-coke display evidence of plasticity. Neither resembles coal macerals or their semi-coke counterparts either in structural or optical properties. For these reasons it is likely that these types form by similar mechanisms.

Solids remaining from the coal. Carbonaceous solids which remain from coal components, essentially unreacted macerals, are volumetrically less important than semi-cokes. Some of the macerals are inherently insoluble in the liquefaction process, and limit the ultimate conversion yield. Fusinite and semifusinite are changed little in the SRC process, although some particles show partial dissolution and others apparently form semi-coke (Figure 5). However,

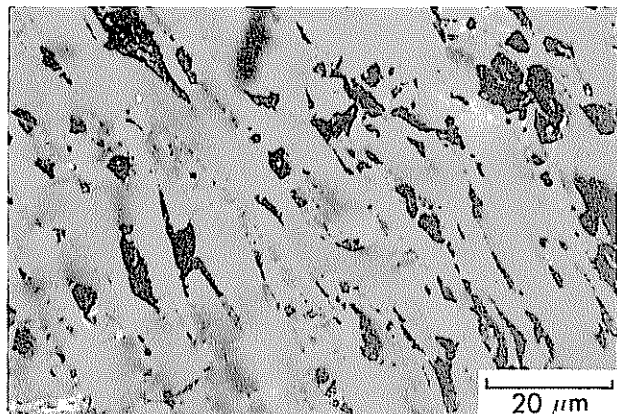


Figure 5 Highly reflecting semi-coke, appearing to be formed directly from semifusinite. West Kentucky reactor solid

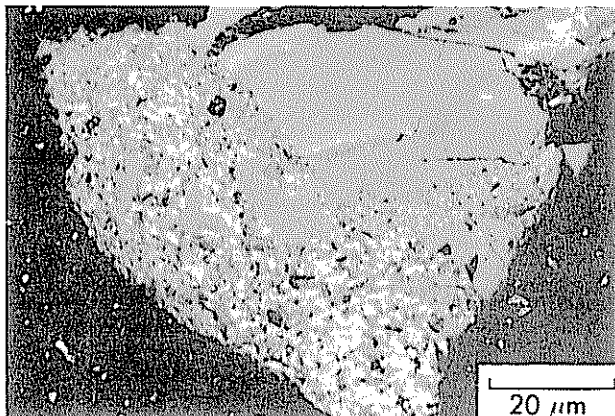


Figure 6 Two forms of highly reflecting semi-coke, one with greater bireflectance. West Kentucky reactor solid

the presence of potentially reactive macerals (e.g. vitrinite) in reactor solids indicates the inability of the process to effect maximum conversion to desired products, probably owing to inadequate residence time, temperature, or contact with the solvent. Vitrinite, nearly all of which is dissolved during this process, is present in an apparently unaltered form in solids from West Kentucky Nos. 9 and 14 coal (Figure 7). It is seen rarely in solids from the other coals. Vitrinite in some particles is associated with semifusinite, fusinite, micrinite, or exinites as it was in the feed coal. Each maceral in the reactor solid has nearly the same optical properties as it displayed in the corresponding feed coal. The only alteration commonly observed is expansion to produce cavities along bedding planes or some disintegration along particle margins.

Mineral components

Minerals predominate in most reactor solids. The solids usually yield more than 60% ash¹ (Table 3), except those from operations during which severe retrogressive reactions occurred. Extensive X-ray diffraction and optical microscopic studies of the mineral-rich solids have revealed the presence of many crystalline minerals in solids from all three coals. Table 3 lists all mineral components identified by X-ray diffraction in samples of solids from several runs with each coal.

Solids from the bituminous coals. The most common minerals identified in reactor solids from the bituminous coals (Illinois No. 6; West Kentucky Nos. 9 and 14) are quartz, pyrrhotite and anhydrite. Minor constituents differ among solids, but consist generally of clays (aluminosili-

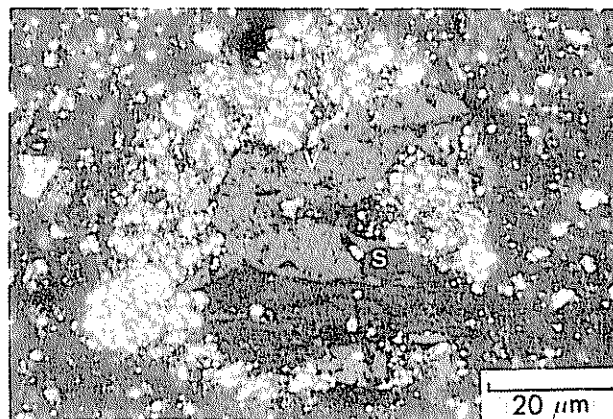


Figure 7 Unreacted macerals (vitrinite (v) centre; also sporinite (s), micrinite) in pyrrhotite agglomerate. West Kentucky reactor solid

Table 3 Mineralogical compositions of reactor solids determined by X-ray diffraction

Feed coal	Major constituents	Minor constituents	Ash from reactor solids (wt %, dry basis)
West Kentucky Nos. 9 and 14	Quartz, pyrrhotite, anhydrite	Calcite, gypsum, illite, kaolinite, montmorillonite, rutile	61 to 71
Illinois No. 6	Quartz, pyrrhotite, anhydrite	Aragonite, bassanite, calcite, gypsum, illite, kaolinite, montmorillonite, rutile, siderite	71 to 80
Wyodak	Calcite, vaterite, quartz	Anhydrite, kaolinite (?), pyrrhotite	60 to 70

Table 4 A classification of mineral components in reactor solids

I.	Unaltered minerals from feed coal (all coals studied) quartz calcite siderite? rutile sphalerite
II.	Minerals from feed coal which undergo fragmentation and changes in hydration in reactor (all coals studied) clays kaolinite montmorillonite illite calcium sulphates gypsum bassanite anhydrite
III.	Major crystallographic changes (all coals studied) pyrite → pyrrhotites
IV.	Minerals formed in reactor (Wyodak subbituminous coal) calcium carbonate: calcite vaterite aragonite

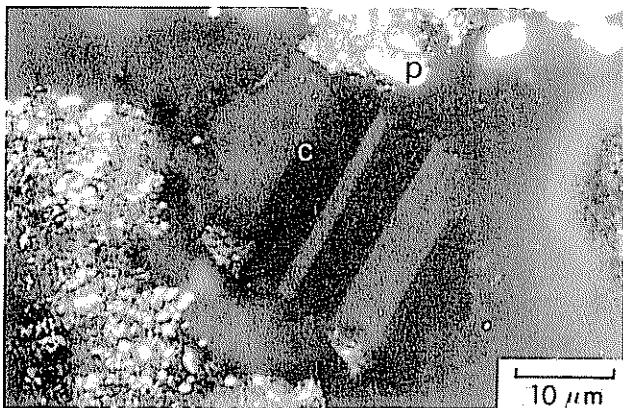


Figure 8 Twinned crystals of calcite (c) derived from feed coal; also pyrrhotite (p). Illinois No. 6 reactor solid

The second group of minerals in reactor solids from bituminous coals consists of those which undergo changes during SRC processing, and includes the clays and calcium sulphates. Clay minerals appear as granular to amorphous masses; individual crystals cannot always be distinguished optically, although the masses usually are crystallized well enough to be detected by X-ray diffraction. Clays undergo fragmentation and probably dehydration during SRC processing. The three calcium sulphate minerals are indistinguishable in reflected light, although they are frequently seen to be well crystallized (Figure 9). The presence of all three crystal forms indicates that the hydration state may change readily during laboratory preparation of coals and reactor solids. Some of the calcium sulphate minerals in reactor solids may be attributable to sulphur being fixed by calcium during liquefaction.

For bituminous coals the most striking mineralogical change caused by liquefaction is the reduction of pyrite (FeS_2) in the feed coals to pyrrhotites (Fe_{1-x}S) in the reactor solids; this major crystallographic change defines the third group of minerals. Pyrrhotites can be distinguished optically from pyrite by their anisotropy (pyrite is isotropic), lower relief (hardness) and lower reflectance.

To investigate the reduction of pyrite to pyrrhotites during liquefaction, pyrite ($<74 \mu\text{m}$) was reacted with tetralin for 1 h at 698 K in a rocking bomb autoclave³. Pyrite was partially reduced to pyrrhotites, producing grains with an outer rim of polycrystalline pyrrhotite and an unaltered inner core (Figure 10).

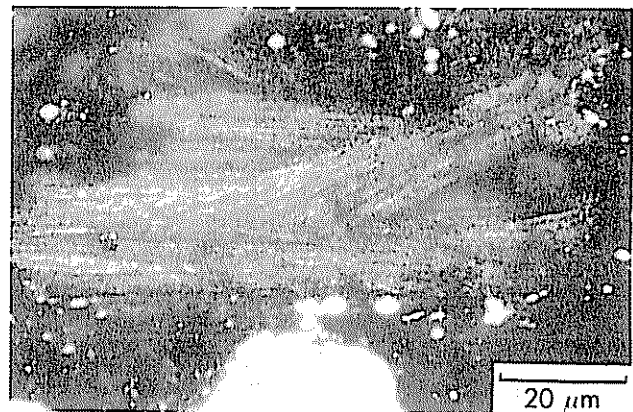


Figure 9 Crystalline calcium sulphate, pyrrhotite in surrounding particles. Illinois No. 6 reactor solid

ates), calcium-containing minerals (carbonates and sulphates), iron-containing minerals (sulphides and carbonate) and rutile. In reactor solids from bituminous coals, these diverse minerals can be classified into three groups on the basis of the extent to which they were altered during the SRC process (Table 4).

Calcite and quartz from these coals remain essentially unchanged during processing, and are the major minerals in the first group. Figure 8 shows a large grain of crystallographically twinned calcite, a common particle in Illinois No. 6 reactor solids. Crystals such as this share with calcite in the feed coal properties such as large size ($>75 \mu\text{m}$), well-developed crystal form and twinning. Quartz in the reactor solids likewise is identical with that of the feed coals. Siderite may remain unaltered through processing, although it was not positively identified optically in any of the residues from bituminous coals. Unaltered sphalerite was identified by its distinctive optical properties¹⁰ during the microscopic studies, but was not detected by X-ray diffraction.

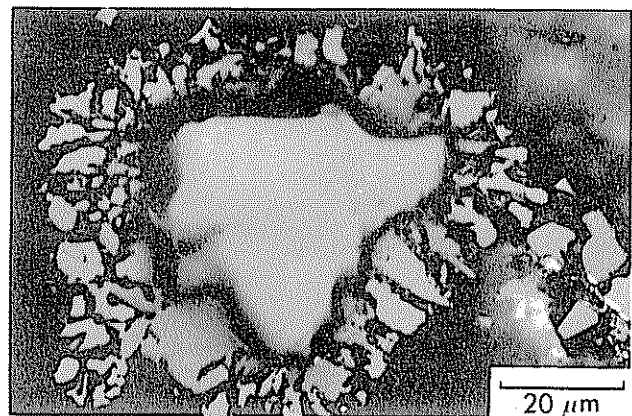


Figure 10 Pyrite (centre, isotropic with higher relief) experimentally recrystallized to pyrrhotite at margins

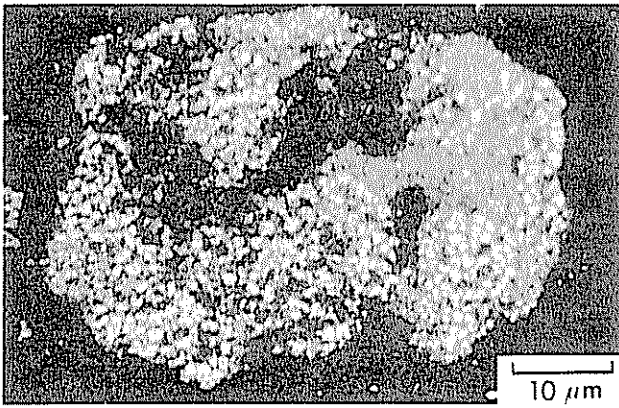


Figure 11 Aggregate of crystalline pyrrhotite. West Kentucky reactor solid

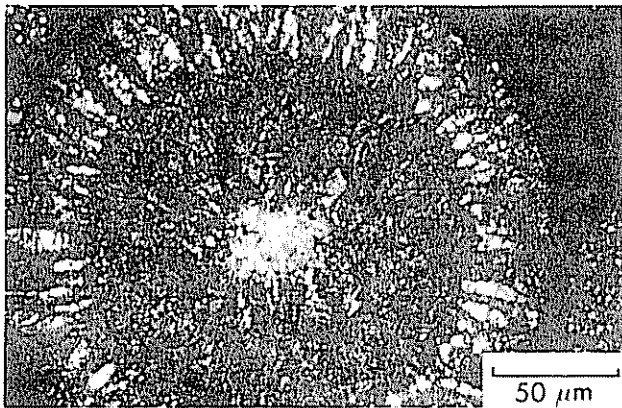


Figure 12 Sphere of calcium carbonate (dark) and radial stacks of pyrrhotite crystals (bright) with pyrrhotite core. Wyodak reactor solid

Pyrrhotites in reactor solids consist of single tabular crystals ($<6 \mu\text{m}$) (Figure 1); crystal aggregates (Figure 11); and finely dispersed grains within larger agglomerates of other minerals and insoluble organic components (Figures 3, 8, and 12). Incorporation in these large agglomerates effects the retention of great amounts of finely divided pyrrhotite in the reactor. Catalytic activity by the pyrrhotites is unlikely when the mineral crystals are encased within complex particles. Disseminated particles, although less common, will be easily accessible to reactants. However, abundant pyrrhotite intimately associated with other insoluble components could enhance magnetic separation of these materials from product streams. The efficiency of magnetic removal of insolubles will depend on the chemical composition of the pyrrhotites in each solid^{7,11}.

Solids from the subbituminous coal. The major mineral components of reactor solids derived from the subbituminous (Wyodak) coal are calcium carbonate (calcite and vaterite) and quartz. Minor constituents are iron sulphides, anhydrite and some clay. The quartz and most minor constituents fit into the three categories of minerals defined for the bituminous coals (Table 4). However, optical examination of Wyodak solids has revealed that much of the calcium carbonate is precipitated during processing of this coal. These carbonates, then, comprise a fourth mineral category: minerals formed in the reactor (Table 4).

The crystallization of additional mineral material during processing accounts for the higher rate of solids build-up occurring during operations with the Wyodak coal¹. Par-

ticles of carbonates precipitated in the reactor are abundant and by optical microscopy are readily distinguished from particles of coal minerals. Granular carbonates comprise spherical particles of distinct concentric layers surrounding a central inert core (Figure 12), usually of semi-coke or a coal-derived mineral. Wall-scale deposits also include layers of granular calcium carbonate. Individual crystals are too small to be resolved. These features are used to differentiate between the reactor-formed carbonates and those from the coal.

In addition to calcite, vaterite also was detected by X-ray diffraction in Wyodak solids. Vaterite is not a mineral found in coals, and is a metastable form of calcium carbonate¹². Its presence must indicate some unusual conditions of formation and subsequent stabilization.

The source of the precipitated calcium carbonate in Wyodak solids is exchangeable calcium cations associated with the carboxylic acid groups in this low-rank coal (subbituminous C). Amounts of exchangeable calcium cations were determined for the three feed coals. These percentages are listed in Table 5, with values for the total amounts of calcium in these coals (determined by extraction with HCl). The absolute and relative amounts of exchangeable calcium are much higher for Wyodak coal than for the two bituminous coals. Bituminous coals do not contain appreciable concentrations of carboxylic acid groups. Also, three to five times more carbon dioxide is produced during liquefaction of Wyodak coal than during processing of bituminous coals¹. The exchangeable cations apparently react with carbon dioxide to precipitate calcium carbonate. Because of the paucity of carboxylic acid groups in the West Kentucky and Illinois coals, it is likely that determined concentrations of exchangeable cations are derived from clays.

Essentially all calcium carbonate spheres in the Wyodak solids include pyrrhotites, usually as stacks of platy crystals radiating outward from the core of the inner surface of each layer (Figure 12). It is unlikely that this structure would result from the capture of discrete pyrrhotite grains from the liquid phase; the radial orientation suggests crystal growth. Pyrrhotites might be formed by reactions of ionic iron species and sulphur. Significantly, pyrrhotite crystals are not present in mesophase semi-coke layers in the spheres in Wyodak solids (Figure 2), showing that grains were not entrapped by the plastic mesophase.

Formation of carbonates during liquefaction of low-rank coals poses significant operational problems: other low-rank coals have even higher concentrations of exchangeable cations than does the Wyodak (e.g. a North Dakota lignite has 1.76% dry weight exchangeable calcium)³. The rate of solids accumulation will be dependent on reactor design and operating conditions (e.g. mass flow rate). Attempts to minimize solids build-up, such as decreasing reaction time or pretreating the coal, must be balanced against cost and the requirements of optimum coal conversion.

Table 5 Amounts of total and exchangeable calcium in feed coals

Feed coal	Total Ca (wt %, dry coal)	Exchangeable Ca ⁺⁺ (wt %, dry coal)
West Kentucky Nos. 9 and 14	0.16	0.09
Illinois No. 6	0.30	0.17
Wyodak	1.05	0.99

SUMMARY

Both carbonaceous and mineral solids which accumulate in an SRC reactor have been identified by optical microscopy and X-ray diffraction, and classified into optically recognizable categories. Substances which cause operational difficulties, i.e. mesophase semi-coke and reactor-formed calcium carbonate, have been identified and their optical properties have been determined.

Carbonaceous solids formed during the SRC-1 process include isotropic pitch-like solids and several types of semi-coke. Some of the anisotropic semi-coke is formed via the mesophase mechanism, while other types have optical properties which distinguish them from the mesophase type. The coal is not completely solvated even in what should be the most favourable conditions; some maceral particles, along with much of the mineral matter, remain in the reactor little changed by this liquefaction process.

A diverse group of minerals is present in the reactor solids, and includes quartz, clay minerals, calcium-containing carbonates and sulphates, iron-containing sulphides and carbonate, and titanium oxide. Pyrite is partially reduced to pyrrhotites in pseudo-liquefaction experiments, and also during SRC processing. Exchangeable calcium cations present in the subbituminous Wyodak coals are responsible for formation of calcium carbonate precipitates during its liquefaction.

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