

PHASE CHARACTERIZATION OF UNMODIFIED PETROLEUM COKE AND COAL GASIFICATION SLAGS

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ABSTRACT

The slags produced in gasifiers using petroleum coke as a feedstock differ compositionally and texturally from the ash and slag formed during combustion of coal. Hence, the chemical and slagging behavior of petroleum-coke ash under gasification conditions must differ markedly from the behavior of coal ash. Whereas the latter is reasonably well understood, the former has been much less well studied. The present work is part of an ongoing study aimed at understanding the physical and chemical characteristics of the phases formed in the slags that are produced during petroleum coke gasification.

INTRODUCTION

The partial oxidation of liquid hydrocarbonaceous fuels such as petroleum products and slurries of solid carbonaceous fuels such as coal and petroleum coke to form alternative fuels is now a common practice. An evolving trend in the feedstocks for such processes is that they are becoming increasingly heavy and of poorer quality. To compensate for this trend, refiners must employ more "bottom of the barrel" upgrading to provide the desired light products. The current industry workhorse to provide this upgrading is some type of coking operation (either delayed or fluid). A good deal of current refinery expansion includes the installation or expansion of coker units, and this coking will be a process of general use for some time to come.

The production of light hydrocarbon fuels from coal or petroleum feedstocks results in the formation of ash or slag which concentrates most of the contaminants originally present in the coal or petroleum. Coals contain significant amounts of clays, quartz, pyrite, and carbonates, along with a broad range of less abundant solid mineral phases (Jenkins and Walker 1978). Petroleum contains less solid mineral matter but may contain significant amounts of other contaminants such as iron, nickel, vanadium and sulfur. Consequently, the residual concentration of elements is significantly different depending upon the feedstock materials. The resulting phases affect gasifier operation and the ultimate use or disposal of the ash or slag.

PROCESS DESCRIPTION

The Texaco Gasification Process is a partial oxidation reaction to produce mixtures of CO and H₂, known as synthesis gas. A carbon containing feedstock is reacted with a controlled, sub-stoichiometric quantity of oxygen in a fuel rich, exothermic reaction. The process is carried out in a pressurized reaction chamber with the temperature maintained above the melting point of the coal or petroleum-coke ash, thus making a slag (molten ash), by controlling the individual feed rates of the reactants. The feeds are introduced together, through the top of the gasifier, and pass through it concurrently with the product gases transporting the solids, making it an entrained flow gasifier. It is fundamentally a simple system that leads to high reliability, and it can be adapted readily to fit many applications economically.

The chemical reaction path is quite complicated, and includes many simultaneous and sequential reactions such as devolatilization, combustion and interactions between the feeds and intermediate or final products. The chemistry is depicted in a schematic sense in Figure 1. The conversion of feedstock slurry to synthesis gas is normally in excess of 95% and can be over 99%.

The use of coal as a feedstock, either in direct combustion or as a gasifier feedstock results in most of the ash being converted to slag, a nearly carbon-free, inorganic material. After water quenching, the slag is normally a glass-like solid, with a maximum size of one-half inch. In all cases evaluated to date, the slag from coal gasification, including the fine fractions that are co-mingled with carbon-rich char, have been classed as a non-hazardous waste.

The high temperature gases, char and molten ash, or slag, produced in the gasifier are normally cooled prior to cleanup, by either of two methods: quenching, i.e., direct contact with water, or indirect heat exchange to make high pressure steam in a special syngas cooler.

The molten slag is cooled with the gas and is collected in a water pool either in the bottom of the radiant cooler or in the quench vessel located under the gasifier. The slag is removed from the system by means of a water-filled lockhopper system. The carbon-rich char can be disposed of with the slag or separated for recycle.

The cooled gas is scrubbed with water to remove the remaining fine particulates. Following particulate scrubbing, gas purification is completed by sulfur removal. A variety of subsequent processes can then be used, with the choice made to fit the overall project needs. The cleaned gas can be used for many purposes, such as fuel for power generation or process heat, synthesis of ammonia or other chemicals, or as a reducing gas.

SAMPLE PREPARATION AND ANALYSIS

The slag samples examined in this study occur both as fragmental materials that are discharged routinely from the gasifiers and as solid incrustations that build up on the interior walls of the gasifier. Megascopically, most samples appear as dark brown to black, porous to solid, irregular masses ranging from less than one-fourth to more than several inches across. The samples removed from the gasifier walls are commonly layered, apparently reflecting episodic buildup.

Representative portions of slags were cast in a low viscosity, cold-setting epoxy resin. Porous samples were vacuum impregnated by placing them in a vacuum desiccator in which vacuum was alternated with normal air pressure. This procedure removed trapped air and forced the epoxy into pores and cracks. Samples were then polished using standard techniques employed for optical microscopy and electron microprobe analysis as described in Craig and Vaughn (1981).

GASIFIER SLAGS

Characterization of slags produced in gasifiers is important in determining the ultimate use and/or disposal of the slags. Furthermore, a prior knowledge of the nature of the slag phases is necessary if it becomes desirable to alter slag properties that adversely affect the operability of gasifiers. To these ends, we have been carrying out investigations on the physical and chemical properties of slags produced both from coal and from petroleum coke feedstock. The slags produced from the different feeds are markedly different, as evidenced in the data presented in Table 1, 2, and 3.

The conditions under which coal and petroleum-coke ash and slags form are similar in that they all involve partial to full combustion. The principal difference is that direct combustion is generally more oxidizing and hence will permit formation of more oxidized phases (eg. ferric rather than ferrous phases). Coal bottom ash, fly ash, and slags have been examined by numerous investigators in recent years as noted in Table 2 and by a wide variety of techniques (eg. Huggins and Huffman, 1979; Weaver 1978; Voina and Todor, 1978; Eriksson et al. 1991). Typical coal ash as noted in Table 1 is rich in SiO_2 with major but variable amounts of Al_2O_3 , Fe_2O_3 , and CaO . Coal slag are generally dominated by glass phases which, though highly variable, are always rich in SiO_2 and contain significant Al_2O_3 . Some glasses are also sufficiently rich in reduced iron to be referred to as "ferrous glasses" (Huffman et al. 1981). The number and variety of other mineral analogues

phases are considerable (Table 2) but often constitute only small proportions of the bulk material. Furthermore, several percent unreacted or partially reacted carbon-char are commonly present.

The glass phases display flow, banding, indicating some flow of compositionally distinct zones. Crystalline phases range from skeletal to fibrous laths (commonly mullite or anorthite; Hulett et al. 1980; Huggins et al. 1981) to skeletal and cruciform spinels (Chen et al. 1986).

Petroleum-coke slags are also highly variable in composition but generally contain less SiO_2 , less Al_2O_3 and less CaO but greater amounts of Fe_2O_3 , V_2O_5 , NiO and sulfur (included in "others" Table 1). The iron and vanadium contents are reported as given by ASTM analytical procedures; however, iron and vanadium actually occur in lower oxidation states in these slags. These gross compositional differences reflect the nature of the source materials. Coals contain abundant included clays and carbonate minerals, whereas petroleum contains less discrete fragmental mineral matter but often contains significant amounts of organic sulfur and porphyrins that hold iron, nickel, vanadium, and chromium.

A general result of these differences in composition is the fusibility of the ash. Typical coal ash has initial deformation (ID) temperatures of 2120°-2140° F, softening temperatures (ST) of 2150°-2210° F, and fluid temperatures (FT) of 2250°-2430° F. In contrast, typical petroleum coke ash remains undeformed and does not melt until temperatures exceed 2700° F.

PETROLEUM COKE SLAGS

The present study has concentrated especially on slags formed during gasifier operation using petroleum coke without any additives to alter constituents or behavior, and are part of an ongoing study to characterize the physical and chemical characteristics of such slags (Craig et al. 1990; Craig and Najjar 1990; Groen et al. 1991).

The investigators have found that the slags formed, display a variety of textures and phases; these apparently reflect differing locations and hence conditions within the gasifiers as well as differences in the feedstock. In general, the types of slags may be summarized as (1) glass-rich, (2) V-oxide rich, (3) sulfide-rich, (4) CaMgFe-silicate-rich. These no doubt represent end members of a continuum, but most samples extracted from the gasifiers conveniently fall into one of these categories. The total of the wide variety of phases that the investigators have found to date are listed in Table 3. Below briefly described are each of the major types of slags noted above:

Glassy Slags - These generally range from black to brown glasses that occasionally exhibit well developed flow textures evidencing their slow flow down the sides of the gasifier. Typically, they contain significant quantities of very fine spherical iron sulfide droplets. The droplets greater than 1 mm in diameter appear to have been formed along with the glass. Finer droplets, down to less than 1 micrometer, appear to have formed primarily through exsolution on cooling. Glassy slags commonly contain dispersed skeletal to cruciform spinels which also appear to have formed on cooling as the liquidus boundary was intersected.

V-oxide-rich slags - These slags are relatively SiO_2 -poor and represent slag formation within the gasifier where vanadium phases crystallize as relatively coarse crystals (~100 micrometers). The V-oxide phases occur as interlocking laths with interstitial spinel crystals and droplets of glass and sulfide-oxide intergrowths. The coarseness of the crystals and the absence of flow structures and exsolution features indicate that the V-oxide phases were stable and forming directly under the conditions of gasifier operation.

Sulfide-rich Slags - Many chunks of slag consist primarily of intimate iron sulfide-iron oxide intergrowths. The iron sulfide ranges from pure FeS (troilite) to Fe_{1-x}S (hexagonal pyrrhotite) and the iron oxide is FeO (wustite). The intergrowths are symplectic in nature and are often so fine (1 micrometer and less) that they are barely resolvable with an optical microscope. The textures are characteristic of the unmixing of phases from a homogenous melt on rapid cooling. Nickel may substitute on a minor scale for the iron in the pyrrhotite and may, in nickel-rich areas, occur as Ni_3S_2 (heazlewoodite) or as (Fe, Ni) $_9\text{S}_8$ (pentlandite). The iron sulfide-iron oxide masses commonly contain dispersed drop-like to cruciform crystals of free iron-nickel alloy. Also scattered throughout

the sulfide-oxide matrix are droplets of glass and euhedral to skeletal iron aluminum spinels which may concentrate significant amounts of vanadium and chromium.

CaMgFe-silicate slags - These occur as local segregations within sulfide-rich slags. The sulfide phase cannot accommodate Ca, Mg, or Si within its structure, hence these elements concentrate sufficiently to form a variety of CaMgFe silicates.

SUMMARY

It is apparent that the differences in the bulk chemistries of the petroleum coke and coal slags are reflected in the behavior and nature of the phases within each. The high silica and alumina contents of the coal slags result in lower melting temperatures and the development of predominantly glassy products. In contrast, the low silica and alumina contents of the petroleum coke slags, coupled with high transition metal contents, result in the development of a variety of crystalline phases. Most notable are aluminates spinel phases that concentrate iron, vanadium, chromium and nickel, and sulfide-oxide intergrowths in which nickel becomes concentrated in both sulfide and accessory alloy phases.

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GASIFICATION REACTION SCHEMATIC

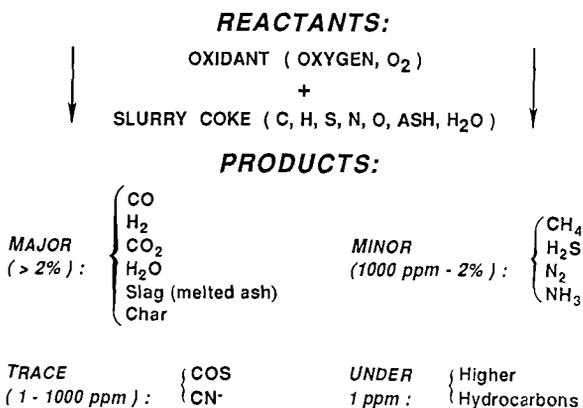


Figure 1. Simplified schematic diagram of the partial oxidation reaction occurring in a petroleum coke gasification.

Table 1. Typical ash composition in wt % of coal and petroleum-coke generated ash.

	Coal		Petroleum Coke	
	Eastern	Western	Type A	Type B
SiO ₂	52.1	42.0	4.4	40.6
Al ₂ O ₃	15.4	25.0	1.5	9.6
Fe ₂ O ₃	7.3	20.9	23.0	6.3
CaO	17.4	9.5	7.5	1.4
MgO	3.7	--	--	2.4
NiO	--	--	20.9	14.0
V ₂ O ₅	--	--	40.3	16.6
Others	4.1	2.6	2.5	9.1
Carbon %	9.5	9.7	0.5	0.9
	<u>Ash Fusibility, °F</u>			
ID	2120	2140	--	--
ST	2150	2210	--	--
FT	2250	2430	>2700	>2700

TABLE 2.

COAL COMBUSTION ASH / SLAG PHASES

Phase Composition	Remarks	Mineral Name	REFERENCE
FREE ELEMENTS:			
C	unreacted char	Graphite	Ouon et al., 1984
FeS	Ouon et al., 1984
SULFIDES:			
FeS ₂	Tronite	Huffman et al., 1981
Fe ₃ S ₄ S	Pyrrhotite	Huffman et al., 1981
SULFATES:			
CaSO ₄	Result of Ca from calcite reacting with SO ₂	Anhydrite	Huffman et al., 1981
OXIDES:			
FeO	Wüstite	Huffman et al., 1981
Fe ₃ O ₄	Magnetite	Ouon et al., 1984
(Fe,Al) ₂ O ₃	Hercynite	Huffman et al., 1981
ferrite phases	Chiefly as mostly Fe ₃ O ₄	Huffman et al., 1981
chromite phases	Chiefly as mostly Fe ₃ O ₄	Huggins et al., 1986
Fe ₂ M ₂ O ₄	M = V, Cr, Mn, Co, Ni, Zn	Spinels	Ouon et al., 1984
Fe ₂ O ₃	In oxidized ash	Hematite	Ouon et al., 1981
Al ₂ O ₃	Cerundum	Huggins et al., 1986
TiO ₂	Rutile	Ouon et al., 1984; Chen et al., 1988
SiO ₂	Residual phase ?	Cristobalite	Huffert et al., 1990; Hulett and Weinberger, 1980;
SiO ₂	Quartz	Rasm, 1982; Ouon et al., 1984; Chen et al., 1988
Class	Highly variable SiAl-dominated	Obsidian	Rasm, 1982; Ouon et al., 1984; Chen et al., 1988
Silicates:			
Fe ₂ SiO ₄	Fayalite	Huffman et al., 1981
Al ₂ SiO ₅	Mullite	Hulett et al., 1980; Hulett and Weinberger, 1980;
CaAl ₂ Si ₂ O ₈	Anorthite	Rasm, 1982; Ouon et al., 1984; Chen et al., 1988
Ca ₂ Al ₂ SiO ₇?	Gaibantite	Huggins et al., 1986; Ouon et al., 1984

TABLE 3.
PETROLEUM COKE GASIFIER SLAG PHASES

Phase Composition	Texture	Ideal Composition	Mineral Name
FREE ELEMENTS:			
Fe-Ni-alloys (up to >70 atomic percent Ni)	Dendritic to blocky crystals & irregular blebs all in sulfide matrix	Complete Fe to Ni solid solution	Native Iron & Native Nickel
C	Aggregates of radiating to fibrous microcrystalline subgrains	C	Graphite
SULFIDES:			
(Fe,Mn)S	Matrix phase often symplectic with TeO^* , & as irreg. blebs in glass	FeS	Troilite
(Fe,Mn) ₂ S	Matrix phase often symplectic with TeO^* , & as irreg. blebs in glass	Fe ₂ S	Pyrrhotite
(Fe,Mn) ₃ S ₂	Irregular separations in sulfide matrix	(Fe,Mn) ₃ S ₂	Psilomelane
(Ni,Fe) ₂ S ₂	Irregular blebs in Y-oxide rich slugs	Ni ₂ S ₂	Heazlewoodite
CeS	Irregular blebs	(Ce,Mn)S	Oldhamite
(Fe,Mn,Cr)VS ₂	Dendritic crystals in sulfide matrix
Undischarged sulfides	Euhedral micron-scale crystals in sulfide matrix
SULFATES (Zr)			
Undischarged Mn-S-O phases	Euhedral micron-scale crystals in sulfide matrix
OXIDES:			
(Fe,Mn) ₂ MnO	Symplectically intergrown in sulfide matrix, and as dendritic crystals and rounded blebs in sulfide matrix	FeO	Wüstite
(Ni,V)PO	Alteration lined on blebs of (Fe,Mn) ₂ S ₂	MnO	Bunsenite
(Fe,Mn,Mg)(Fe,Al,V) ₂ O ₄	Euhedral massive crystals in Y-oxide rich matrix	Fe ₂ O ₃	Magnetite

Phase Composition	Textural	Ideal Composition	Mineral Name
(Fe,Mg)(Cr,V) ₂ O ₄	Euhedral crystals in glassy matrix (residual from refractory bricky)	FeCr ₂ O ₄	Chromite
(Mg,Fe)(Cr,Fe,Al) ₂ V ₂ O ₄	Euhedral crystals in glassy matrix (residual from refractory bricky)	MgCr ₂ O ₄	Magnesiochromite
(V,Cr) ₂ V ₂ O ₄	Euhedral massive crystals in sulfide matrix	V ₂ O ₅
(Fe,V,Cr,NI) ₂ V ₂ O ₄	Euhedral massive to dendritic crystals in sulfide matrix	FeV ₂ O ₅	Coulsonite
(Mg,NI,Fe)(Al,V,Cr,Fe) ₂ O ₄	Euhedral massive to dendritic crystals in sulfide matrix	FeAl ₂ O ₃	Spinel
Fe(Al,Fe) ₂ O ₄	Irregular grains w/ FeS interstitial between dendritic FeO crystals	FeV ₂ O ₅	Hercynite
(NI,Fe)(Fe,Al) ₂ O ₄	Euhedral skeletal crystal in V-oxide rich matrix	NIFe ₂ O ₄	Tironite
(NI,Mg)(V,Fe,Al) ₂ Cr ₂ O ₄	Euhedral massive crystals in V-oxide rich matrix
(Fe,V,Al) ₂ Cr ₂ O ₄	Oxidation crusts on sulfide-rich and glassy slag surfaces	Fe ₂ O ₃	Hematite
(V,Fe,Al) ₂ Cr ₂ O ₄	Slender acicular crystals in chromite crystals	Cr ₂ O ₃
(V,Fe,Al) ₂ Cr ₂ O ₄	Bladed euhedral crystals & as irregular cores of spinel crystals	Al ₂ O ₃	Korundum
(V,Fe,Al) ₂ Cr ₂ O ₄	Bladed euhedral crystals in V-oxide rich slag	VO ₂
(V,Fe,Al) ₂ Cr ₂ O ₄	Bladed to feathery euhedral crystals in V-oxide rich slag	V ₂ O ₅	Karelianite
(Fe,Mg,NI)(V,Al)Fe ₂ O ₅	Bladed to feathery euhedral crystals in V-oxide rich slag	CaV ₂ O ₇
(NI,Fe)(V,Al,Fe) ₂ O ₅	Bladed to feathery euhedral crystals in V-oxide rich slag	FeV ₂ O ₆
(Ni,Cr,NI)(Cr,NI)(V,Fe,Al) ₂ Cr ₂ O ₂₀	Bladed to feathery euhedral crystals in V-oxide rich slag	NaCaV ₂ O ₇
(Fe,Ca)VO ₄ or CaFeV ₂ O ₇ (?)	Bladed to feathery euhedral crystals in sulfide- and V-oxide rich slugs	FeVO ₄ or CaFeV ₂ O ₇
(Si,Al) ₂ VO ₂	Matrix phase & as rounded bits in sulfide- and V-oxide rich slugs	SiO ₂	Obsidian
Sulfides:			
(Al,Fe) ₂ (Si,V,Cr,Al) ₂ O ₃	Euhedral, diamond shaped, acicular crystals in glass matrix	Al ₂ SiO ₅	Andalusite or Sillimanite
(Fe,Mg,Ca,NI) ₂ (Si,Al) ₂ O ₄	Matrix of tiny subhedral crystals intergrown w/ Pigeonite crystals	Fe ₂ SiO ₅
(Mg,Fe,Al,NI) ₂ (Mg,Fe)(Si,Al) ₂ O ₄	Matrix of tiny subhedral crystals interg. w/ Fayalite crystals	(Mg,Fe,Ca)(Mg,Fe) ₂ Si ₂ O ₆	Pigeonite
(Mg,Fe)(Cr,Al) ₂ O ₇	Equant euhedral in glass matrix w/ spinel, sulfide, & other silicates	MgCa ₂ Si ₂ O ₇
(Ni,Cr,Al) ₂ (Al,SI,V,Fe) ₂ Si ₂ O ₇	Euhedral, w/ spinel, glass spherul, & Fe ₂ O ₃ in V-oxide rich slag	(Ca,NI) ₂ Al ₂ (Al,SI) ₂ Si ₂ O ₇	Sarcosite
Undeveloped silicates	Small euhedral crystals