

CHEMICAL PHASES IN PETROLEUM COKE GASIFICATION SLAG

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ABSTRACT

The gasification of petroleum coke results in the generation of complex slags. The broad variability in the physical and chemical properties of these slags will be described. The slags were examined primarily by means of reflected light optics using standard polished sections. These sections were also used directly for electron microprobe analysis where quantitative data on elemental distribution and partitioning was gathered and will be presented. Scanning electron microscopy (SEM) techniques were also used to characterize the presence of numerous phases including spinels of variable composition, glass droplets of variable composition, iron sulfide/oxide intergrowths often with tiny Fe-Ni alloy grains, and calcium silicates.

INTRODUCTION

The Texaco partial oxidation gasification process makes use of petroleum coke to produce a synthesis gas for use as a fuel for power generation or process heat, a chemical feedstock, or as a reducing gas. The petroleum coke 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 at 2200-2600°F (1200-1450°C), which promotes efficient reaction and facilitates the formation of a partially to wholly molten slag by controlling the 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. The slags that form in the gasifiers result from the accumulation of residual, noncombustible elements either on the refractory linings of the gasifiers, or as droplets that fall into water quench baths.

The slags produced during the high temperature gasification of petroleum coke can be generally characterized into three principal types: 1.- relatively fluid homogeneous silicate melts that solidify on cooling to brownish-black glass with minor to significant amounts of sulfide droplets, spinel crystals (Fe,Mg,Ni)²⁺(Fe,Al,V,Cr)₂³⁺O₄, plus other minor phases; 2.- sulfide dominant slag of generally troilitic composition (FeS), frequently but not always symplectically intergrown with wüstite (FeO), and usually containing smaller amounts of native Fe-Ni alloy grains, spinels (as above), glass droplets, and other phases; 3.- highly viscous slags comprised of masses of coarse interlocking vanadium-oxide-rich crystals, with major amounts of CaV₂O₆, (Fe,Ca)VO₄ or CaFeV₂O₇, VO₂, spinels (as above), glass droplets, plus other minor phases. These generalized compositions are shown in Table 1, which also lists in more detail the specific nature of some of the minor phases observed.

CHEMICAL PHASES

Spinel is both the most ubiquitous and the most compositionally variable crystalline phase. Hence it is instructive to consider the potential structural site occupancies and the degree of partitioning that the spinels exhibit with coexisting phases. The most apparent spinel compositional trend, as shown in Figure 1, is that which exists among spinels hosted by Ca-Fe-V oxides. Most of these spinels lie in the Ni to Mg, Al-V-(Fe³⁺+Cr) prism, and cluster toward the Al-rich corner. These spinels commonly contain more than 20 mol% Ni in the 2+ site, and some contain more than 80%. In contrast, the spinels in sulfide-rich slags tend to be Ni-poor; the Ni in such slags concentrates in the Fe-Ni-S monosulfide solid solution and in the Fe-Ni alloy.

The spinels in FeS-FeO-rich, glassy, and Ca-Fe silicate-rich slags are in general considerably more V-rich (Fig. 2) than are the spinels in Ca-Fe-V oxide-rich slags where the V is more highly partitioned into the host phases. The lower V contents of the spinels in Figure 1 is compensated by increases in the Al and Fe³⁺+Cr contents. The scarcity of Fe²⁺ in these spinels implies that the oxidation potential at the time of slag generation was high enough to keep most of the iron in the Fe³⁺

state; this is also supported by the observation that the vanadium in the coexisting Ca-Fe-V oxides is all present as V^{4+} and V^{5+} .

Spinel structures that occur in the sulfide rich slags (Fig.'s 2a-c) exhibit a fairly tight clustering of compositions that are relatively Fe^{2+} and V-rich and Al-poor. The enrichment of these spinels in Fe^{2+} is obviously due to the abundant available reduced iron in the Fe-S-O melt. Vanadium, as a general rule, partitions out of Fe-S-O melts, however, residual V that is present, clearly prefers filling 3+ sites, and then 2+ sites in spinel to forming V-sulfides. Strong verification of this phenomenon comes from the common observation of V-bearing spinels occurring in V-deficient Fe-Ni sulfides. The efficacy of V-partitioning into spinels is so strong, in fact, that even when present as V^{2+} , the V ions still enter spinel structures preferentially to forming sulfides as analyzed in several samples. Furthermore, only one sample of slag was found to contain V-rich sulfides, and in that sample, the euhedral spinels had already been virtually saturated with V, such that their compositions were essentially that of the pure endmember V_3O_4 (unplottable in Figure 2, and unknown as a mineral), leaving no oxygen for the additional V to react with, instead only sulfur. The oxidation state present during the formation of this slag must have been unusually low to facilitate the formation of V-sulfides. The low Al content of many of the spinels in the sulfide-rich slags (Fig. 2b), no doubt results from the virtually complete exclusion of Al from Fe-S-O melts. The relative deficiency of Mg in these spinels (Fig. 2c), can most likely be explained by a similar argument. The sulfide-rich slags also contain an interesting spinel with a rather unique composition approaching that of the mineral coulsonite (FeV_2O_4).

Glass-rich chunks of slag contain variable to large quantities of sulfide droplets, and thus form a continuum of slag types between sulfide-rich and glass-rich. This is probably the main reason that the spinels within glass hosts are compositionally similar to spinels within sulfide hosts. The primary compositional difference between these two groups is the Al-content (Fig. 2b), which is considerably higher in the glass-hosted spinels. Such a variation would be expected, because of the relatively high Al-content of the glasses, where Al substitutes for Si. The analyses of glass-hosted spinels that plot on or near the V - $Fe^{3+}+Cr$ join, are of spinels in sulfide-droplet-rich glassy slags (as described above), suggesting that these spinels experience compositional influences from both sources. The "ideal" glass hosted spinel composition, therefore, appears to be represented by the higher Al-content points shown in Figure 2b. The anomalous, isolated group of V-poor, and $Fe^{3+}+Cr$ -rich spinels in the glass-hosted family are unusually Cr-rich, and are interpreted to result from reaction with the refractory brick in the gasifiers.

Only a few pieces of slag have been found which contain significant quantities of crystalline Ca-Fe silicates; hence any discussion of the composition of their associated spinels is very preliminary. The highly variable V-content of all the spinels (and probably of the slags in general) most likely reflects the variable nature of the source petroleum for the feed cokes. Many crude oils are naturally enriched in V (carried as organic porphyrin complexes), as a result of the type of source materials and source rocks from which the oil was derived. Ni is another common element in petroleum and is also carried in large part as porphyrin complexes; hence its abundance in the slags may also be largely a function of its source crude. The Fe, Al, Si, Mg, Ca, Na, and S found in the slags are derived primarily by residual accumulation of minute entrained mineral particles (such as clays, Fe-oxides, Fe-sulfides, etc.) and hence tend not to vary considerably from slag to slag because of the common, but variable occurrence of these minerals. Chromium contents of petroleum are very low, hence, most of the Cr found in the slags probably originates from reaction of the molten slag with the Cr-rich refractory brick lining the gasifiers. The elemental Cr-content of most of the spinels is generally less than 15 mol%; and as of yet has not been found to show any relationship to host slag type.

The dominant sulfide phase found in the petroleum coke gasification slags is troilite (FeS). This composition may, however, grade from pure FeS to that of hexagonal pyrrhotite ($Fe_{1-x}S$, $0.0 < x < 0.125$) as shown in Figure 3. Distinguishing the compositions of these phases by means of electron microprobe analysis is quite difficult, and is better accomplished (if sufficient quantities exist), by X-ray diffraction, TEM, or other such techniques. The iron-sulfide often occurs as a very fine symplectitic intergrowth with iron oxide (presumably wüstite, FeO), that can barely be resolved by optical techniques. These intergrowths appear to be the result of the rapid cooling of an initially homogeneous Fe-S-O melt; such melts cannot be quenched to glasses. Nickel can substitute for iron in pyrrhotite in minor amounts, but may also form a discrete Ni-sulfide phase (Heazlewoodite, Ni_3S_2) and an Fe-Ni-sulfide phase (Pentlandite, $(Fe,Ni)_9S_8$). The crystals/grains of free metal (F.M.) that form in the sulfide matrix generally contain iron plus 10 to 28 atomic percent Ni but have been found to range from pure Fe to more than 70 atomic percent Ni (Fig. 3). In addition to the Fe-monoxide wüstite phase observed in the sulfide bearing slags, NiO (bunsenite) has also been found as well as a few grains of mixed $(Fe,Ni)O$ composition.

Vanadium oxide rich slags have been found to contain at least five distinct V-bearing phases. One

is CaV_2O_6 which is not known as a mineral but has been synthesized in phase equilibria studies. Euhedral Na-V-oxide crystals of apparent stoichiometry equal to $\text{NaV}_6\text{O}_{15}$ occur with CaV_2O_6 crystals, and correspond well with a β -solid solution phase along the experimental $\text{Na}_2\text{O-V}_2\text{O}_5$ join. This experimental β -solid solution phase has been found to be in equilibrium with CaV_2O_6 at 650° . A third phase, which occurs with the two phases above, has an apparent chemical formula of $\text{NaCaV}_8\text{O}_{20}$; this phase, however, does not correspond to any phases known from the literature. A fourth V-phase which is quite common, is problematic in that it is most favorably represented as a Ca-bearing variety of the synthetic FeVO_4 phase, from charge balance considerations; yet it is conceptually difficult to imagine a Ca ion substituting for Fe^{3+} in the structure. Alternatively, this phase might be a hypothetical CaFeV_2O_7 phase extrapolated from such known phases as $\text{Ca}_2\text{V}_2\text{O}_7$ and $\text{Ni}_2\text{V}_2\text{O}_7$; however, CaFeV_2O_7 does not charge balance well, and, the coexistence of Fe^{2+} and V^{5+} in the same structure may be unlikely. A fifth and less common V-phase is VO_2 . VO_2 is known as the mineral paramontroseite, however, this mineral forms as a metastable, low temperature oxidation product of the mineral montroseite and is a polymorph of synthetic VO_2 . The euhedral VO_2 crystals we observe in the slags grew at high temperatures and are therefore most likely not paramontroseite, but instead equivalent to its synthetic, high temperature polymorph. Spinel and variable composition glasses are the other main constituents of this type of slag; many additional minor phases occur in this type of slag as listed in Table I.

The sulfide-dominant slags occasionally contain pieces of slag which have several different euhedral $\text{Ca,Mg,Fe} \pm \text{Na}$ silicates worth noting. Though still in need of further verification, some of the phases have tentatively been identified as Akermanite ($\text{MgCa}_2\text{Si}_2\text{O}_7$, observed= $(\text{Mg,Fe})\text{Ca}_2(\text{Si,Al})_2\text{O}_7$), Fayalite (Fe_2SiO_4 , observed= $(\text{Fe,Mg,Ca,Na})_2(\text{Si,Al})\text{O}_4$), and Pigeonite ($(\text{Mg,Fe,Ca})(\text{Mg,Fe})\text{Si}_2\text{O}_6$, observed= $(\text{Ca,Fe,Mg,Na})(\text{Mg,Fe})(\text{Si,Al})_2\text{O}_6$). These phases are well known in geological realms and should be useful for estimating the conditions under which crystallization occurred.

TABLE 1.

SLAG TYPE	COMMON PHASES	MINOR PHASES
Glassy	<ul style="list-style-type: none"> * Glasses of variable composition * Spinels of variable composition (Fig.'s 1&2) * Droplets of Fe sulfide and/or Fe sulfide/oxide intergrowths, often with tiny Fe-Ni alloy grains (Fig. 3) 	<ul style="list-style-type: none"> * Al_2SiO_5: Andalusite or sillimanite, needs crystal structure work * Corundum: Al_2O_3, needles * Eskolaite: Cr_2O_3, exsolution lamellae in Cr-rich spinels * Karelianite: V_2O_3, crust on sulfide bleb * Hematite: Fe_2O_3, irreg. chunk
Sulfide rich . . .	<ul style="list-style-type: none"> * Fe-sulfide: $\sim FeS$, and/or FeS/FeO intergrowths, often with tiny Fe-Ni alloy inclusions (Fig. 3) * Spinels of variable composition (Fig.'s 1&2) * Glass droplets of variable composition * FeO dendritic crystals and blebs 	<ul style="list-style-type: none"> * long acicular sulfide crystals of unknown phase, need crystal structure analysis to identify * $\sim 1 \mu m$ blocky sulfide crystals? * Pentlandite: $(Fe,Ni)_9S_8$ or monosulfide solid solution (?) * $(Fe,Ni,Cr)VS_2$: not a known mineral * Unknown euhedral CaFeMg-silicate phase * Hercynite: $FeAl_2O_4$, or (?) * $FeAlO_3$: (not a known mineral) * V_3O_4: (not a known mineral)
CaFeMg-silicate rich subgroup of sulfide rich slags:	<ul style="list-style-type: none"> * CaFeMg-rich glasses * Akermanite: $Ca_2MgSi_2O_7$, with Fe and Al partially substituting for Mg * Pigeonite: $(Mg,Fe,Ca)(Mg,Fe)Si_2O_6$, with minor Na substituting for Ca and minor Al substituting for Si * Fayalite: Fe_2SiO_4, with Mg,Ca and Na partially substituting for Fe and minor Al substituting for Si * Unknown euhedral CaFeMg-silicate phase * Spinels of variable composition (Fig.'s 1&2) * Droplets of Fe-sulfide and/or Fe-sulfide/oxide intergrowths, often with tiny Fe-Ni alloy grains (Fig. 3) 	
V-oxide rich . . .	<ul style="list-style-type: none"> * CaV_2O_6: not a known mineral * NaV_6O_{15}: not a known mineral * $NaCaV_8O_{20}$: not a known mineral * $FeCaV_2O_7$ or $(Fe,Ca)VO_4$: need crystal structure analysis to determine actual phase * VO_2: Paramontroseite polymorph * Spinels of variable composition (Fig.'s 1&2) * Glass droplets of variable composition 	<ul style="list-style-type: none"> * Hematite: Fe_2O_3, with Al & V partially substituting for Fe * Corundum: Al_2O_3, with an unknown element partially substituting for Al * Sarcosite: $(Ca,Na)_4Al_3(Al,Si)_3Si_3O_{24}$ with Mn(?) partially substituting for Ca * Heazlewoodite: Ni_3S_2 * Bunsenite: NiO * FeV_2O_6: not a known mineral * unidentifiable submicroscopic V-oxide bearing crystals

Petroleum Coke Slag Spinel

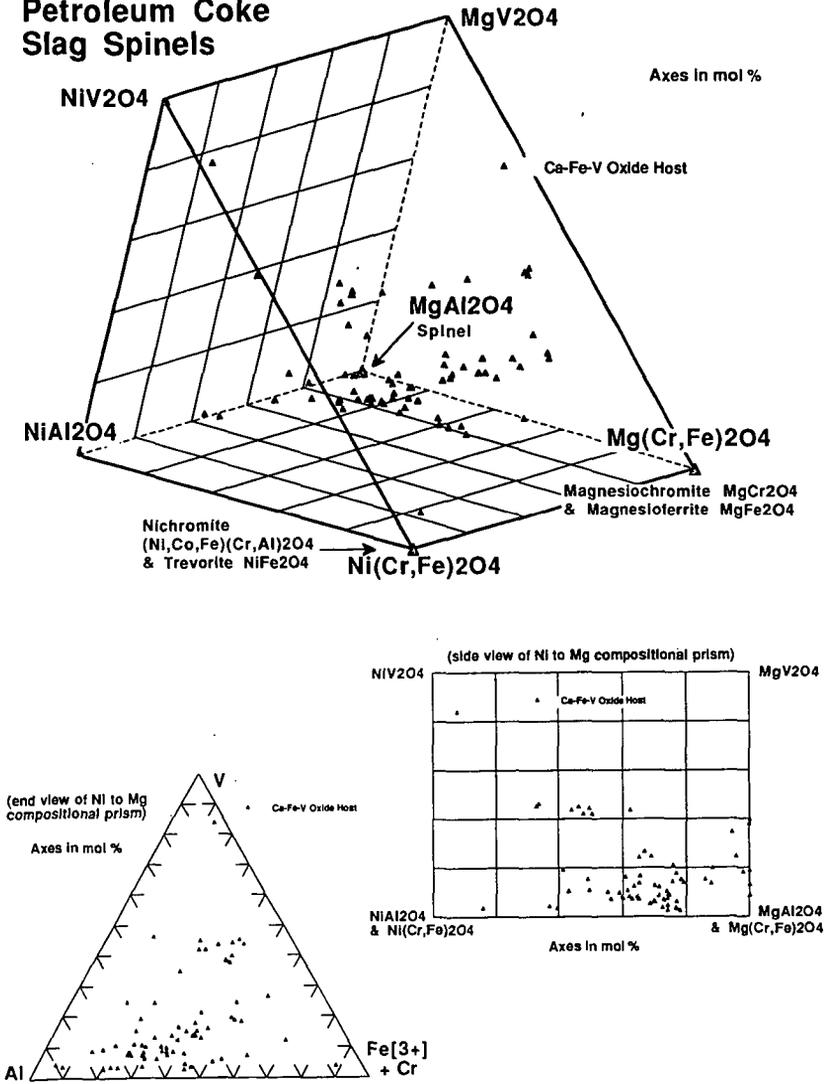


FIGURE 1.

Petroleum Coke Slag Spinel

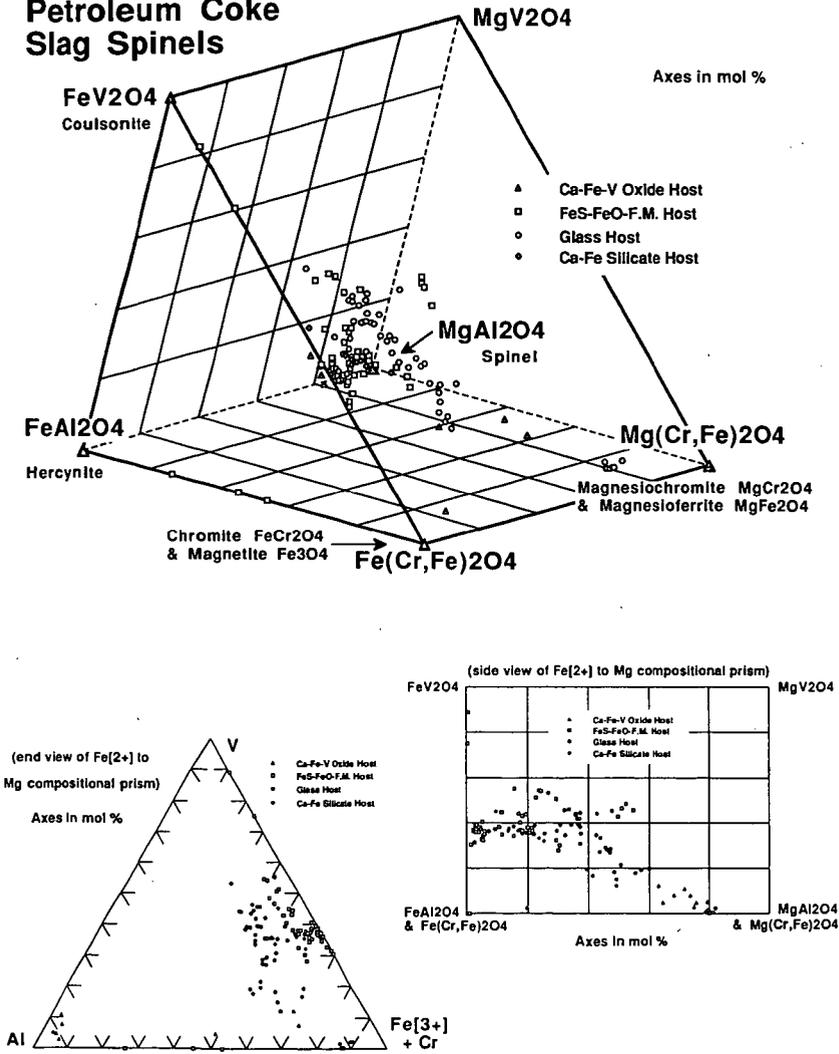
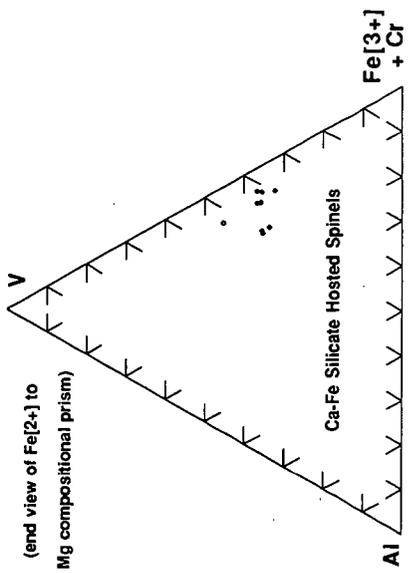
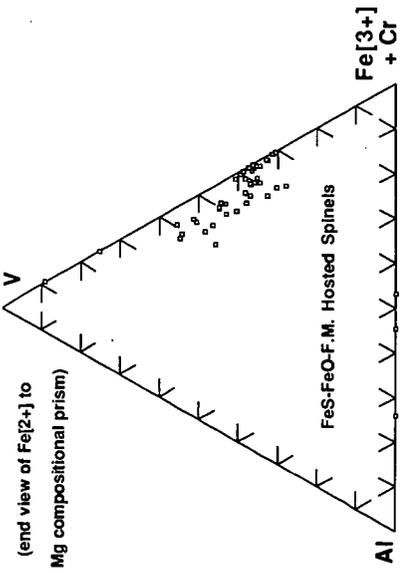
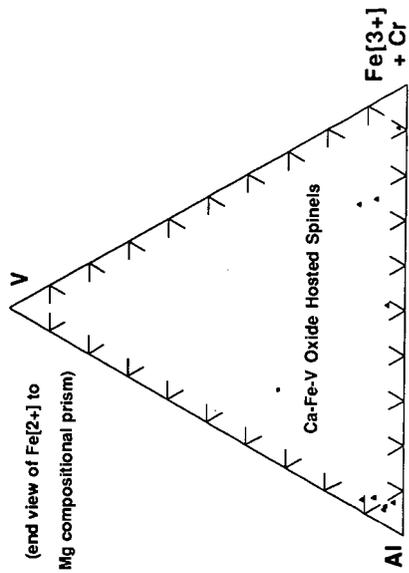
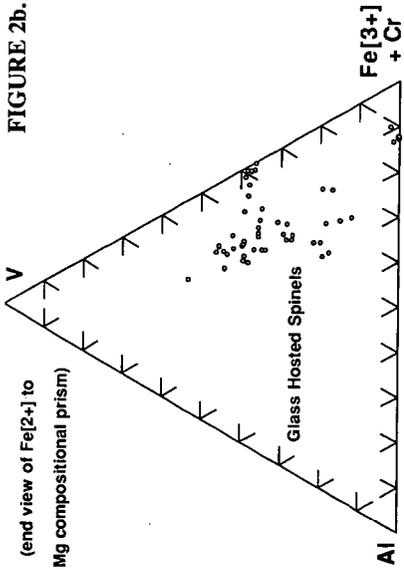


FIGURE 2a.

FIGURE 2b.



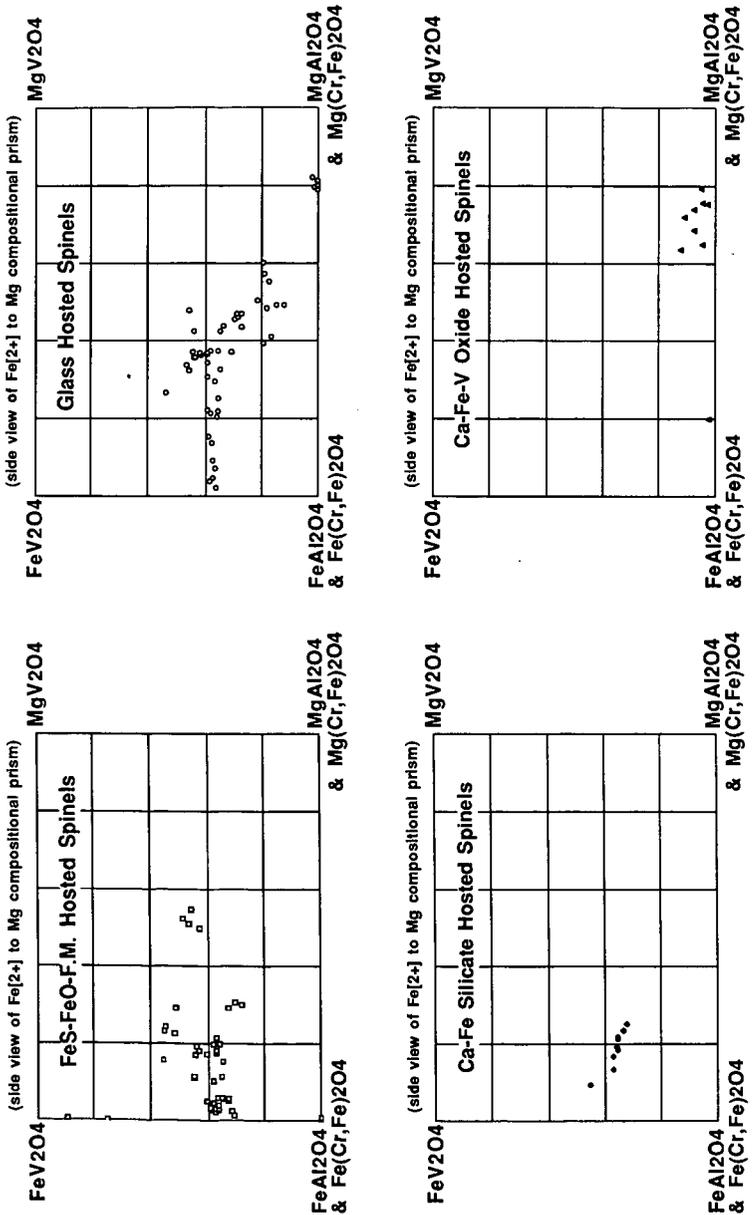


FIGURE 2c.

Petroleum Coke Slag Fe-Ni-S-O Phases

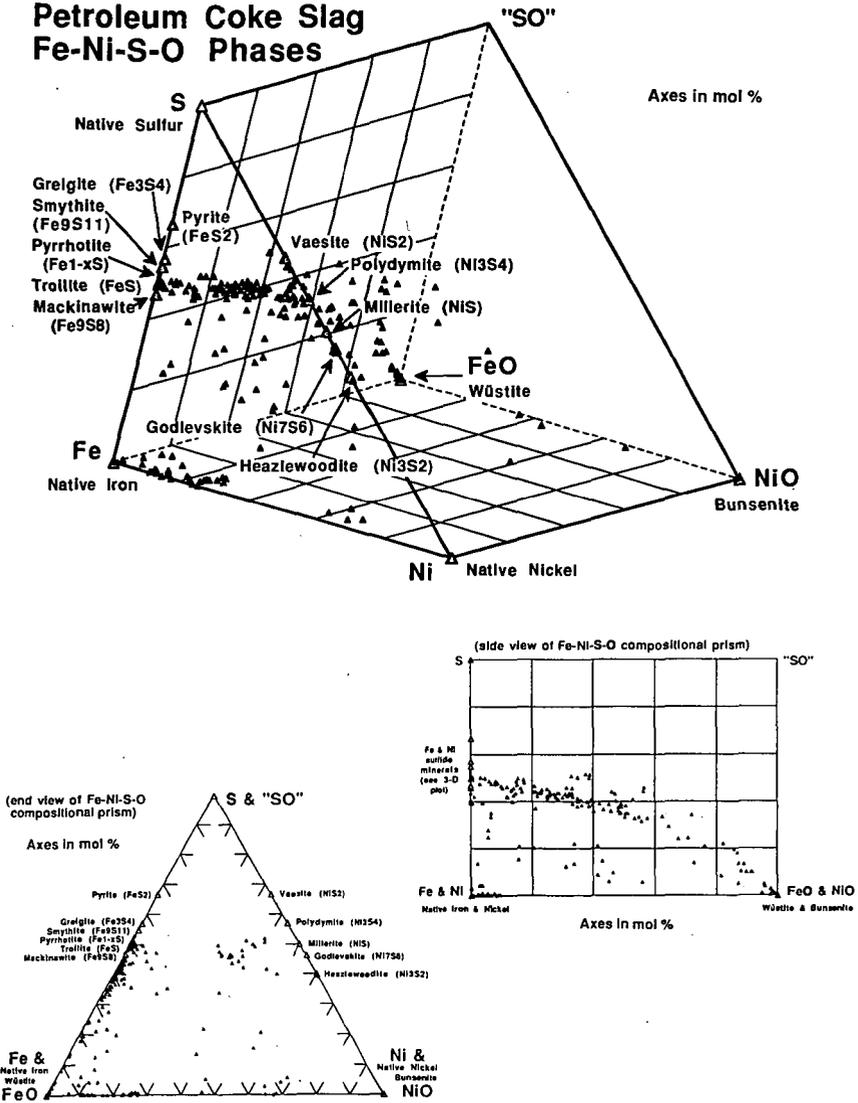


FIGURE 3.