Industrial uses of high sulfur petroleum coke
by Lance Harold Ulrich

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

Abstract:

The purpose of this thesis is to find a use or uses for high sulfur petroleum coke. Research was conducted to determine if high sulfur petroleum coke can be used as a reagent to convert molybdenum ore, MoS2, to MoO2. The second experiment was to determine if the petroleum coke can be used as a reagent to convert Cu2S ore to copper at a lower temperature than is currently used in industry. The third area of research was to determine if high sulfur petroleum coke could be used in place of regular coke to reduce iron ore, Fe3O4, to pig-iron (Fe). The last experiment was to determine if petroleum coke could be substituted for regular coke in the initial lead ore roasting process.

Each of these experiments used a similar procedure. The petroleum coke was mixed with the metal ore, and the mixture was heated in either an oxidizing or reducing atmosphere until the ore had been converted to the final product. Then the product was chemically analyzed to determine purity and percent conversion. For molybdenum, the ore/coke mix was cooked in air to facilitate the conversion of MoS2 to MoO2. Air was blown through an experimental blast furnace to help convert Cu2S ore to elemental copper. A reducing atmosphere was required to convert iron ore, Fe3O4, to iron, so the ore/coke mix was insulated from the atmosphere with a top layer of coke. Lastly, air was blown through the lead ore/coke mix to help convert PbS to Pb.

An 83% conversion of MoS2 to MoO2 was obtained by roasting an. 8:1 coke:ore mixture in air at 500°C for 38 minutes. The iron ore didn't reduce to iron at 1350°C. The best result with copper ore was achieved by roasting a 0.5:1 coke:ore ratio at 700°C with a small amount of air blowing through it. After two hours a 6 0% conversion of Cu2S to Cu was achieved. A 43% conversion of PbS to Pb was obtained by roasting a 0.167:1 coke:ore ratio in air for 8 minutes at 800°C.

It was concluded that it is highly probably that high sulfur petroleum coke is effective in converting MoS2 to MoO2 and it is highly probable that the petroleum coke can be used to convert lead ore to lead. The coke is effective in converting copper ore to copper. Lastly, high sulfur petroleum coke cannot convert Fe3O4 to iron at 1350°C; a higher temperature is probably needed.

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

June 6, 1991
Date

Lloyd Berg
Chairperson, Graduate Committee

Approved for the Major Department

June 7, 1991
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

July 25, 1991
Date

Henry L Parsons
Graduate Dean

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Symbol	Definition	Units
ΔG_T°	Gibbs standard energy change of reaction at constant temperature T	kcal/mol
ΔH_T°	Standard enthalpy change of reaction at constant temperature T	kcal/mol
T	Temperature	K
ΔS_T°	Standard entropy change of reaction at constant temperature T	cal/(K*mol)
ΔC_p°	Standard heat capacity of reaction at constant pressure	cal/(K*mol)
v_i	Stoichiometric coefficient of each component in the reaction, i (+) for products, (-) for reactants	none
C_{pi}°	Standard heat capacity of each component in the reaction, i	cal/(K*mol)
R	Gas constant	cal/(mol*K)
K	Equilibrium constant	none
$H^\circ_{prod,\ 298}$	Sum of the standard enthalpies of the products of reaction	kcal/mol
$H^\circ_{react,\ 298}$	Sum of the standard enthalpies of the reactants in the reaction	kcal/mol
$S^\circ_{prod,\ 298}$	Sum of the standard entropies of the products of reaction	cal/(K*mol)
$S^\circ_{react,\ 298}$	Sum of the standard entropies of the reactants in the reaction	cal/(K*mol)

ABSTRACT

The purpose of this thesis is to find a use or uses for high sulfur petroleum coke. Research was conducted to determine if high sulfur petroleum coke can be used as a reagent to convert molybdenum ore, MoS_2, to MoO_2. The second experiment was to determine if the petroleum coke can be used as a reagent to convert Cu_2S ore to copper at a lower temperature than is currently used in industry. The third area of research was to determine if high sulfur petroleum coke could be used in place of regular coke to reduce iron ore, Fe_3O_4, to pig-iron (Fe). The last experiment was to determine if petroleum coke could be substituted for regular coke in the initial lead ore roasting process.

Each of these experiments used a similar procedure. The petroleum coke was mixed with the metal ore, and the mixture was heated in either an oxidizing or reducing atmosphere until the ore had been converted to the final product. Then the product was chemically analyzed to determine purity and percent conversion. For molybdenum, the ore/coke mix was cooked in air to facilitate the conversion of MoS_2 to MoO_2. Air was blown through an experimental blast furnace to help convert Cu_2S ore to elemental copper. A reducing atmosphere was required to convert iron ore, Fe_3O_4, to iron, so the ore/coke mix was insulated from the atmosphere with a top layer of coke. Lastly, air was blown through the lead ore/coke mix to help convert PbS to Pb.

An 83% conversion of MoS_2 to MoO_2 was obtained by roasting an 8:1 coke:ore mixture in air at 500°C for 38 minutes. The iron ore didn't reduce to iron at 1350°C. The best result with copper ore was achieved by roasting a 0.5:1 coke:ore ratio at 700°C with a small amount of air blowing through it. After two hours a 60% conversion of Cu_2S to Cu was achieved. A 43% conversion of PbS to Pb was obtained by roasting a 0.167:1 coke:ore ratio in air for 8 minutes at 800°C.

It was concluded that it is highly probably that high sulfur petroleum coke is effective in converting MoS_2 to MoO_2 and it is highly probable that the petroleum coke can be used to convert lead ore to lead. The coke is effective in converting copper ore to copper. Lastly, high sulfur petroleum coke cannot convert Fe_3O_4 to iron at 1350°C; a higher temperature is probably needed.

BACKGROUND

Petroleum Coke

Heavy oils that are left over after vacuum distillation in a refinery are worth very little since they can only be used as fuel. However, light oils can be further processed to make saleable products. Lighter oils can be produced from very heavy ones solely by thermal cracking. This process is called "coking" because the by-product is petroleum coke.

The feed to a coker is usually the heavy gas oil that is left over from vacuum distillation of the lubricating residue. The lubricating residue comes from crude oil distillation. The coker produces either delayed coke or fluid coke. Delayed coke is available in chunks while fluid coke is in the form of small spherical balls. In either case, the chemical composition of the coke is 93 - 99% carbon and the balance is sulfur. [1]

Both delayed and fluid coke are valuable as electrolytic reducing agents if their sulfur content is below 3%. In the refining of sulfur containing crude oil, the pitch, asphalt and coke fractions contain the most sulfur. If the crude is a high sulfur crude, the coke fraction can become 5 - 7% sulfur. After coking, most of the sulfur in this fraction ends up in the petroleum coke. Currently, high sulfur petroleum coke is almost worthless. Even as a fuel, the current restriction is one pound of sulfur per million BTU's. [2]

The EXXON refinery in Billings, Montana uses a high sulfur crude as its feedstock. The petroleum coke produced by this refinery is about 94% carbon and 6% sulfur so it cannot be used as an electrolytic reducing agent or as a fuel. The research in this thesis is based upon trying to find a use for the high sulfur petroleum coke produced at the EXXON Refinery in Billings. [3] The properties of the EXXON fluid coke are presented in Table 1. Properties of EXXON Fluid Petroleum Coke.

Table 1. Properties of EXXON Fluid Petroleum Coke [4]

Sieve Analysis

Cumulative, % Retained		Non-cumulative, % Retained	
on: 10m	2	on: 12m	4.2
20	5	20	3.9
48	11	40	6.4
60	20	50	37.6
80	44	70	29.2
100	65	100	10.0
150	88	200	6.4
200	95	325	1.2
Through 200	5	Through 325	1.1

Particle Density, g/cm^3		1.3
Bulk Density, lb/ft^3		55.9
Calorific Value, BTU/lb	(ASTM D-271)	14,100
Proximate Analysis, wt. %	(ASTM D-271)	
Moisture		0.3
Volatile Matter		6.0
Fixed Carbon		93.4
Ash		0.3
Ultimate Analysis, wt. %	(ASTM D-271)	
Carbon		90.0
Hydrogen		2.0
Sulfur		6.0
Metals, (wt. % on coke)		
Nickel		0.013
Vanadium		0.034
Iron	less than	0.01
Calcium	less than	0.01
Silicon	less than	0.005
Titanium	less than	0.001
Sodium	less than	0.02

Molybdenum

Molybdenum was discovered in 1778 by C. W. Scheele when he produced a new oxide from molybdenite (MoS_2), thus distinguishing the mineral from graphite, with which it had been thought to be identical. Today, molybdenum is obtained from molybdenite and is a byproduct from the production of copper. In both cases, MoS_2 is separated by floatation and then roasted in air to produce MoO_3. About 85% of the MoO_3 is used in the manufacture of stainless steel and high-speed tools. It is used directly or after conversion to ferromolybdenum by the aluminotherimc process.

Molybdenum chemicals are synthesized from ammonium molybdate which is obtained by dissolving MoO_3 in aqueous ammonia, then crystallizing the ammonium molybdate. Pure molybdenum, which is used in catalysts for a variety of petrochemical processes and as an electrode material, is obtained from hydrogen reduction of ammonium molybdate. [5]

The intent of the molybdenum research is to determine if molybdenum ore, MoS_2, can be converted to MoO_2 using high sulfur petroleum coke as a reagent, thus demonstrating a use for the coke. MoO_2 is of interest because it contains 11% more molybdenum per pound than MoO_3.

Several investigators have reported methods of converting molybdenite to MoO_2:

> "V. H. Zazhigalov (1975) employed hydrogen and elemental sulfur. N. Satani (1975) used hydrogen-thiophene mixtures to reduce the MoO_3 hydrate to MoO_2. J. O. Besenhard (1976) carried out the reduction of MoS_2 in dimethylsulfoxide. A. Wold (1964) prepared pure MoO_2 crystals by the electrolytic reduction of MoO_3--$NaMoO_4$ solution. W. Kunnman (1961) used a mixture of CO and CO_2 to reduce MoO_3 to MoO_2. S.I. Sobol (1961) used hydrogen and CO under pressure at 200°C. to reduce $NaMoO_4$ to MoO_2. V. Angelova (1972) reacted molybdenite with TiO_2 at 500°--900° C to produce MoO_2, SO_2 and elemental Ti. F. Zabo (1963) reduced MoO_3 with ammonia." [6]

Additional work on the subject includes Conversion of Molybdenite to Molybdenum Dioxide Using Petroleum or Coal Tar Pitches. This patent states that "Molybdenite, MoS_2, is completely converted into molybdenum dioxide, MoO_2 by mixing MoS_2 with petroleum or coal tar pitches and heating in air at 400°-600° F." [7]

Copper

Copper is one of the most important metals in the history of man. It was in use as far back as 5000 BC, was obtained from charcoal reduction in 3500 BC, and was combined with tin to establish the "Bronze Age" in about 3000 BC. Today, copper is still one of man's most important metals.

The majority of copper comes from huge open pit mines. The ore only contains about 1/2% Cu so it is concentrated to 15-20% Cu by froth floatation before further processing.

Silica is added to the concentrate, and the mixture is melted in a reverberatory furnace at about 1400°C. The iron in the melt (FeS) is more readily converted to the oxide than the Cu_2S ore, so it forms an upper layer of iron silicate slag. This leaves a lower layer of copper matte which is mostly Cu_2S and FeS. The liquid matte is poured into a converter, more silica is added, and a blast of air is forced through it. The air and silica transforms the remaining FeS to FeO and then to slag, while the Cu_2S is converted to Cu_2O and then to copper:

$$2FeS + 3O_2 \text{--->} 2FeO + 2SO_2$$

$$2Cu_2S + 3O_2 \text{--->} 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \text{--->} 6Cu + SO_2$$

This "blister" copper is usually further purified electrolytically for use in the electronics industry. [8]

The research in this thesis involves using petroleum coke as a reagent to convert Cu_2S ore to Cu at a lower temperature. If this is proven, it will demonstrate a use for the high sulfur petroleum coke. The probable reaction is as follows:

$$Cu_2S + C + 2O_2 \text{--->} 2Cu + SO_2 + CO_2$$

This reaction represents the overall conversion of Cu_2S to Cu. There is probably an intermediate step where the copper is in an oxidized state, but this is not important because the above equation is only used to obtain a rough approximation of temperatures at which Cu_2S can be converted to Cu.

Iron

As with copper, iron has had a tremendous impact on man's history. Iron beads dating from about 4000 BC were probably of meteoric origin. Iron was first made by low temperature reduction methods, but this produces a spongy material that could only be shaped by prolonged hammering. The high temperature smelting process did not evolve until about 1200 BC--the start of the "Iron Age". More recently, the use of coke as the reducing agent had far-reaching effects, such as the start of the Industrial Revolution.

Today, most iron is used as steel of one form or another. The first step to convert iron ore to steel is the blast furnace. The Fe_2O_3 ore is reduced to Fe using coke as the reducing agent while limestone ($CaCO_3$) removes sand or clay as slag (see Figure 1, Iron Blast Furnace). The molten iron is cast into molds or ingots for further processing. This iron is in an impure form containing about 4% carbon and is called "cast-iron" or "pig-iron". [9]

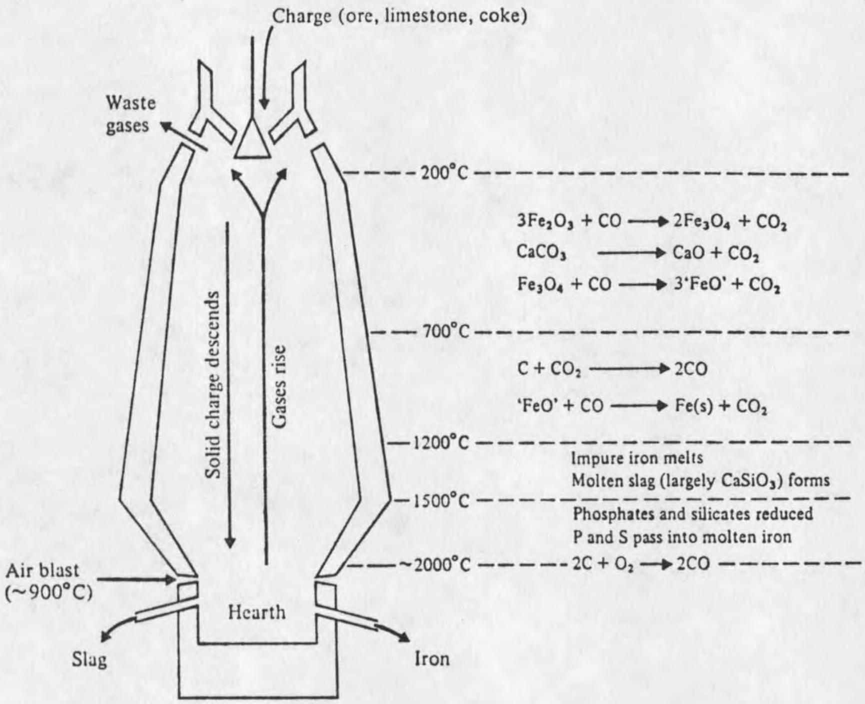

Figure 1, Iron Blast Furnace

The purpose for this research on iron is to find out if petroleum coke could be used in place of regular coke to reduce the iron ore to pig-iron.

Lead

Lead is another of man's oldest metals. It was used in ancient Egypt for glazing pottery in 7000-5000 BC. The Romans used lead for water pipes and plumbing, extracting 6-8 million tons in four hundred years. Today, over half the lead produced is used in batteries. The remaining amount is used in cable sheathing, sheet, pipe, foil, tubes, $Pb(CH_2CH_2)_4$, solders, pigments, and chemicals. $Pb(CH_2CH_2)_4$ is used as an antiknock additive in gasoline, but is being phased out by the Environmental Protection Agency.

Most lead is obtained from PbS ore. This is concentrated from low-grade ores by froth flotation, then roasting in air to produce PbO. The PbO is then mixed with coke and limestone, and the mixture is reduced in a blast furnace. The following equations illustrate the process:

$$PbS + 1.5O_2 \text{ ---> } PbO + SO_2$$

$$PbO + C \text{ ---> } Pb(liq) + CO$$

$$PbO + CO \text{ ---> } Pb(liq) + CO_2$$

Another possible reduction method is to replace the reduction of the roasted ore with fresh ore (PbS):

$$PbS + 2PbO \text{ ---> } 3Pb(liq) + SO_2(g) \quad [10]$$

The "Green Ore" used at the ASARCO lead refinery in East Helena has the following composition:

Table 2. Composition of Lead Green Ore [11]

Element	Wt. %
Lead (PbS)	34-36
Copper (Cu_2S)	3.9-4.1
Arsenic (As_2S_2, As_2S_3)	0.8-1.0
Antimony (Sb_2S_3)	1.1-1.3
Sulfur (as the metal sulfides)	57.6-60.2

The ASARCO lead refinery in East Helena uses the roasting/blast furnace process. However, they combine the lead ore with regular coke in the initial roasting process to speed up the production of SO_2. The SO_2 is then used to produce sulfuric acid. The purpose of the lead research in this thesis is to determine if petroleum coke could be substituted for regular coke in the initial roasting process.

THEORETICAL ASPECTS

All of the reactions for molybdenum, copper, iron and lead involve rather high temperatures. If petroleum coke is going to be used in the production of the metals in question, it would be useful to know the thermodynamics of the systems. Since the reactions for each experiment are fairly well known, as are the thermodynamic properties for the compounds in question, one can calculate the temperature of neutral equilibrium, the Gibbs standard energy change of reaction, and the heat of reaction. Since the Gibbs standard energy change of reaction must be equal to or less than zero for a feasible reaction, and $\Delta G = 0$ at neutral equilibrium, one can find the feasible temperature range for the reaction (see Thermodynamics of Molybdenum Oxidation). Once a feasible temperature range is known, one can use it to design appropriate experiments and to better evaluate the results of these experiments.

Thermodynamics of Molybdenum Oxidation

Molybdenite is to be converted to molybdenum dioxide by the following reaction:

$$MoS_{2(s)} + C_{(s)} + 4O_{2(g)} \text{ ---> } MoO_{2(s)} + 2SO_{2(g)} + CO_{2(g)}$$

This reaction is probably not the only reaction taking place when MoS_2 is oxidized to MoO_2, but it will allow a good estimate of the temperature of neutral equilibrium and the heat of reaction. The following information is available from the Handbook of Chemistry and Physics: [12]

Table 3. Thermodynamic Properties of Some Molybdenum Compounds

Compound	Standard Entropy cal/deg*mol	Gibbs Standard Energy kcal/mol	Standard Enthalpy kcal/mol
MoS_2	14.96	-54	-56.2
C	1.372	0	0
O_2	49.003	0	0
MoO_2	11.06	-127.40	-140.76
MoO_3	18.58	-159.66	-178.08
SO_2	59.30	-71.748	-70.944
CO_2	51.06	-94.254	-93.963

The heat of reaction is calculated by subtracting the sum of the enthalpies of the reactants from the sum of the enthalpies of the products. A negative quantity indicates an exothermic reaction, a positive quantity means the reaction is endothermic. [13]

$$\text{Heat of Reaction} = \Sigma(\text{Product Enthalpies}) - \Sigma(\text{Reactant Enthalpies})$$

$$\text{Heat of Reaction} = [-140.76 + 2(-70.944) + -93.963] - [-56.2 + 0 + 4(0)]$$

Heat of Reaction = -320.411 kcal/mol

So the reaction is very exothermic.

An approximation of the temperature range at which a reaction is feasible can be determined by calculating the Gibbs standard energy change of reaction and the neutral equilibrium temperature. A proof of this begins with:

$$\Delta G^{\circ}_{T} = \Delta H^{\circ}_{T} - T\Delta S^{\circ}_{T} \quad (1)$$

The equation for ΔG at one temperature, using ΔH and ΔS at another temperature is:

$$\Delta G^{\circ}_{T} = \Delta H^{\circ}_{298} + \int_{298}^{T} \Delta C^{\circ}_{p} dT - T\left[\Delta S^{\circ}_{298} + \int_{298}^{T} \frac{\Delta C^{\circ}_{p}}{T} dT\right] \quad (2)$$

Since

$$\Delta C^{\circ}_{p} = \Sigma v_{i} C^{\circ}_{pi} \quad (3)$$

If you assume that $Cp_{(products)} = Cp_{(reactants)}$ then Equation 2 becomes:

$$\Delta G^{\circ}_{T} \approx \Delta H^{\circ}_{298} - T\Delta S^{\circ}_{298} \quad (4)$$

It is also know that

$$\Delta G_T^\circ = -RT\ln K \quad (5)$$

If you arbitrarily choose K = 1 for a feasible reaction, (K = 1 gives about a 50% conversion) then lnK = 0, and Equations 4 and 5 can be combined as:

$$\Delta G_T^\circ \approx \Delta H_{298}^\circ - T\Delta S_{298}^\circ = 0 \quad (6)$$

Equation 6 can be rearranged as:

$$T_{N.E.} = \frac{\Delta H_{298}^\circ}{\Delta S_{298}^\circ} = \frac{H_{prod,\,298}^\circ - H_{react,\,298}^\circ}{S_{prod,\,298}^\circ - S_{react,\,298}^\circ} \quad (7)$$

where $T_{N.E.}$ is the "Temperature of Neutral Equilibrium". [14]

For the molybdenum reaction, the temperature of neutral equilibrium is:

$$T_{N.E.} = \frac{\frac{1000\ cal}{kcal}\biggl[-140.76\frac{kcal}{mol} + 2(-70.944)\frac{kcal}{mol} + -93.963\frac{kcal}{mol} - \frac{1000\ cal}{kcal}\biggl[-56.2\frac{kcal}{mol} + 0\frac{kcal}{mol} + 4(0)\frac{kcal}{mol}\biggr]}{\biggl[11.06\frac{cal}{^{\circ}K{\cdot}mol} + 2(59.30)\frac{cal}{^{\circ}K{\cdot}mol} + 51.06\frac{cal}{^{\circ}K{\cdot}mol}\biggr] - \biggl[14.96\frac{cal}{^{\circ}K{\cdot}mol} + 1.372\frac{cal}{^{\circ}K{\cdot}mol} + 4(49.003)\frac{cal}{^{\circ}K{\cdot}mol}\biggr]}$$

$$T_{N.E.} = 10{,}131\ ^{\circ}K$$

By observation of Equation 5, one can determine that ΔG_T° must be less than or equal to zero for a feasible reaction. The Gibbs standard energy change of reaction is calculated by subtracting the sum of the ΔG_{298}°'s of the reactants from the sum of the ΔG_{298}°'s of the products. [15] A negative quantity indicates a feasible reaction at 298 K, a positive quantity means that the reaction is not feasible.

$$\text{Gibbs Standard Energy Change of Reaction} = \Sigma(\Delta G_{298}^{\circ}\ \text{Products}) - \Sigma(\Delta G_{298}^{\circ}\ \text{Reactants})$$

$$\text{Gibbs S.E.C.R} = [-127.40 + 2(-71.748) + -94.254] - [-54 + 0 + 4(0)]$$

$$\text{Gibbs S.E.C.R} = -311.15\ \text{kcal/mol}$$

Since the Gibbs S.E.C.R is negative, the reaction is thermodynamically feasible from 298 K to 10,131 K, the temperature of neutral equilibrium. Note that the compounds in question probably do not exist at 10,131 K, but the thermodynamics state that if they did exist at that temperature, the reaction would be feasible.

In addition, the following thermodynamic properties are calculated for

$$MoS_{2(s)} + C + 9/2O_{2(g)} \text{ ---> } MoO_{3(s)} + 2SO_{2(g)} + CO_{2(g)}$$

using the methods outlined above:

Heat of Reaction (ΔH^f_{298})..............-357.64 kcal/mol

Gibbs Energy of Reaction (ΔG^f_{298}).....-343.41 kcal/mol

Temp. of Neutral Equilibrium ($T_{N.E.}$)...7.36 K

Figure 2, Delta G vise Temperature for Oxidation of MoS_2 to MoO_2, and Figure 3, Delta G vise Temperature for Oxidation of MoS_2 to MoO_3 provide a comparison of the thermodynamic feasibility for the reactions in question.

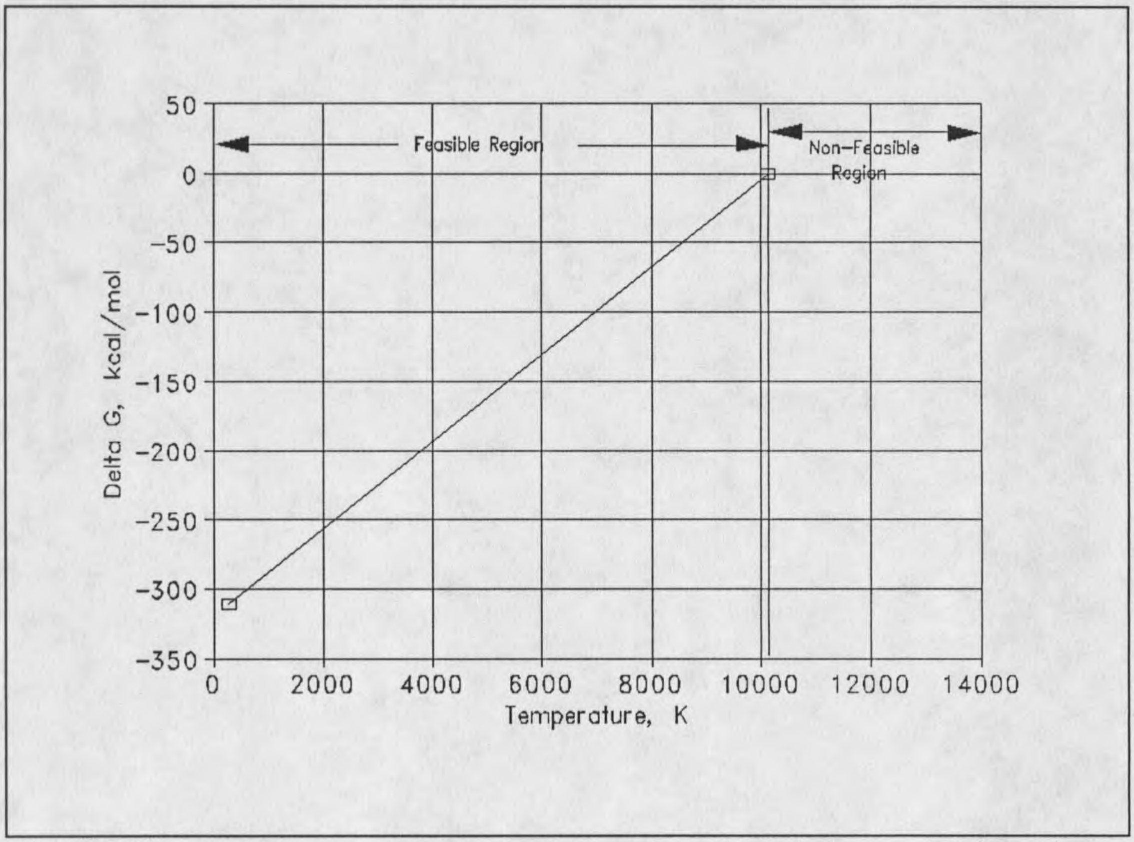

Figure 2, Delta G vs Temperature for Molybdenum Oxidation

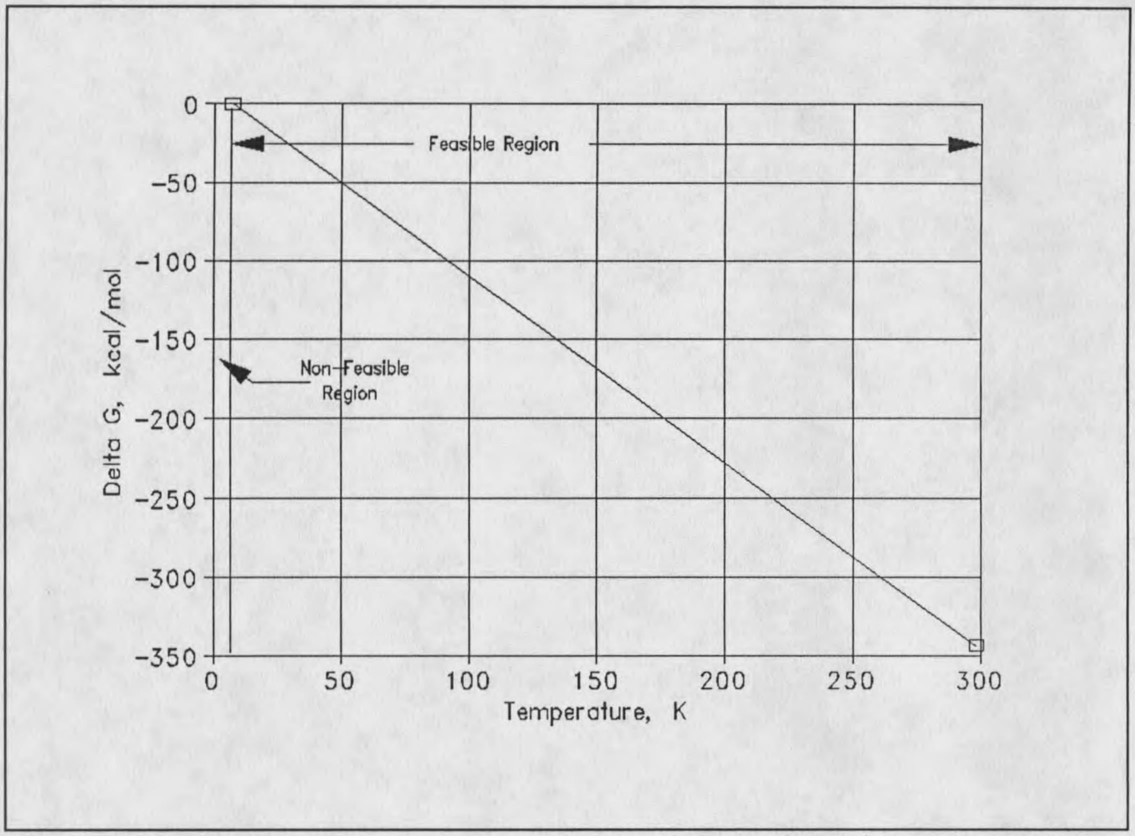

Figure 3, Delta G vs Temperature for Oxidation of MoS_2 to MoO_3

Note that ΔG is more negative at lower temperatures in the MoS_2 ---> MoO_3 case than in the MoS_2 ---> MoO_2 case. This shows that it is more thermodynamically feasible for molybdenum ore to oxidize to MoO_3 than to MoO_2. However, limiting the amount of oxygen would modify reaction conditions to favor oxidizing the ore to MoO_2, and make MoS_2 ---> MoO_2 possible.

Thermodynamics of Copper Reduction

Copper ore is converted to blister copper by the following reaction:

$$Cu_2S_{(s)} + C_{(s)} + 2O_{2(g)} \text{---}> 2Cu_{(s)} + SO_{2(g)} + CO_{2(g)}$$

The thermodynamic properties of copper are listed in the Handbook of Chemistry and Physics: [16]

Table 4. Thermodynamic Properties of Some Copper Compounds

Compound	Entropy cal/deg*mol	Gibbs Standard Energy kcal/mol	Standard Enthalpy kcal/mol
Cu_2S	28.9	-20.6	-19.0
C	1.372	0	0
O_2	49.003	0	0
Cu	7.923	0	0
SO_2	59.30	-71.748	-70.944
CO_2	51.06	-94.254	-93.963
Cu_2O	22.26	-34.9	-40.3

The following thermodynamic properties are calculated for

$$Cu_2S_{(s)} + C_{(s)} + 2O_{2(g)} \text{---}> 2Cu_{(s)} + SO_{2(g)} + CO_{2(g)}$$

using the methods outlined above:

Heat of Reaction (ΔH^f_{298}).............-145.907 kcal/mol

Gibbs Energy of Reaction (ΔG^f_{298}).....-145.402 kcal/mol

Temp. of Neutral Equilibrium ($T_{N.E.}$)...70,418 K

In addition, the following thermodynamic properties are calculated for

$$2Cu_2S_{(s)} + 3O_{2(g)} \text{ ---> } 2Cu_2O_{(s)} + 2SO_{2(g)}$$

using the methods outlined above:

Heat of Reaction (ΔH^f_{298})..............-184.48 kcal/mol

Gibbs Energy of Reaction (ΔG^f_{298}).....-172.096 kcal/mol

Temp. of Neutral Equilibrium ($T_{N.E.}$)...4.12 K

Both of these reactions are very exothermic. In addition, the Gibbs energy of reaction is negative for both reactions. This means that the reaction Cu_2S ---> Cu is feasible for all real temperatures and the reaction Cu_2S ---> Cu_2O is feasible from 4.12 K on up.

The feasibility of making Cu is shown in Figure 4, Delta G vs Temperature for Reducing Cu_2S to Cu:

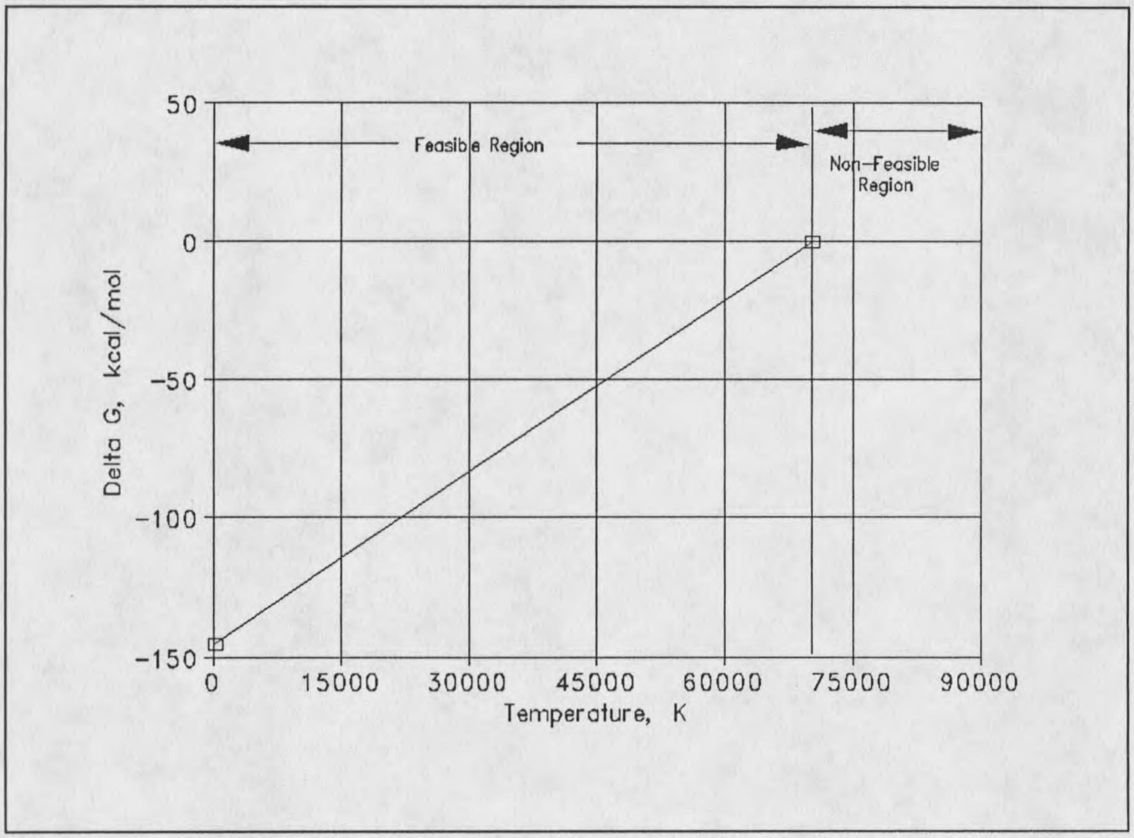

Figure 4, Delta G vs Temperature for Reducing Cu_2S to Cu

The feasibility of making Cu_2O from Cu_2S is shown in Figure 5, Delta G vs Temperature for Reducing Cu_2S to Cu_2O:

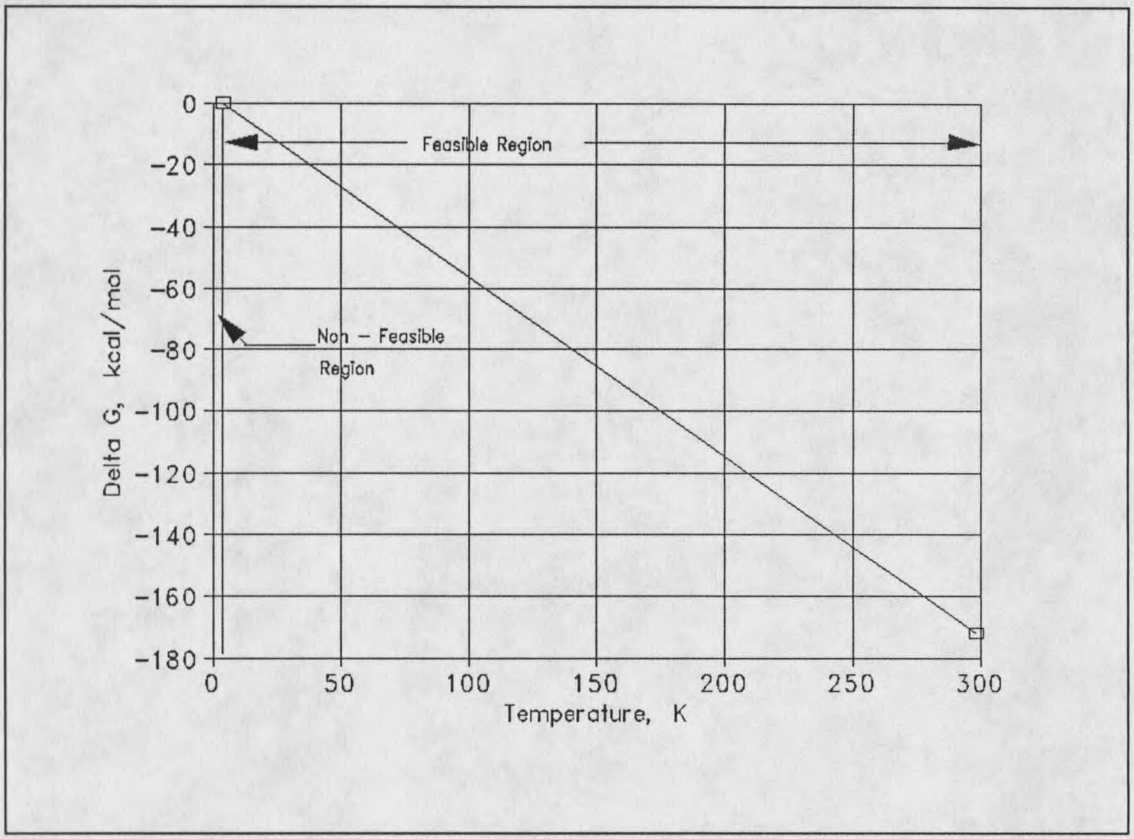

Figure 5, Delta G vs Temperature for Reducing Cu_2S to Cu_2O

A comparison of Figures 4 and 5 indicates that the reduction to Cu_2O is more thermodynamically feasible than the reduction to Cu because the ΔG is more negative for all temperatures in the $Cu_2S \text{ ---> } Cu_2O$ case. However, if the reaction conditions favor the Cu_2S ---> Cu reaction, it could happen. Notice that the Cu_2O reduction requires three oxygens but the Cu reduction only requires two oxygens. If oxygen is limited in the reaction atmosphere, the reduction to Cu would probably be favored.

Thermodynamics of Iron Reduction

The iron ore under consideration for this project is primarily Fe_3O_4, not the traditional Fe_2O_3 because this is what is available in Montana mines which are close to Billings. For this particular ore, the reaction in question is:

$$Fe_3O_{4(s)} + 2C_{(s)} \text{ ---> } 3Fe_{(s)} + 2CO_{2(g)}$$

The thermodynamic properties of these iron compounds are listed in the Handbook of Chemistry and Physics: [17]

Table 5. Thermodynamic Properties of Some Iron Compounds

Compound	Entropy cal/deg*mol	Gibbs Standard Energy kcal/mol	Standard Enthalpy kcal/mol
Fe_3O_4	35.0	-242.7	-267.3
C	1.372	0	0
Fe	6.52	0	0
CO_2	51.06	-94.254	-93.963

The following thermodynamic properties are calculated for

$$Fe_3O_{4(s)} + 2C_{(s)} \text{ ---> } 3Fe_{(s)} + 2CO_{2(g)}$$

using the methods outlined above:

Heat of Reaction (ΔH^f_{298}).............+79.374 kcal/mol

Gibbs Energy of Reaction (ΔG^f_{298}).....+54.192 kcal/mol

Temp. of Neutral Equilibrium ($T_{N.E.}$)...946 K

The reaction is endothermic. In addition, since ΔG^f_{298} is positive, this particular reaction is only feasible above 946 K, the temperature of neutral equilibrium, as shown in Figure 6, Delta G vs Temperature for Iron Reduction:

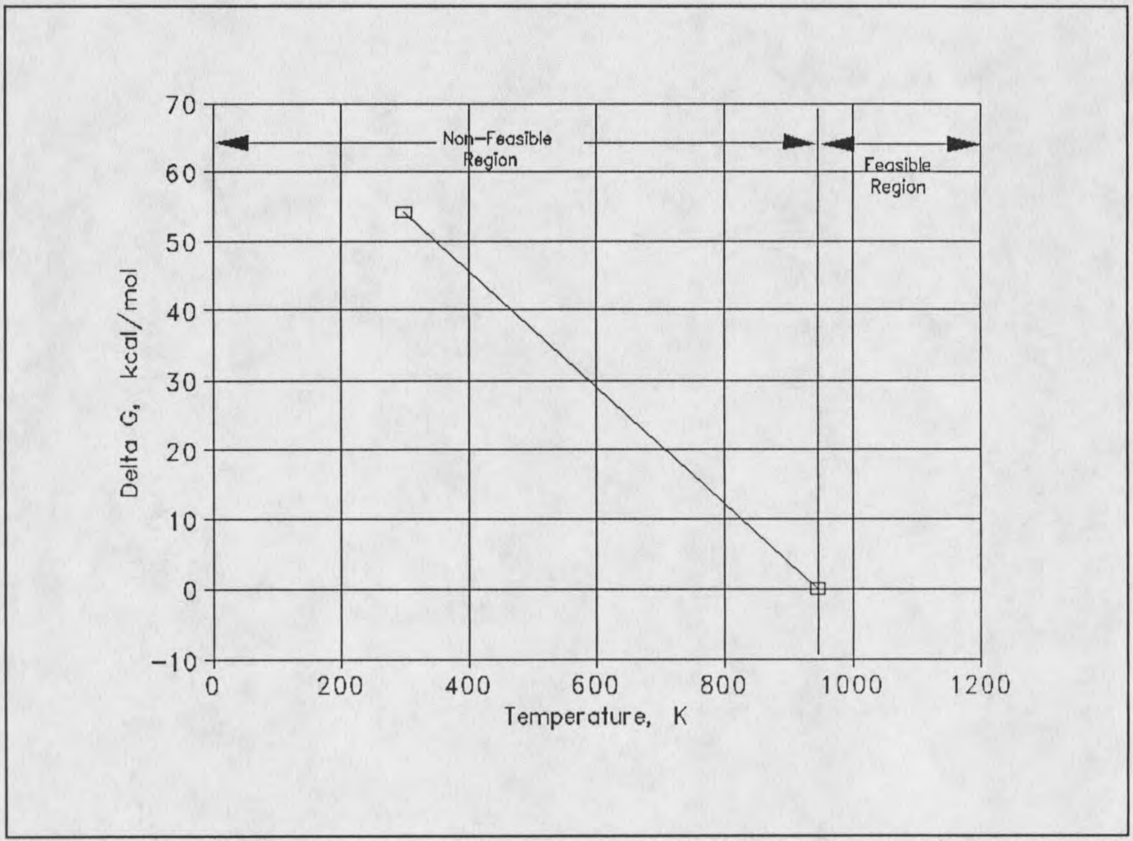

Figure 6, Delta G vs Temperature for Iron Reduction

Thermodynamics of Lead Reduction

The lead reaction in question is a combination of the reactions mentioned in the **BACKGROUND:**

$$PbS + C + 2O_2 \text{ ---> } Pb + SO_2 + CO_2$$

The thermodynamic properties of these lead compounds are listed in the Handbook of Chemistry and Physics: [18]

Table 6. Thermodynamic Properties of Some Lead Compounds

Compound	Entropy cal/deg*mol	Gibbs Standard Energy kcal/mol	Standard Enthalpy kcal/mol
PbS	21.8	-23.6	-24.0
C	1.372	0	0
O_2	49.003	0	0
Pb	15.49	0	0
SO_2	59.30	-71.748	-70.944
CO_2	51.06	-94.254	-93.963

The following thermodynamic properties are calculated for

$$PbS + C + 2O_2 \text{ ---> } Pb + SO_2 + CO_2$$

using the methods outlined above:

Heat of Reaction (ΔH^f_{298})..............-140.907 kcal/mol

Gibbs Energy of Reaction (ΔG^f_{298}).....-142.402 kcal/mol

Temp. of Neutral Equilibrium ($T_{N.E.}$)..-30,159 K

Once again, the reaction is very exothermic. The temperature of neutral equilibrium is below 0 K, absolute zero, so it is only hypothetical. However, the ΔG vs T line slopes downward from $\Delta G = 0$ on, so the reaction is feasible for all real temperatures. The ΔG vs T line is shown in Figure 7, Delta G vs Temperature for Lead Reduction:

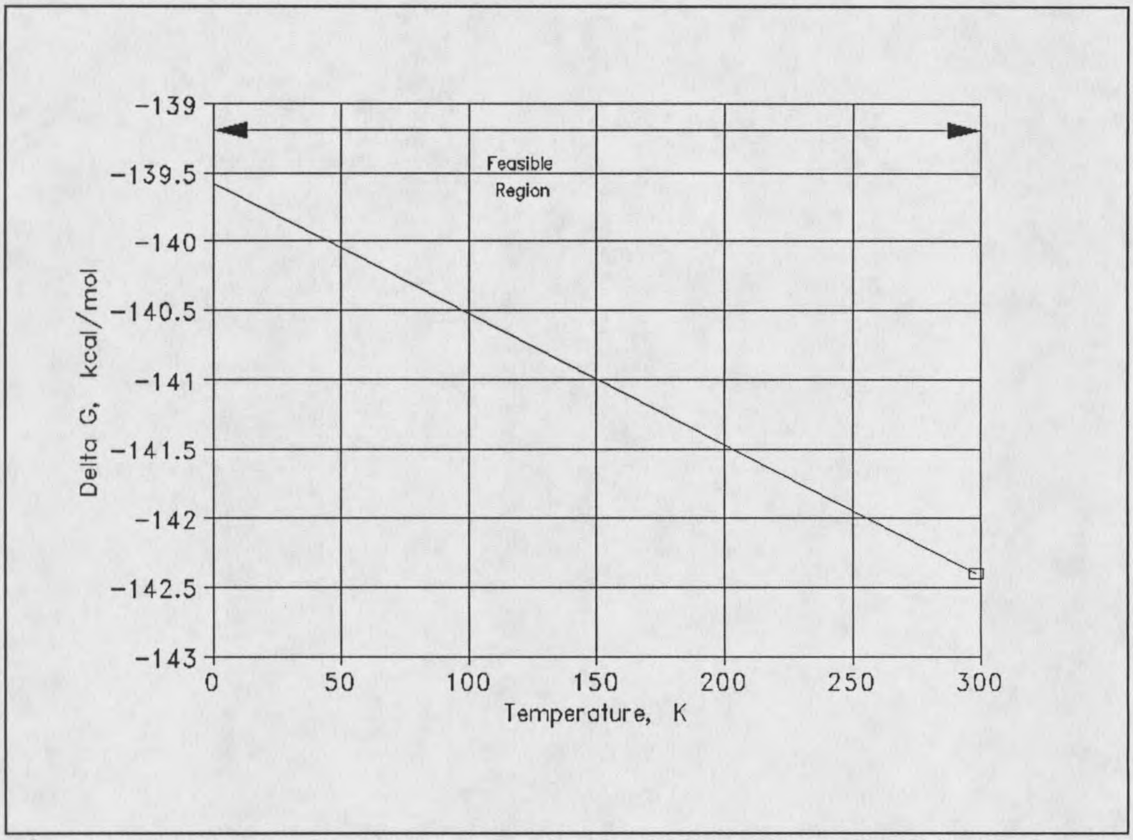

Figure 7, Delta G vs Temperature for Lead Reduction

RESEARCH OBJECTIVES

The primary objective of this research is to find a use or uses for high sulfur petroleum coke. To this end, research was conducted on molybdenum, copper, iron, and lead ores.

The objective of the molybdenum research is to find a use for high sulfur petroleum coke in the molybdenum processing industry. This is done by determining if molybdenite, MoS_2, can be converted to MoO_2 using the high sulfur petroleum coke as a reagent. This is an attractive area of research because most molybdenum used in steel making is currently obtained by the conversion of molybdenite to MoO_3 by roasting the MoS_2 in a kiln at about 1100 °F. If the ore could be converted to MoO_2 at 500 °F by using coke as a reagent, the molybdenum processing companies would probably save energy. In addition to the energy savings, the processing companies could save shipping charges because MoO_2 contains 11% more molybdenum per pound than MoO_3.

The objective of the copper research is to find a use for high sulfur petroleum coke in the copper industry. The experimental approach is to determine if copper ore concentrate, Cu_2S, can be converted to elemental copper at about 700°C using high sulfur petroleum coke as a reagent. This objective was chosen because the current industrial process requires a furnace temperature of about 1400°C and a silica reagent. Producing copper at a 700°C lower temperature would probably result in energy savings and therefore a market for the high sulfur petroleum coke.

The objective of the iron research is to find a use for the petroleum coke in the iron smelting industry. The possible use is substituting high sulfur petroleum coke for coke obtained from coal in the iron ore smelting process. Regular coke costs about $70 a ton plus shipping; high sulfur petroleum coke would probably only cost the freight to ship it. The reason for this is that high sulfur petroleum coke has to much sulfur to be used in traditional petroleum coke applications. With this in mind, an iron smelter would save a lot if the substitution is successful and the cost of petroleum coke remains less than regular coke.

Similarly, the objective of the lead research is to determine if high sulfur petroleum coke can be substituted for regular coke in the initial ore roasting process. The economic incentive is the same as in the iron case.

MOLYBDENUM RESEARCH

Molybdenum Experiments

Recall that the purpose of this experiment is to find a use for high sulfur petroleum coke in the molybdenum industry and that using the coke a reagent to convert MoS_2 to MoO_2 is the specific area of interest. The experiment is graphically depicted in Figure 8, Molybdenum Experimental Procedure. The coke was ground to a fine powder in a ball mill before use. After grinding, a known ratio of coke to molybdenum ore is cooked in a crucible for about 38 minutes. As the mixture cooked, a white gas was evolved, probably SO_3. The mixture turned from black to a lead gray, and yellow crystals formed a thin crust on the top of the mixture and on the sides of the crucible. The yellow crystals turned white after cooling.

The ratio calculations considered coke as 94% carbon 6% sulfur. The experimental ratios were 4:1 moles carbon to moles molybdenum, 8:1 moles carbon to moles molybdenum, and 16:1 moles carbon to moles molybdenum. It was assumed that burning the coke and ore resulted in a mixture of unconverted ore (MoS_2), MoO_2, and MoO_3. This is verified in Molybdenum Results and Discussion. The white crystals on the sides of the crucible were assumed to be MoO_3 since it is the

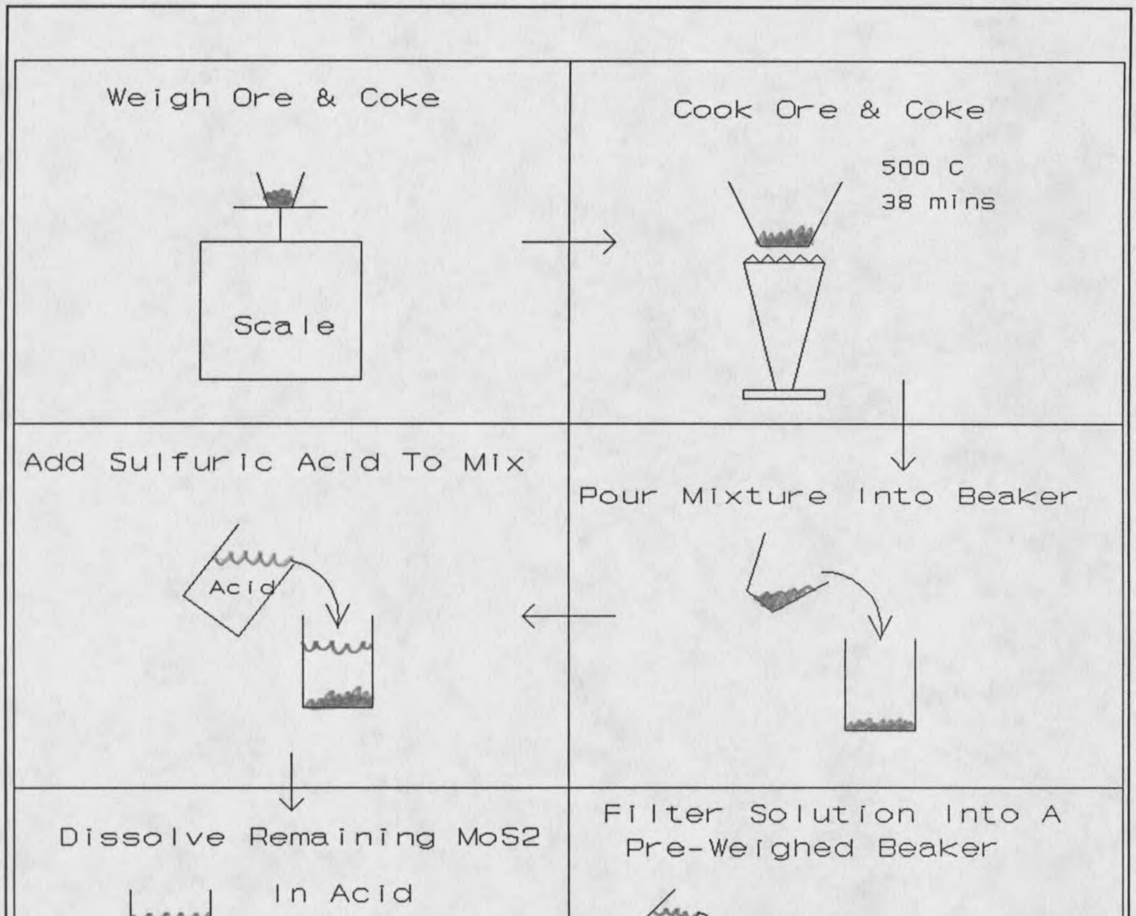

Figure 8, Molybdenum Experimental Procedure

most probable solid molybdenum compound which can be both yellow or white in crystalline form. [19]

After burning, the mixture was cooled and then leached with sulfuric acid to remove any MoO_3, MoS_2, MoS_4, and Mo that may have been in the mixture while leaving MoO_2. [20] [21] [22] [23] The leaching involved heating the mixture in a beaker with various concentrations of sulfuric acid for about 30 minutes. Different concentrations of H_2SO_4 were tried to determine if acid concentration had an effect on the leaching process.

The compound(s) that dissolved in the sulfuric acid were assumed to be primarily unconverted MoS_2. It is unlikely that MoS_4 or Mo were created by roasting MoS_2 in air, but this assumption is noted. To determine yield, the sulfuric acid was evaporated to dryness in a pre-weighed beaker, see Figure 8. The pre-weighed beaker was weighed after the sulfuric acid had evaporated to determine the amount of MoS_2 that did not convert to MoO_2, and the yield was calculated.

Molybdenum Results and Discussion

A problem with the procedure was determining if all the unconverted MoS_2 had been dissolved in that particular acid concentration, or if a more concentrated sulfuric acid solution was necessary. To determine this, three samples at

20, 40, 60, and 70 weight% H_2SO_4 were tested. This was done for the 4:1, 8:1, and 16:1 Carbon:Mo molar ratios, for a total of 36 tests. The averages of each three-run phase are graphically depicted below in Figure 9, Molybdenum Results:

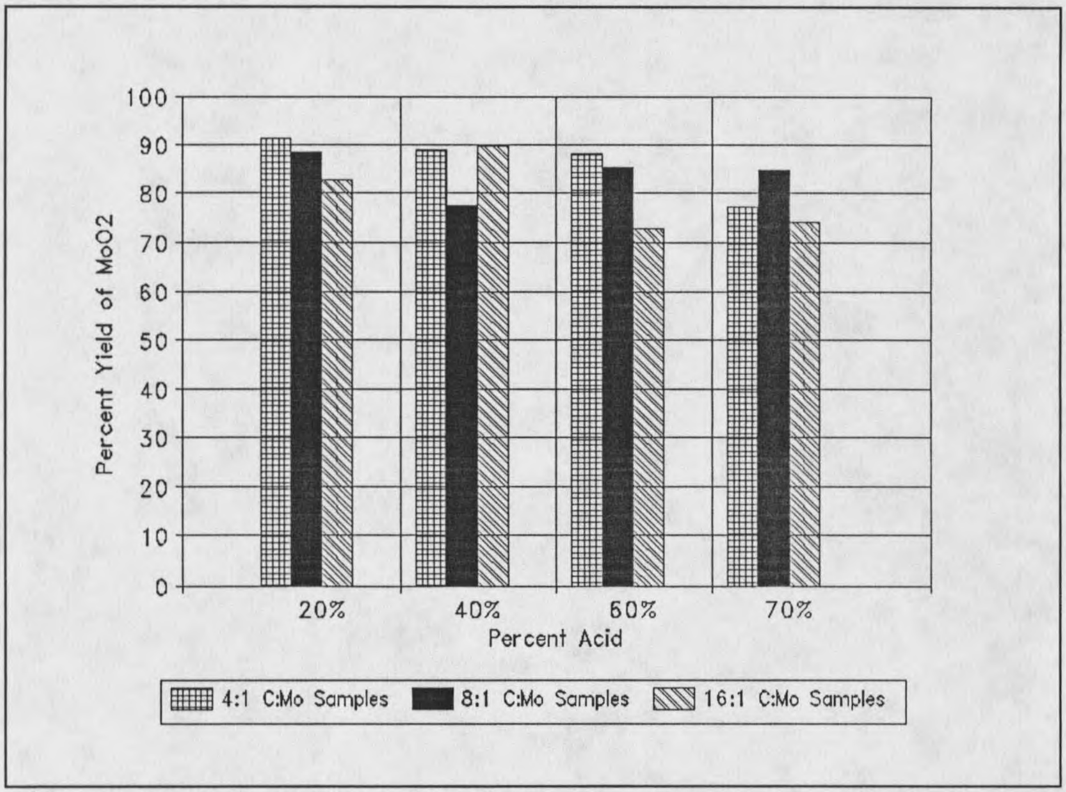

Figure 9, Molybdenum Results

As can be see, the acid concentration had no significant effect on yield. However, the molar ratio of carbon:Mo seems to have a significant effect. This is better demonstrated in Figure 10, Molybdenum Average Yields which shows the average yield for each carbon:Mo molar ratio.

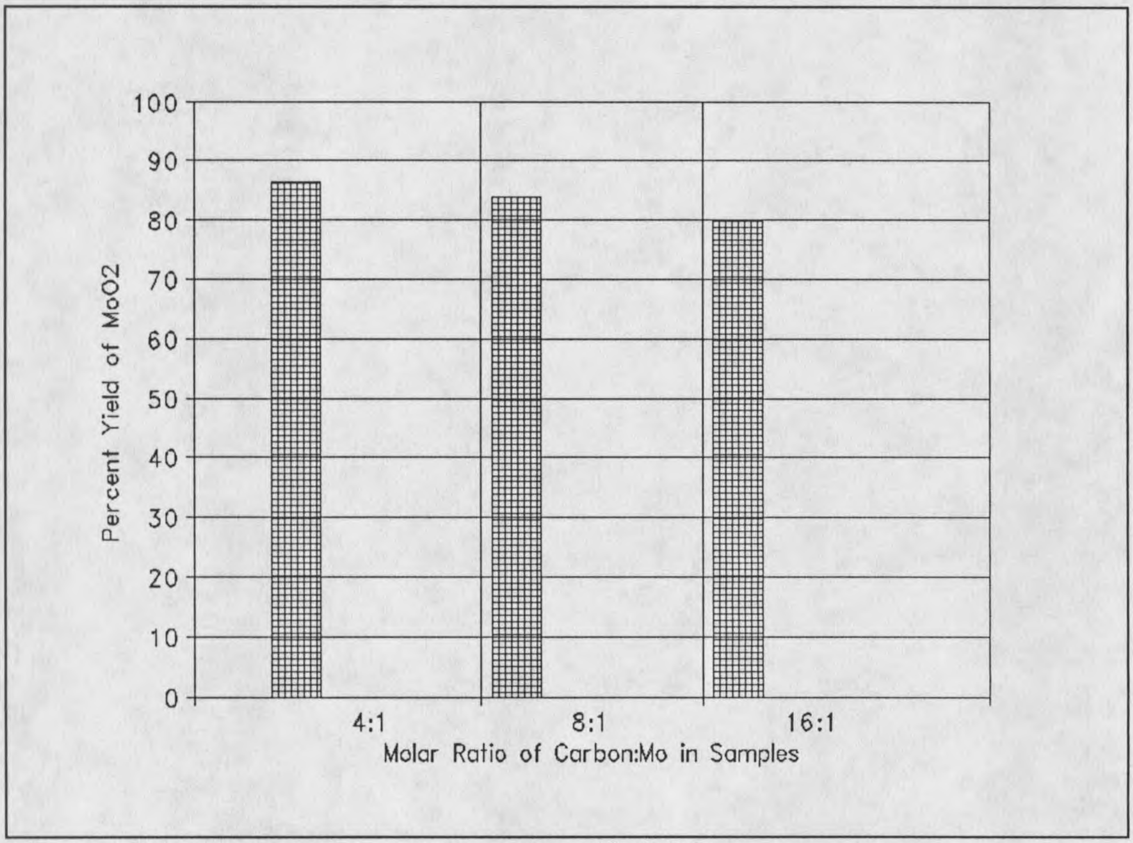

Figure 10, Molybdenum Average Yields

Excellent yields of MoO_2 were obtained, from 79%-85%. The yield of MoO_2 seems to get better as the ratio of Carbon to

Molybdenum decreased, however, a Population Standard Deviation was calculated on the Percent Yield in each category to determine data consistency. The results are shown on Figure 11, Molybdenum Data Consistency. The standard deviations ranged from 1.5% to 5.7%, so the data is quite consistent. However, the range of Percent Yields in Figure 10 is only 5%. This means that experimental error could be the cause of Percent Yield getting better as carbon:Mo ratio decreased, so the trend illustrated in Figure 10 should not be taken as absolute fact.

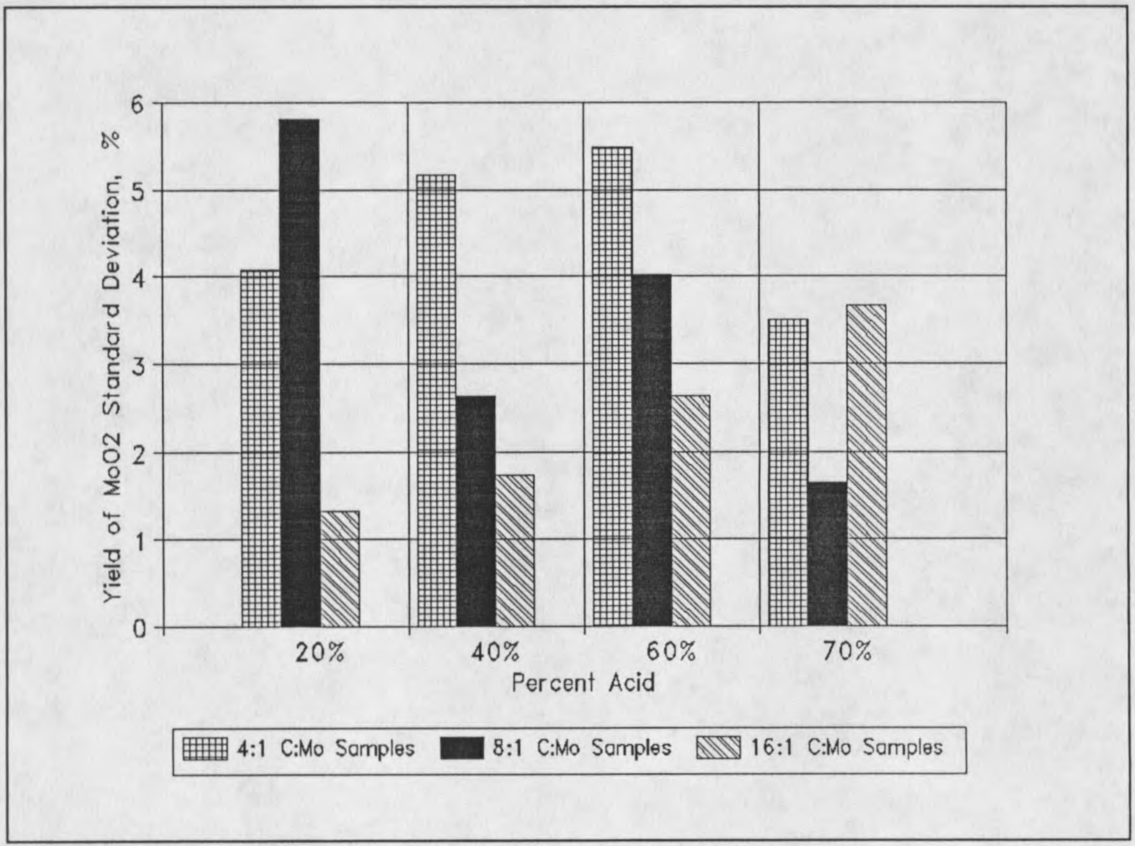

Figure 11, Molybdenum Data Consistency

The data is very consistent, but is it correct? Recall that the mixture in the crucible was assumed to be primarily MoO_2. Analytical tests were performed on the mixture to eliminate other possible molybdenum compounds. Table 7, Properties of Some Molybdenum Compounds is an exhaustive list of all known compounds that have any combination of molybdenum, carbon, sulfur, and oxygen.

Table 7. Properties of Some Molybdenum Compounds [24]

Compound	Color/form	Density, g/cm^3	Solubility
MoS_2	Black	4.80	H_2SO_4
MoO_2	Lead Grey	6.47	-------
MoO_3	White	4.692	H_2SO_4
MoC	Grey	8.20	-------
Mo_2C	White	8.9	-------
Mo_2S_3	Steel Grey	5.91	d h HNO_3
MoS_4	Brown Powder	----	h H_2SO_4
MoS_3	Black Plates	----	-------

MoS_3 can be eliminated from the list of possible compounds since no black plates were observed. MoS_2, MoO_3, and MoS_4 can be eliminated because they dissolve in sulfuric acid and would have been removed in the leaching process. To confirm that all the soluble compounds were completely removed, two leaches were performed. The weight of the solids was reduced by only 0.7% after the second leach. This was probably the weight of the fines that were entrained in the filter paper, so only one leach was necessary. Some of the mixture was place in 100+°C nitric acid to see if it would decompose, indicating the presence of Mo_2S_3. Nothing happened after 20 minutes so there was no Mo_2S_3 present. Only MoC and Mo_2C are left. Since both of these compounds are only slightly soluble in concentrated H_2SO_4, the MoO_2 was cooked until it turned to white crystals, probably MoO_3. The crystals were then dissolved in 50% H_2SO_4. If all the crystals dissolved, then no MoC or Mo_2C was present. All but 0.8% of the crystals dissolved easily in hot H_2SO_4. The compound that didn't dissolve was probably unreacted coke, so very little MoC and Mo_2C were present. These tests confirm that the mixture is, with high probability, MoS_2, MoO_2, and MoO_3 as was assumed in the experimental procedure.

Finally, a density test showed that the density of the mix was 6.0 g/cm^3. Since the mixture was a powder, it was firmly packed into a graduated cylinder. However, there probably was a small void fraction which would give a slightly lower density. In any case, the experimentally determined density of 6.0 g/cm^3 is consistent with a mixture of 80% MoO_2 and 20% MoS_2 which would have a calculated density of 6.136 g/cm^3. This provides more supporting evidence that the mixture was MoS_2, MoO_2, and MoO_3.

Experimental error could produce misleading data. There are several possible sources of error in this experiment. When filtering the solution, the filter paper would occasionally float, and some of the solid would get into the filtrate. On these occasions, the faulty test was disregarded.

Another source of error occurred when the solids were washed out of the beaker during filtration. The literature stated that MoS_2 was only soluble in hot H_2SO_4 [25]. Room temperature distilled water was used to wash the solids into the filter, thus lowering the temperature and diluting the solution. This did not have a major effect since very little wash water was used, so the temperature was only lowered 2 - 3°C.

The analytical tests show that no other known compounds that contain molybdenum, sulfur, oxygen, or carbon were present. However, without evidence confirming the presence of MoO_2, one can only say that there is a high probability that the data is both correct and consistent. Therefore, it is highly probably that high sulfur petroleum coke can be used to convert molybdenum ore (MoS_2) to MoO_2.

COPPER RESEARCH

Copper Experiments

Recall that the purpose of the copper research is to find a use for high sulfur petroleum coke in the copper industry, specifically, converting Cu_2S to copper at 700°C using the coke as a reagent. The copper concentrate that was used in the experiments came from Montana Resources in Butte. This concentrate contained about 26 wt% copper. The experiment began by combining 66 wt% concentrate and 33 wt% Coke in an experimental blast furnace (see Figure 12, Experimental Copper Blast Furnace):

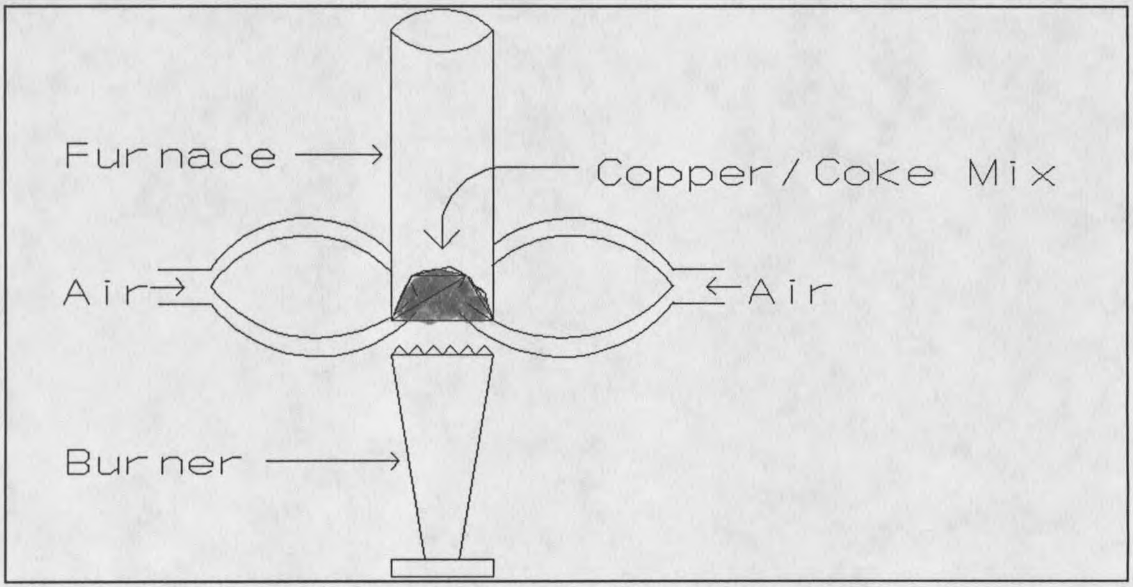

Figure 12, Experimental Copper Blast Furnace

About 2 standard cubic feet per hour of air was then blown into the "furnace" to provide the necessary oxygen for the copper reduction reaction. Very little air was blown into the furnace to try to maintain a reducing atmosphere. This was necessary to minimize the conversion of Cu_2S to CuO. Little, if any, CuO was produced as shown in the analytical test for pure copper in <u>Copper Results and Discussion</u>.

The furnace was heated to about 700°C. This temperature was measured on the outside of the furnace, so it only approximates the actual temperature of the reaction. Since the reaction is very exothermic, the actual temperature inside the furnace was probably much higher. Because of the design of the furnace, it was not possible to measure the temperature inside it. After heating for two hours, the powdered ore and coke had formed a lump of solid copper at the bottom of the furnace. The copper was separated from the ore and excess coke by water flotation. This procedure separates components on the basis of density--the lighter components float away, leaving the heavier ones. The table below shows the properties of the copper compounds in question.

Table 8. Properties of Some Copper Compounds [26]

Compound	Color	Density, g/cm^3
Cu_2S	Black	5.6
CuO	Black	6.3
Cu	Reddish	8.92

Since the unconverted ore, Cu_2S, and coke are much lighter than copper, the ore and coke would be washed away, leaving the copper.

The actual procedure is as follows: the lump of copper, along with the unconverted ore and excess coke was scraped out, and placed in a large beaker. A hose was placed with its end about 1/4" from the bottom of the beaker and water was forced into the beaker. The upward momentum of the water carried the lighter components (Cu_2S and coke) away, while leaving the solid copper lump on the bottom of the beaker. After the lump was washed, its color was reddish, and it felt like metallic copper. The blister copper was then dried and weighed, and the percent conversion was calculated.

Copper Results and Discussion

The data that was obtained from using the method outlined in **EXPERIMENTAL PROCEDURE** is shown Figure 13, Copper Percent Conversion vs Time in Blast Furnace:

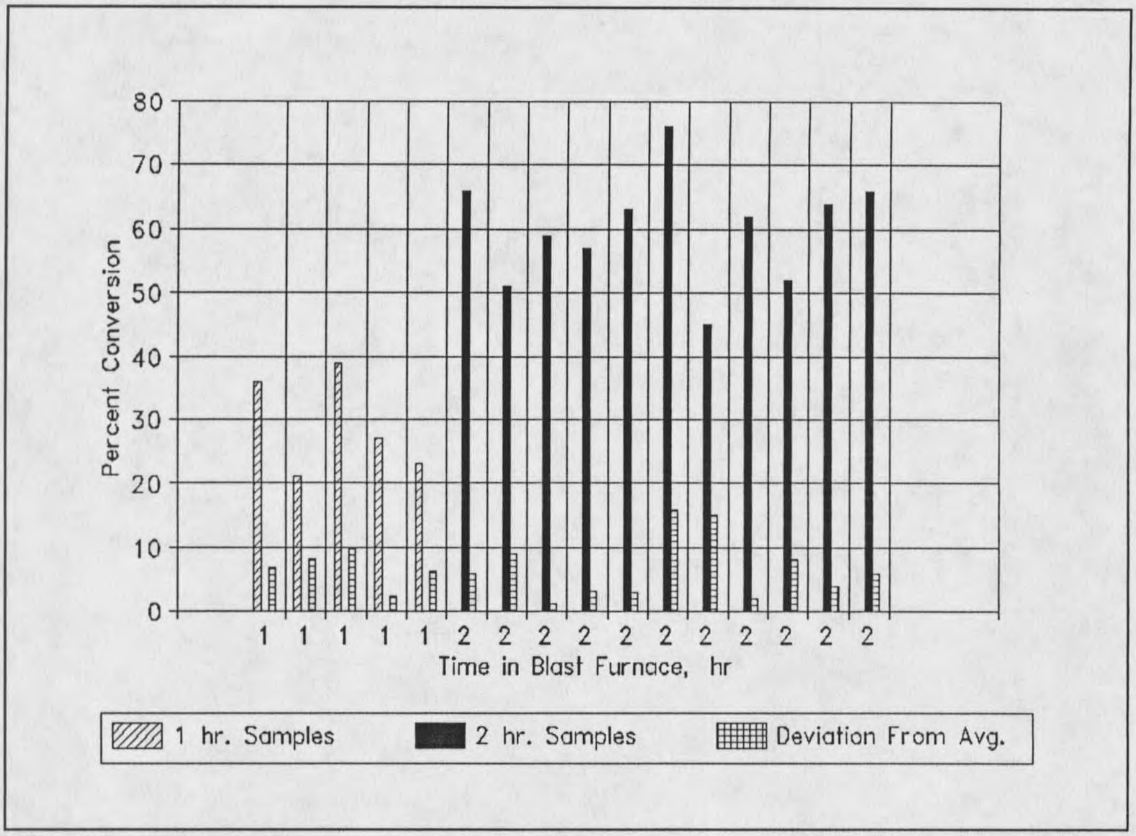

Figure 13, Copper Percent Conversion vs Time in Blast Furnace

The average conversion of Cu_2S to blister copper was 60%. If the reaction continued for one hour, the average conversion was reduced to about 30%. The data is very consistent, as shown by the Deviation from Avg. series.

Again, one must ask if the data is correct. The only assumption in the procedure was assuming the solid at the bottom of the experimental blast furnace was blister copper. The color of the lump was the same as copper, so it couldn't have been CuO which is black. However, to show that the lump was pure copper, it was analytically tested by the following procedure:

1. Dissolve the questionable copper in concentrated nitric acid
2. The acid will turn from clear to green
3. Boil the solution, evolving brown fumes
4. If the copper has 95% or better purity, the solution will turn from green to blue, indicating the presence of the Cu^{2++} anion.
5. If the copper does not have a 95% purity or better, the solution will remain green, the color of the Cu^{1+} anion. [27]

This procedure is represented by the following reaction:

$$Cu + NO_3^- + 2H^+ \underset{\Delta}{\rightarrow} Cu^{2++} + NO_2\uparrow + H_2O$$

The solid on the bottom of the blast furnace turned green when it was dissolved in nitric acid. The solution was heated and brown fumes (NO_2) were evolved as the solution turned from green to a bright blue. The bright blue color positively confirms the presence of the Cu^{2+} ion which will only form if the copper has a purity of 95% or better. If the copper does not have this purity, it will not form the Cu^{2+} ion, instead, it will remain as the green Cu^{1+} ion. Therefore, the lump in the bottom of the furnace was at least 95% pure copper, and the above assumption is valid.

The experimental error in this procedure is very minimal. While separating the unconverted ore from the copper, some copper could have been washed away. Since the copper came out of the furnace in large lumps, this error is negligible.

After evaluating the assumptions and experimental error, it has been shown that the data is consistent and correct so high sulfur petroleum coke can be used to reduce copper ore to copper.

IRON RESEARCH

Iron Experiments

The experiments began by combining various ratios of ore to coke in a porcelain crucible. Both the coke and ore were in a powdered form. The crucible was then heated with a Fisher Blast Burner. This burner resembles a regular bunsen burner, but it uses compressed air. Propane was used as the fuel and pure oxygen was added to the forced air stream in an effort to increase the flame temperature. The coke/ore mix was cooked in this manner for about one hour at 1350°C. If elemental iron was created, the ore would have become liquid iron. However, during the cook the ore changed color, from a dark black to dark red to grey, but never actually became a liquid. After cooling, it was observed that the ore/coke did not form a lump of iron, instead, the ore had changed color but was still in a powder form. The experiment was terminated at this point.

Iron Results and Discussion

The iron experiments did not go as planned. The solid iron ore, Fe_3O_4, remained in the powdered form, never entering the liquid phase. Instead, it underwent two color changes from black to dark red, then to lead grey. Since Fe_3O_4 is black, Fe_2O_3 is rust, and FeO is lead grey [28], it is assumed that the iron ore was reduced to FeO, but not all the way to elemental iron. Since iron melts at 1535°C and the blast burner only achieved 1350°C, it probably did not get hot enough to complete the reduction from Fe_3O_4 to Fe. Many different heat sources were used in an attempt to get the crucible hotter, but none were able to exceed the oxygen/propane blast burner temperature of 1350°C.

LEAD RESEARCH

Lead Experiments

The information in this section is pictorially presented in Figure 14, Lead Experimental Procedure. To begin, the Green Ore used in ASARCO's East Helena plant and powdered coke were weighed in specific ratios. Then the mix was cooked in a crucible above a bunsen burner at about 800°C for about 8 minutes. A constant air flow was directed through the mixture while it was stirred continuously. During this time, the ore reacted vigorously, evolving much white gas (SO_3) and forming little liquid spheres of metal. Recall that the green ore contains lead, copper, arsenic, and antimony sulfides. All of the sulfides except lead are in small concentrations, but they can still introduce experimental error. Because of this, the unreacted PbS as well as the copper sulfide impurity were dissolved in hot sulfuric acid. [29] These compounds had to be removed from the mixture because both PbS and the copper sulfide are soluble in nitric acid, and would have produced experimental error later in the procedure. [30] The hot sulfuric acid did not dissolve either the arsenic or antimony sulfides. However, these compounds don't have to be removed because they won't dissolve in any acid, so they won't cause

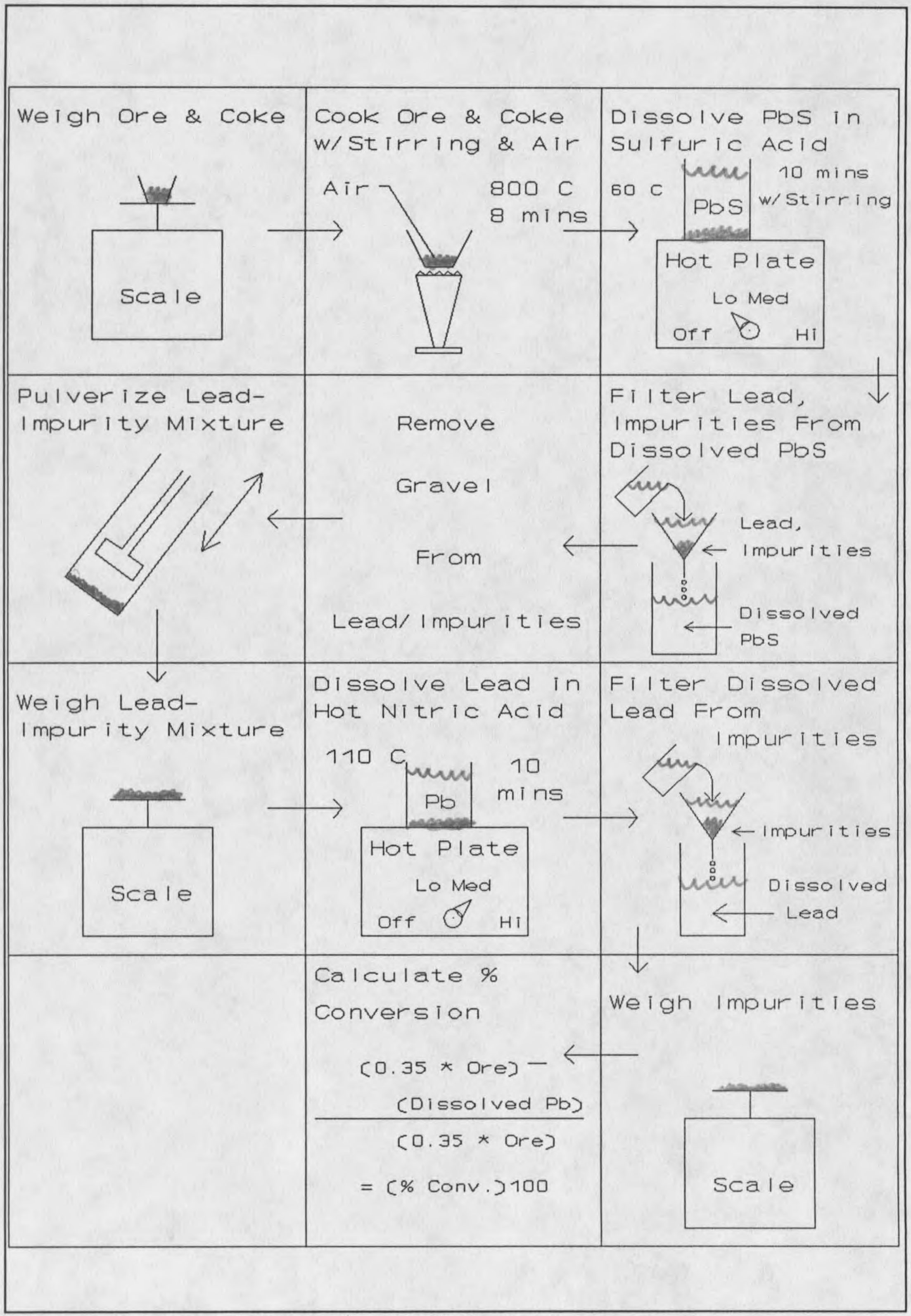

Figure 14, Lead Experimental Procedure

experimental error later in the procedure. [31] The dissolved PbS and Cu_2S were then filtered from the lead/impurities mixture and the mixture was dried. The green ore contained some 1/8" pieces of gravel. The gravel was easily identified at this point because the sulfuric acid bleached them from grey to white. The pieces of gravel were removed from the mixture by hand. The gravel was not weighed because this information is not necessary to determine the percent conversion of lead ore to lead. The mix was then pulverized. After pulverization, the mix was weighed. The lead in the mixture was then dissolved in nitric acid, and filtered. The filtrate was dried and weighed, then by subtraction the amount of pure lead created in the initial cook could be calculated. Since the Green Ore contains 35 wt.% lead, the percent conversion from Green Ore to lead could then be calculated.

Lead Results and Discussion

Various ratios of coke/ore were tested. The 6:1 grams ore to grams coke ratio was best because the reaction went to lead in the least amount of time. Figure 15, Lead Conversion vs Weight Ratio of Ore to Coke, graphically shows the experimental results.

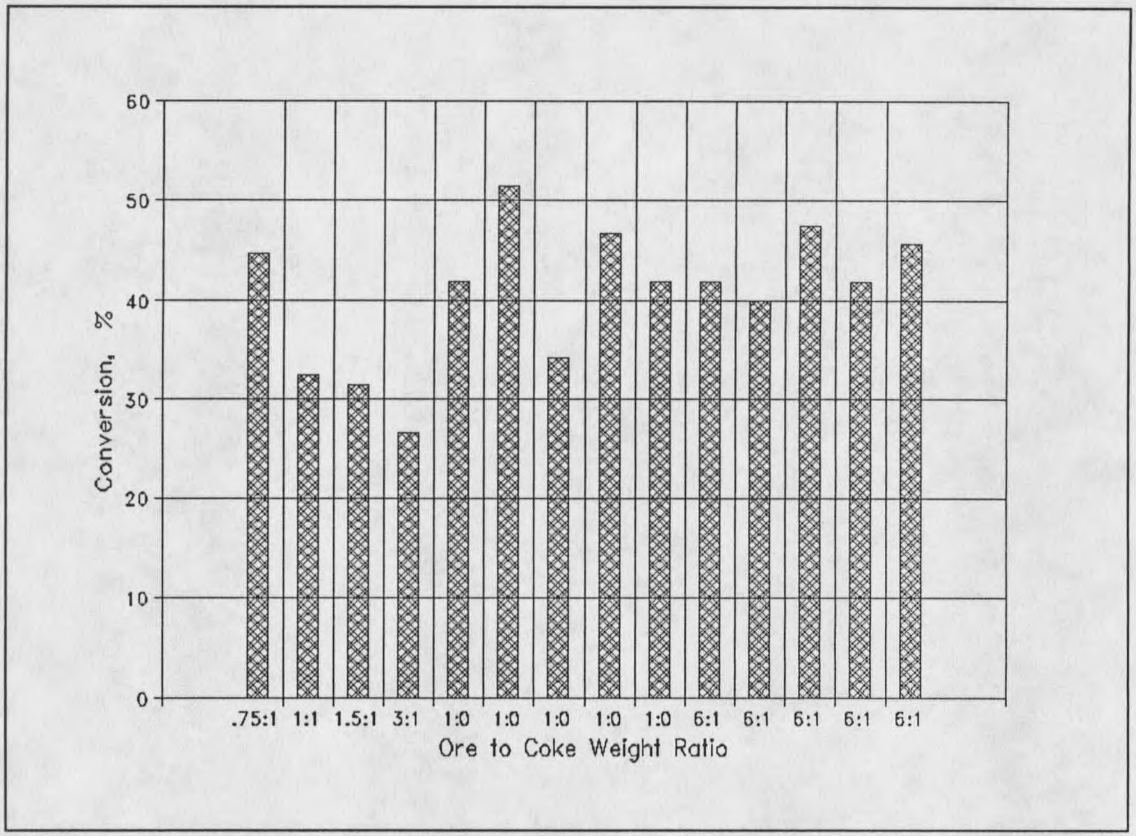

Figure 15, Lead Conversion vs Weight Ratio of Ore to Coke

The average conversion with the 6:1 weight ratio is 43%, with a 2.8% Standard Deviation.

It is possible to reduce lead ore (PbS) directly to lead without a reducing agent. N. N. Greenwood and A. Earnshaw state that "Alternatively, the carbon reduction can be replaced by reduction of the roasted ore with fresh galena: [32]"

$$2PbS + 3O_2 \xrightarrow[\Delta]{} 2PbO + 2SO_2\uparrow$$

$$PbS + 2PbO \xrightarrow[\Delta]{} 3Pb(liq) + SO_2\uparrow$$

The samples that were tried without coke for this research (1:0 grams ore to grams coke) appear to have a high conversion, see Figure 14. However, they took longer to react, 15+ minutes compared to 8 minutes.

Figure 14 shows that the data is consistent. However, is it correct? The first assumption made in the procedure is that the sulfuric acid dissolves all of the unreacted PbS, but none of the lead. To begin, PbS dissolves completely in sulfuric acid. [33] Since the sulfuric acid was used at a 50% concentration, and the dissolving process took place at 60°C, only a very negligible amount of lead would have been dissolved in the H_2SO_4. [34] The second assumption is that all the lead is dissolved in nitric acid. The Handbook of Chemistry and Physics states that lead is soluble in HNO_3. To insure that all the lead would dissolve, 150 grams of hot concentrated HNO_3 was added to a maximum of 1.05 grams lead. [35]

There is only one source of experimental error in this procedure. When filtering the solutions, the filter paper would occasionally float, and some of the solid would get into the filtrate. On these occasions, I would disregard the faulty test and start over from the beginning of the procedure, so the amount of experimental error is negligible.

Since there is little experimental error, and no obviously bad assumptions, the data appears to be correct and consistent. However, since the mix was never analytically tested to confirm the presence of lead, one can only say that it is highly probable that lead was created. This is acceptable because the intent of the lead research is to see if high sulfur petroleum coke can be used in any capacity in the lead refining industry.

SUMMARY AND CONCLUSIONS

Through carefully selected and conducted experiments, it was found that:

1. It is highly probable that high sulfur petroleum coke can be used to convert molybdenite to MoO_2 because 83% of molybdenite, MoS_2, was oxidized to MoO_2 by combining 0.660 grams high sulfur petroleum coke with one gram of MoS_2 and roasting in air at 500°C for 38 minutes.

2. High sulfur petroleum coke can be used to reduce copper concentrate to copper because 60% of the Cu_2S in copper concentrate can be converted to blister copper. The procedure is to mix 66 wt% concentrate with 34 wt% high sulfur petroleum coke and roast the mixture in a blast furnace at 700°C for two hours.

3. Iron ore, Fe_3O_4, cannot be converted to elemental iron by combining it with high sulfur petroleum coke and roasting in air at 1350°C. Instead, it is reduced to FeO.

4. It is highly probable that high sulfur petroleum coke can be substituted for regular coke to reduce lead ore to lead because 43% of the PbS in lead ore was converted to elemental lead by combining 17 wt% high sulfur petroleum coke with 83 wt% ore and roasting in air at 800°C for 8 minutes while blowing air through the mixture.

Three of the four areas of research show promise for uses for high sulfur petroleum coke, a substance that was previously thought of as an unwanted waste product. This research should be very useful to any refinery that produces fluid petroleum coke with a sulfur content over 3%, high sulfur petroleum coke.

RECOMMENDATIONS FOR FUTURE RESEARCH

This research is only the first step in the process to use high sulfur petroleum coke in the metals refining industries. Future research should include finding and employing an analytical test to absolutely confirm the presence of MoO_2 and elemental lead. Since the iron experiments at 1350°C were not successful, future experiments should be conducted at 1600°C, above the melting point of iron. Other than that, there is little research that can be performed in a lab. The experiments, when run on a lab scale, were usually successful. However, the coke needs to be proven on an industrial scale before total success can be claimed.

More specifically, the scale up in the molybdenum industry should include mixing the MoS_2 with powdered coke and then roasting at a lower temperature to obtain MoO_2 instead of MoO_3. The copper industry should try adding coke to the ore/silica mix in the blast furnace. The experiments in this thesis indicate that adding the coke would allow the conversion to proceed at a lower temperature. Finally, the lead industry could prove the utility of petroleum coke by combining it with the lead ore in the initial roast. If the petroleum coke works as well in the actual industry as it worked in the lab, it could be substituted for the regular coke breeze the lead industry is currently using.

REFERENCES CITED

1. Austin, G., Shreve's Chemical Process Industries, 5th ed., McGraw-Hill, New York, 1984, pp. 722-742.

2. Berg, L., and L. Ulrich, U.S. Patent Application 00/000,000, filed on May 1, 1991, p. 3.

3. Ibid., p. 4.

4. Suiter, R.C., Silicon Carbide Synthesis Using High-Sulfur Petroleum Fluid Coke and Montana Silicon, Ph.D. Thesis in Chemical Engineering, Montana State College, Bozeman, Montana, June 1965.

5. N. N. Greenwood and A. Earnshaw, Chemistry of the Elements, 1st ed., Pergamon Press Inc., New York, 1984, p. 1168.

6. Berg, L., U.S. Patent Application 4,687,647, January 1, 1991.

7. Ibid., p. 2.

8. N. N. Greenwood and A. Earnshaw, op. cit., pp. 1365-1366.

9. Ibid., pp. 1243-1244.

10. Ibid., pp. 429-430.

11. McIntyre, T.F., Process Engineer, ASARCO Lead Refinery, Letter to L. Berg, December 7, 1990.

12. Weast, R.C., M.J. Astle, and W.H. Beyer, CRC Handbook of Chemistry and Physics, 65th ed., CRC Press, Boca Raton, Florida, 1984, pp. B-116 to B-117.

13. Felder, R., and R.W. Rousseau, Elementary Principles of Chemical Processes, 2nd ed., John Wiley and Sons, New York, 1986, p. 422.

14. Dr. Frank P. McCandless, Ph.D., Chemical Engineer, private communication, May 8, 1991.

15. Smith, J.M., and H.C. Van Ness, Introduction to Chemical Engineering Thermodynamics, 4th ed., McGraw-Hill, New York, 1987, p. 504.

16. Weast, R.C., M.J. Astle, and W.H. Beyer, op. cit., pp. B-92 to B-94.

17. Ibid., p. B-104.

18. Ibid., pp. B-105 to B-107.

19. Ibid., p. B-116.

20. Ibid., pp. B-116 to B-117.

21. Parker, G.A., Analytical Chemistry of Molybdenum, Springer-Verlag, Berlin, Germany, 1983, pp. 8-32.

22. Browning, P.E., Introduction to the Rarer Elements, 2nd ed., John Wiley and Sons, New York, 1908, pp. 125-131.

23. Samsonov, G., The Oxide Handbook, 2nd ed., IFI/Plenum Data Company, New York, 1982, pp. 329-330.

24. Weast, R.C., M.J. Astle, and W.H. Beyer, op. cit., pp. B-116 to B-117.

25. Ibid., p. B-117.

26. Ibid., pp. B-92 to B-94.

27. Dr. Kenneth Emerson, Ph.D., Physical Chemist, private communication, June 25, 1990.

28. Weast, R.C., M.J. Astle, and W.H. Beyer, op. cit., pp. B-105 to B-107.

29. Ibid., pp. B-94 to B-107.

30. Ibid., p. B-107.

31. Ibid., pp. B-74 to B-75.

32. N. N. Greenwood and A. Earnshaw, op. cit., p. 430.

33. Weast, R.C., M.J. Astle, and W.H. Beyer, op. cit., p. B-107.

34. Hofmann, W., Lead and Lead Alloys Properties and Technology, 2nd ed., Springer-Verlag, New York, 1970, pp. 268-275.

35. Weast, R.C., M.J. Astle, and W.H. Beyer, op. cit., p. B-107.

APPENDICES

APPENDIX A

MOLYBDENUM EXPERIMENTAL DATA

Table 9. 4:1 Molybdenum:Coke Samples

4:1 Samples 20% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
2.85	70.34	70.43	0.09	96.84	91.23	4.06
2.85	69.05	69.35	0.30	89.47		
2.85	111.10	111.46	0.36	87.37		

4:1 Samples 40% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
2.85	69.01	69.53	0.52	81.75	88.77	5.16
2.85	67.28	67.45	0.17	94.04		
2.85	69.58	69.85	0.27	90.53		

4:1 Samples 60% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
2.85	68.90	69.06	0.16	94.39	88.19	5.48
2.85	67.28	67.59	0.31	89.12		
2.85	69.50	70.04	0.54	81.05		

4:1 Samples 70% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
2.85	69.00	69.78	0.78	72.63	77.31	3.50
2.85	67.26	67.88	0.62	78.25		
2.85	69.48	70.02	0.54	81.05		

Table 10. 8:1 Molybdenum:Coke Samples

8:1 Samples 20% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
1.43	69.01	69.24	0.23	83.86	88.30	5.80
1.43	67.27	67.49	0.22	84.56		
1.43	68.34	68.39	0.05	96.49		

8:1 Samples 40% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
1.43	68.32	68.60	0.28	80.35	77.54	2.63
1.43	70.35	70.66	0.31	78.25		
1.43	68.90	69.27	0.37	74.04		

8:1 Samples 60% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
1.43	69.66	69.82	0.16	88.77	85.26	4.01
1.43	70.33	70.51	0.18	87.37		
1.43	68.90	69.19	0.29	79.65		

8:1 Samples 70% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
1.43	67.15	67.35	0.20	85.96	84.80	1.65
1.43	67.46	67.71	0.25	82.46		
1.43	69.60	69.80	0.20	85.96		

Table 11. 16:1 Molybdenum:Coke Samples

16:1 Samples 20% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
0.72	68.30	68.43	0.13	81.82	82.75	1.32
0.72	70.30	70.41	0.11	84.62		
0.72	68.88	69.01	0.13	81.82		

16:1 Samples 40% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
0.72	67.15	67.22	0.07	90.21	89.74	1.74
0.72	67.45	67.54	0.09	87.41		
0.72	69.59	69.65	0.06	91.61		

16:1 Samples 60% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
0.72	68.33	68.51	0.18	74.83	72.96	2.64
0.72	70.34	70.56	0.22	69.23		
0.72	68.90	69.08	0.18	74.83		

16:1 Samples 70% Acid

Starting MoS2 Weight (g)	Beaker Before Filtrate (g)	Beaker After Dried Filtrate (g)	Unreacted MoS2 Weight (g)	% Yield MoO2	Average Yield (%)	Population Standard Deviation (%)
0.72	68.31	68.47	0.16	77.62	74.36	3.67
0.72	70.31	70.53	0.22	69.23		
0.72	67.43	67.60	0.17	76.22		

APPENDIX B

COPPER EXPERIMENTAL DATA

Table 12. Copper Experimental Data

Time in Blast Furnace (min)	Starting Copper Ore Weight (g)	Starting Copper Weight (g)	Starting Coke Weight (g)	After Cook Cu Weight (g)	Copper Yield (%)
120	50	13	25	8.6	65.8
120	50	13	25	6.6	50.8
120	50	13	25	7.7	59.5
120	50	13	25	7.5	57.3
120	50	13	25	8.2	62.7
120	50	13	25	9.9	76.2
120	50	13	25	5.9	45.1
120	50	13	25	8.1	62.5
120	50	13	25	6.2	51.6
120	50	13	25	8.4	64.3
120	50	13	25	8.6	66.2
120	50	13	25	4.6	35.4
60	50	13	25	4.7	36.0
60	50	13	25	2.8	21.5
60	50	13	25	5.1	39.4
60	50	13	25	3.5	26.9
60	50	13	25	3.1	23.5

APPENDIX C

LEAD EXPERIMENTAL DATA

Table 13. Lead Experimental Data

Green Ore (g)	Coke (g)	Ore:coke Ratio	Lead in Green Ore (35% of Green Ore, g)	Wt. After Gravel Removed, Sulfuric Acid Treatment, (g)	Wt. After Nitric Acid Treatment (g)	Lead in Sample (g)	% Conversion Green Ore to Lead, (%)
3.00	4.00	.75:1	1.05	1.39	0.92	0.47	44.76
3.00	3.00	1:1	1.05	0.90	0.56	0.34	32.38
3.00	2.00	1.5:1	1.05	1.15	0.82	0.33	31.43
3.00	1.00	3:1	1.05	0.84	0.56	0.28	26.67
3.00	0.00	1:0	1.05	1.50	1.06	0.44	41.90
3.00	0.00	1:0	1.05	1.90	1.36	0.54	51.43
3.00	0.00	1:0	1.05	1.90	1.54	0.36	34.29
3.00	0.00	1:0	1.05	1.85	1.36	0.49	46.67
3.00	0.00	1:0	1.05	1.70	1.26	0.44	41.90
3.00	0.50	6:1	1.05	1.35	0.91	0.44	41.90
3.00	0.50	6:1	1.05	1.28	0.86	0.42	40.00
3.00	0.50	6:1	1.05	1.26	0.76	0.50	47.62
3.00	0.50	6:1	1.05	1.35	0.91	0.44	41.90
3.00	0.50	6:1	1.05	1.35	0.87	0.48	45.71
							Standard Deviation of 17% Coke Samples: 2.80
							Average %Conv. of No Coke Samples: 43.24