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DIRECT REDUCTION OF IRON AND NICKEL SULPHIDES BY CALCIUM OXIDE AND CARBON MONOXIDE, WITH SUBSEQUENT RECOVERY OF ELEMENTAL SULPHUR

by

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ABSTRACT

A process is proposed for the direct reduction of nickel and iron sulphides, with the subsequent recovery of nickel and iron powder and elemental sulphur. The direct reduction step takes place at 830°C in the presence of CaO and CO. After separating the nickel and iron powder from the reaction product, either magnetically or by the carbonyl process, the resulting CaS is carbonated and recycled to the reduction roast. The H_2S off-gas is converted to elemental sulphur in a Claus reactor. The proposed process has the advantage that nickel and iron powder are recovered directly and that sulphur is recovered in the elemental form rather than being released as gaseous sulphur oxides.

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CONTENTS

FIGURES

TABLES

INTRODUCTION

A number of conventional pyrometallurgical processes used to recover metals from sulphide concentrates release large amounts of sulphur oxides to the atmosphere. As air pollution standards related to sulphur oxide emissions become more stringent many smelters are faced with either making expensive modifications to existing plants or adopting new processes which will meet these new standards. Consequently, a number of novel, non-polluting pyrometallurgical processes are currently under review or development.

This study is concerned with the development of a pyrometallurgical process which would recover the metals and elemental sulphur from sulphide concentrates while effectively eliminating sulphur oxide emissions. The process involves the direct reduction of sulphide concentrates in the presence of calcium oxide and carbon monoxide at 700-1000° C, with the formation of the respective metals, calcium sulphide, and carbon dioxide. After separation of the reduced metals and the calcium sulphide, the calcium sulphide is carbonated and recycled, while the hydrogen sulphide off-gas is converted to elemental sulphur.

PROCESS OUTLINE

A simplified flow-sheet for the proposed process is shown in Figure 1. The various steps of the process are described below.

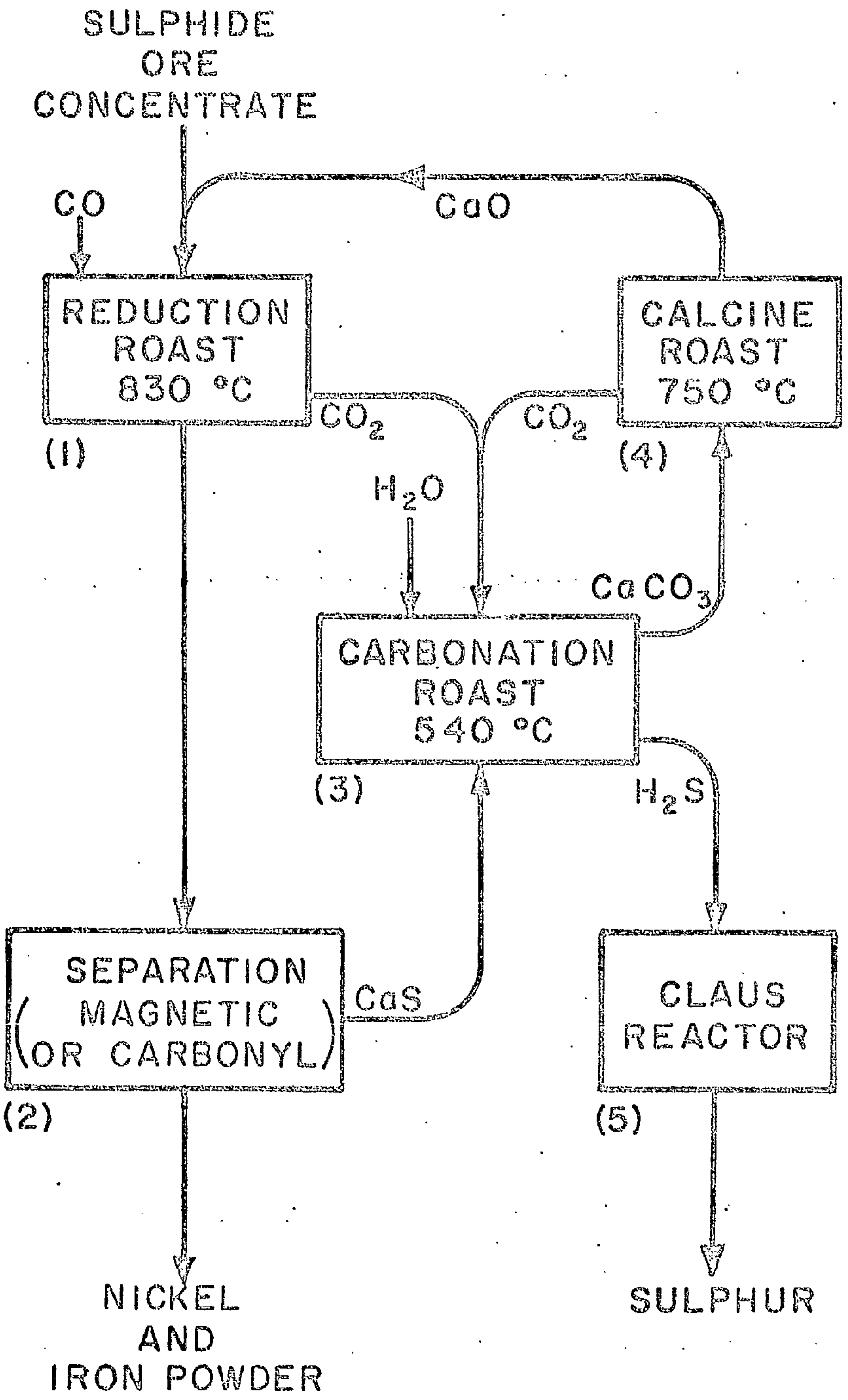

Figure 1: Flow sheet of direct reduction of nickel and iron sulphides and recovery of elemental sulphur.

Step 1: Direct Reduction of Sulphide Concentrates

The basic reactions involved in Step 1 are shown in the following equations:

$$MS_{(s)} + CaO_{(s)} + CO_{(g)} \rightarrow M_{(s)} + CaS_{(s)} + CO_{2(g)} \qquad [1]$$

$$MS_{(s)} + CaO_{(s)} + C_{(s)} \rightarrow M_{(s)} + CaS_{(s)} + CO_{(g)} \qquad [2]$$

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)} \qquad [3]$$

The reduction roast of the sulphide ore concentrates is done under an inert or reducing atmosphere to prevent oxidation of the metals and calcium sulphide. As shown by the thermochemical analysis (Appendix 1) of the above reactions, the reduction of a number of metal sulphides (except ZnS) in the presence of calcium oxide and carbon is favourable at temperatures above 700°C, whereas reduction in the presence of calcium oxide and carbon monoxide is favourable except for ZnS at all the temperatures considered.

The reduction of ferrous sulphide (FeS) by the interaction of CaO and carbon has been studied previously both as solid mixtures(1,2,3) and as constituents of molten iron(4). The reactions were found to proceed rapidly at temperatures above 800°C. Excess CaO helped drive the reaction to completion, whereas excess carbon had the opposite effect. Synthetic nickel sulphide (Ni_3S_2) was reduced rapidly in the presence of CaO and carbon at temperatures above 800°C, but the reaction did not go to completion(3). In the Waelz process, sulphide concentrates containing Zn, Pb, and Cd are mixed with CaO and carbon and heated to 1200°C to drive off metal oxide fumes which are further processed (5,6). Several empirical studies on the direct reduction of metal sulphides using mixtures of calcium or sodium carbonates and carbon (7,8,9) as reductants have been reported.

In this study, only the direct reduction of nickel and iron sulphides was considered because this allowed the magnetic and/or carbonyl separation of the reduced metals from the reaction products. The conditions necessary for the selective reduction of Ni_3S_2 in preference to FeS in the presence of CaO and CO are given in Appendix 1. The selective reduction of Ni_3S_2 is possible if certain ratios of P_{CO_2}/P_{CO} are maintained; this aspect was studied only briefly.

Step 2: Separation of the Reduced Metals from the Reaction Products

There are several dry and wet separation techniques which could be used to separate the reaction products. Wet separation techniques have the disadvantage that some of the reduced metal will oxidize during separation and that part of the calcium sulphide will undergo hydrolysis and oxidation and will liberate hydrogen sulphide.

The first dry separation technique tried in this study was a magnetic/density separation. This yields an iron-nickel powder and a light, non-magnetic residue consisting of calcium sulphide plus unreacted material.

The second dry separation technique used was the carbonyl separation of nickel from either the reaction products or the iron-nickel powder product of the magnetic/density separation.

The carbonyl separation of nickel at 50°C depends on the nickel being in an "activated" state, usually the result of reducing nickel oxide(10) with hydrogen.

Step 3: Conversion of Calcium Sulphide to Calcium Carbonate, with the Liberation of Hydrogen Sulphide

The basic reactions of Step 3 are shown in the following equations:

$$CaS_{(s)} + CO_2{}_{(g)} + H_2O_{(g)} \rightarrow CaCO_3{}_{(s)} + H_2S_{(g)} \qquad [4]$$

$$CaS_{(l)} + CO_2{}_{(g)} + H_2O_{(l)} \rightarrow CaCO_3{}_{(s)} + H_2S_{(g)} \qquad [5]$$

The reaction shown in Equation 4 represents the solid-state carbonation of calcium sulphide in the presence of moist carbon dioxide, whereas Equation 5 represents the aqueous carbonation of dissolved calcium sulphide by carbon dioxide. A thermochemical analysis (Appendix 1) of Equation 4 indicates that these reactions are favourable at temperatures below 700°C.

The aqueous carbonation of CaS has been proposed previously, but requires complex reactors(11-15). The solid-state carbonation of CaS at atmospheric pressure is also difficult, because the temperature at which the reaction reverses (700° to 750°C) limits any increase in reaction rate by an increase in temperature(16). However, recent studies have shown that the solid-state carbonation of calcium sulphide will proceed at a satisfactory rate when increased pressures of carbon dioxide and water vapour are used(17,18). Typical operation parameters are temperature between 530 and 540°C and 220 psia CO_2-steam pressure. With a stainless-steel reactor, conversion exceeded 90 % within six hours.

The solid-state carbonation step was chosen as the method for carbonating calcium sulphide. Even though it is necessary to use a pressurized reactor in this step, with its attendant engineering problems, operating problems should be less than with the aqueous carbonation process. Previous experience with the solid-state carbonation of sodium sulphide has shown that these reactions tend to be reasonably trouble-free(19,20).

Step 4: Calcination of Calcium Carbonate to Form Calcium Oxide

The calcination of $CaCO_3$ to form CaO is a common industrial process which usually takes place at approximately 780°C in a rotating kiln(21,2[illegible]). In the present process, the $CaCO_3$ from Step 3 can be either calcined to CaO prior to entry to the reduction roast furnace (Step 1) or added directly to the reduction roast furnace, with the calcination occurring below the reaction temperature. The liberated CO_2 gas, along with water vapour, is recycled to the carbonation roast autoclave (Step 3). It would be necessary to remove gangue and unreacted material from the recycled $CaCO_3$ at this point in order to prevent a build-up of waste material in the system. The alternative is to discard the calcium carbonate formed during the carbonation roast (Step 3), along with any unreacted concentrate, and to add either fresh $CaCO_3$ or CaO to the reduction roast furnace. However, there would likely be a pollution problem associated with the practice of discarding the used $CaCO_3$ due to the presence of small amounts of metal sulphides.

Step 5: Recovery of Elemental Sulphur from Hydrogen Sulphide Gas

The conversion of hydrogen sulphide gas to elemental sulphur is accomplished industrially by means of the Claus reaction(23). The technology for this process is well established, particularly in the natural gas industry.

EXPERIMENTAL

Materials

Both synthetic and natural iron and nickel sulphides were used in the reduction experiments. All materials were minus 200 mesh. Chemical analyses of the sulphides are listed in Table 1. Reagent-grade calcium oxide, calcium carbonate powders, and lamp black were used to prepare the reduction mixtures. Purified calcium sulphide, previously heated to 1000°C in nitrogen, was used for the carbonation experiments. Purified nickel powder was used in the carbonyl experiments. High-purity nitrogen gas (99.996 %) was used to provide an inert atmosphere for the experiments. The other gases used were standard cylinder grades.

Apparatus and Procedure

The kinetics of the reduction, carbonyl separation, and carbonation reactions were followed by measuring the weight change of the reaction mixtures as a function of time, using a Cahn electrobalance(24). One-gram powdered samples were placed in size-0000 porcelain crucibles and heated at 5°/min to the reaction temperature. In the case of the reduction mixtures containing carbon, some reaction occurred before the process temperature was reached, so this minor initial reaction was compensated for by extrapolation of the reaction curves back to zero weight loss.

TABLE 1

Chemical Analysis of Metal Sulphides

ND = not determined

No.	Metal Sulphides	Component (wt %)							
		Fe	Ni	S	SO_4/S	Cu	Ca	Mg	SiO_2
1.	Pyrrhotite Concentrate								
	A. Falconbridge	55.6	1.09	35.5	0.53	0.115	0.25	0.35	1.62
	B. Cominco	46.3	0.006	30.6	1.40	0.033	0.17	0.31	ND
	C. Falconbridge #2	54.3	1.08	34.2	1.33	0.100	0.086	0.23	ND
2.	Pyrite Crystal	46.4	--	53.2	ND	--	ND	ND	ND
3.	Pyrite Concentrate	42.6	0.007	44.8	2.79	0.015	0.12	0.42	ND
4.	Synthetic Ni_3S_2	ND	72.9	26.2	ND	ND	ND	ND	ND
5.	Pentlandite Concentrate (Texmont)	18.6	16.7	13.7	0.83	0.19	0.29	10.7	ND

In the other cases, the initial reaction occurred when the flow of reactive gas over the samples was started. Temperatures were measured by a thermocouple located within 1 cm of the sample. The weight changes and temperatures were recorded on a strip chart and a digital print-out. The resulting weight changes were used to calculate the percentage reaction for comparison with the total theoretical weight change in the respective reactions.

Differential thermal analysis of the reactions were done in a Fisher DTA controlled-atmosphere system at heating rates of 1°C/min. The gaseous reaction products were analyzed on a MS-10 mass spectrometer connected to the effluent gas line.

Lab-scale reduction roast tests were done on 100-gram samples contained in porcelain boats enclosed in a 46-mm-ID silica tube. The reaction mixtures were heated by a horizontal Lindberg heavy-duty tube furnace. Nitrogen was used to flush the apparatus, prior to reaction and during the reaction while carbon was present. Carbon monoxide was passed over the reaction mixture at flows between 50 and 150 cc/min for some of the tests. The temperature of the reaction mixtures was measured by a thermocouple beside the porcelain crucible. Sheathed thermocouples were used to measure the actual reaction temperatures of several of the mixtures. No appreciable temperature rise was found during reaction. The reaction products were identified by chemical, X-ray, and microprobe analyses. Some difficulties were experienced in the chemical analyses; they are detailed elsewhere(26).

The apparatus used to make the magnetic/density separations of the reduction roast products is shown in Figure 2. The apparatus is based on the principle that the iron and nickel powders contained in the products are both more magnetic and denser than the calcium sulphide, calcium oxide, and the unreacted gangue. Some retention of unreacted magnetic pyrrhotite (Fe_xS) would be expected. Twenty grams of minus 100-mesh reaction product was added to the vertical column and nitrogen flowing at 500 cc/min was used to create a fluid bed. The magnets kept the iron and nickel powders in the fluid bed, while the non-magnetic calcium sulphide, calcium oxide, and gangue were swept by the gas to the cyclone and caught in the test tube. Both fractions were then analyzed chemically.

RESULTS

Kinetic Analysis of the Metal Sulphide Reduction Reactions

The metal sulphides listed in Table 1 were reduced at 830°C, in the presence of carbon monoxide gas and either calcium oxide or reduced calcium carbonate, and at 960°C in the presence of carbon and either calcium oxide or reduced calcium carbonate. These reaction temperatures were chosen on the basis of preliminary experiments over a range of temperatures. The rates of reduction were followed by measuring the weight changes of 1-gram powdered samples. The results of the kinetic studies, calculated as the fraction reduced per unit of time, are shown in Table 2. Also given are the molar ratios of the various components used in the reaction mixtures. A hyperbolic regression analysis of the results was made using the Programma 601. The

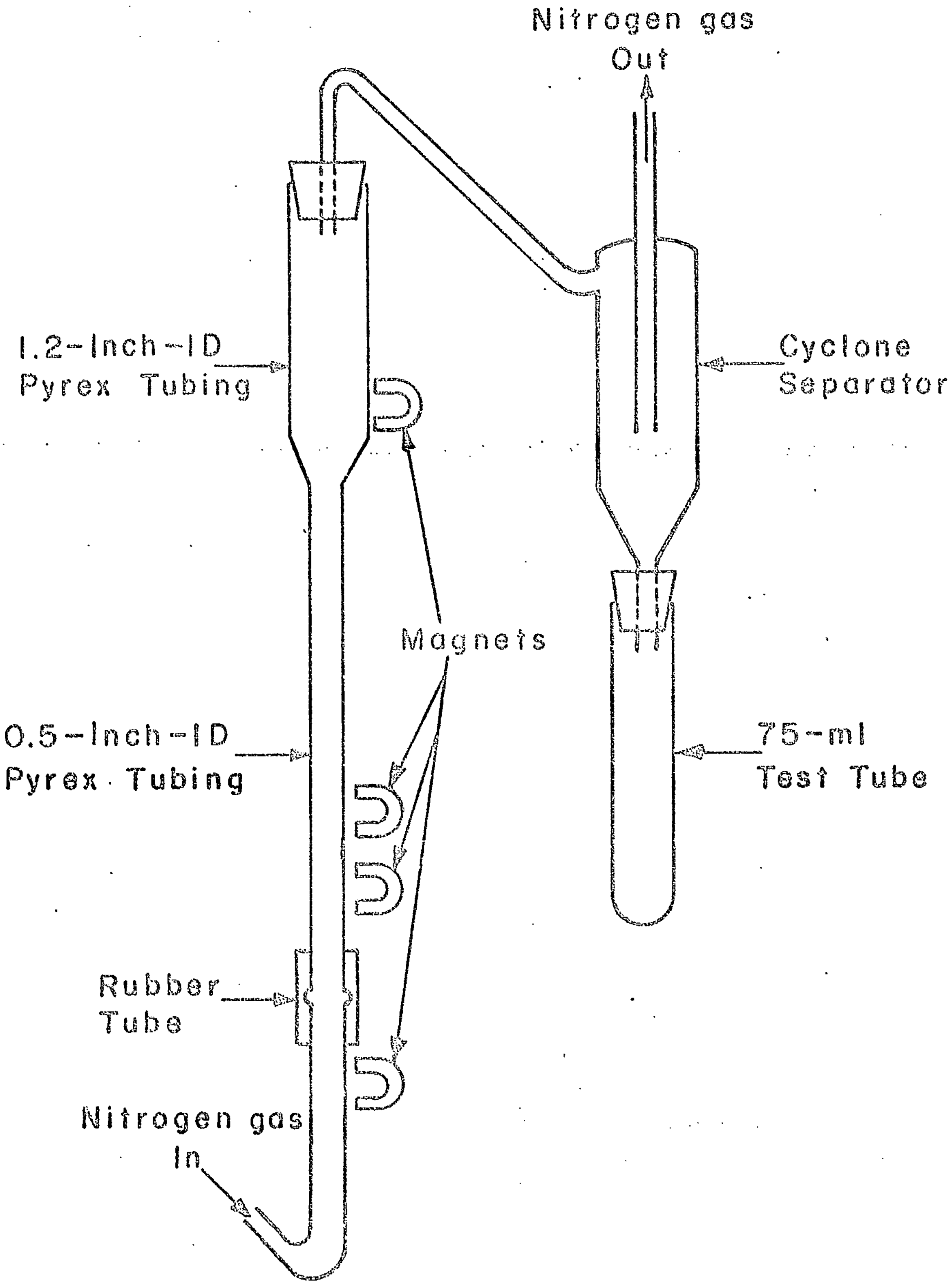

Figure 2: Schematic diagram of the apparatus used to magnetically separate the reduced metal sulphides.

TABLE 2

Rates of Reduction of Metal Sulphides

Fraction reduced = $\frac{bt}{1 + ct}$ where t = time in minutes

Std = standard deviation

Reaction Stoichiometry	Temp. (°C)	Initial Reaction Rate (min^{-1})	% reduction in one hour	b	c	Std
Pyrrhotite Conc. No. 1A						
$Fe_xS + CaO + C$	965	0.010	35	0.0132	0.0216	0.013
$Fe_xS + 2CaO + 2C$	963	0.018	61	0.0208	0.0183	0.021
$Fe_xS + 3CaO + 3C$	964	0.020	74	0.0277	0.0224	0.053
$Fe_xS + CaCO_3 + C$	963	0.017	39	0.0220	0.0403	0.015
$Fe_xS + CaO + CO_{(g)}$	831	0.064	99	0.1329	0.1131	0.220
$Fe_xS + 2CaO + CO_{(g)}$	830	0.064	99	0.1020	0.0693	0.122
$Fe_xS + 3CaO + CO_{(g)}$	832	0.071	99	0.1406	0.1045	0.136
$Fe_xS + CaCO_3 + CO_{(g)}$	830	0.040	99	0.0549	0.0287	0.115

...cont'd

TABLE 2 (cont'd)

Reaction Stoichiometry	Temp. (°C)	Initial Reaction Rate (min^{-1})	% reduction in one hour	b	c	Std
Pyrrhotite Conc. No. 1B						
$Fe_xS + CaO + C$	951	0.035	93	0.0364	0.0220	0.029
$Fe_xS + CaO + C$	931	0.022	54	0.0297	0.0244	0.160
$Fe_xS + CaO + C$	904	0.012	27	0.0164	0.0407	0.013
$Fe_xS + 2CaO + 2C$	956	0.029	79	0.0334	0.0263	0.020
$Fe_xS + 3CaO + 3C$	959	0.025	74	0.0261	0.0191	0.028
$Fe_xS + CaCO_3 + C$	965	0.015	28	0.0117	0.0253	0.015
$Fe_xS + CaO + CO_{(g)}$	836	0.064	99	0.0949	0.0598	0.095
$Fe_xS + 2CaO + CO_{(g)}$	832	0.040	85	0.0661	0.0618	0.056
$Fe_xS + 3CaO + CO_{(g)}$	835	0.055	99	0.1040	0.0870	0.130
$Fe_xS + CaCO_3 + CO_{(g)}$	829	0.038	91	0.0624	0.0521	0.050

...cont'd

TABLE 2 (cont'd)

Reaction Stoichiometry	Temp. (°C)	Initial Reaction Rate (min^{-1})	% reduction in one hour	b	c	Std
Pyrrhotite Conc. No. 1C						
$Fe_xS + CaO + C$	966	0.012	33	0.0213	0.0477	0.030
$Fe_xS + 2CaO + 2C$	964	0.018	66	0.0246	0.0210	0.023
$Fe_xS + 3CaO + 3C$	965	0.017	64	0.0164	0.0097	0.025
$Fe_xS + CaO + CO_{(g)}$	834	0.050	99	0.0761	0.0579	0.172
$Fe_xS + 2CaO + CO_{(g)}$	836	0.070	99	0.0936	0.0422	0.066
$Fe_xS + 3CaO + CO_{(g)}$	835	0.049	96	0.0486	0.0183	0.013
$Fe_xS + CaCO_3 + CO_{(g)}$	831	0.051	99	0.0783	0.0596	0.030
Pyrite Crystal (crushed) No. 2						
$FeS_2 + 2CaO + 2C$	962	0.023	72	0.0287	0.0226	0.016
$FeS_2 + 4CaO + 4C$	964	0.023	92	0.0293	0.0174	0.084
$FeS_2 + 6CaO + 6C$	965	0.023	96	0.0328	0.0202	0.123
$FeS_2 + 2CaCO_3 + 2C$	968	0.001	2	--	--	--

...cont'd

TABLE 2 (cont'd)

Reaction Stoichiometry	Temp. (°C)	Initial Reaction Rate (min^{-1})	% reduction in one hour	b	c	Std
Pyrite Concentrate No. 3						
$FeS_2 + 2CaO + 2C$	967	0.030	52	0.0110	0.0218	0.051
$FeS_2 + 4CaO + 4C$	965	0.023	52	0.0106	0.0218	0.048
$FeS_2 + 6CaO + 6C$	964	0.023	48	0.0082	0.0156	0.042
$FeS_2 + 2CaCO_3 + 2C$	968	0.001	2	--	--	--
$FeS_2 + 2CaO + 2CO_{(g)}$	833	0.038	97	0.1378	0.1246	0.092
$FeS_2 + 4CaO + 2CO_{(g)}$	835	0.031	92	0.0857	0.0759	0.062
$FeS_2 + 6CaO + 2CO_{(g)}$	832	0.036	89	0.1128	0.1090	0.108
$FeS_2 + 2CaCO_3 + 2CO_{(g)}$	829	0.001	2	--	--	--

...cont'd

TABLE 2 (cont'd)

Reaction Stoichiometry	Temp. (°C)	Initial Reaction Rate (min^{-1})	% reduction in one hour	b	c	Std
Synthetic Ni_3S_2 No. 4						
Ni_3S_2 + 2CaO + 2C	965	0.012	27	0.0166	0.0439	0.015
Ni_3S_2 + 4CaO + 4C	966	0.011	29	0.0145	0.0326	0.030
Ni_3S_2 + 6CaO + 6C	969	0.013	29	0.0183	0.0475	0.012
Ni_3S_2 + 4CaO + 2C	968	0.011	38	0.0140	0.0217	0.027
Ni_3S_2 + $2CaCO_3$ + 2C	963	0.007	18	0.0064	0.0186	0.009
Ni_3S_2 + 2CaO + $2CO_{(g)}$	835	0.024	41	0.0610	0.1307	0.026
Ni_3S_2 + 4CaO + $2CO_{(g)}$	833	0.029	61	0.0496	0.0658	0.040
Ni_3S_2 + 6CaO + $2CO_{(g)}$	832	0.035	77	0.0534	0.0531	0.048
Ni_3S_2 + $2CaCO_3$ + $2CO_{(g)}$	830	0.038	99	0.0359	0.0196	0.027

...cont'd

TABLE 2 (cont'd)

Reaction Stoichiometry	Temp. (°C)	Initial Reaction Rate (min^{-1})	% reduction in one hour	b	c	Std
Pentlandite Concentrate No. 5						
$(Fe,Ni)_9S_8 + 8CaO + 8C$	950	0.024	81	0.0479	0.0455	0.128
$(Fe,Ni)_9S_8 + 16CaO + 16C$	949	0.039	82	0.0448	0.0400	0.078
$(Fe,Ni)_9S_8 + 32CaO + 32C$	968	0.020	88	0.0308	0.0229	0.142
$(Fe,Ni)_9S_8 + 48CaO + 48C$	956	0.017	61	0.0213	0.0179	0.024
$(Fe,Ni)_9S_8 + 16CaCO_3 + 16C$	968	0.012	24	0.0097	0.0233	0.012
$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(g)}$	832	0.102	78	0.2615	0.3153	0.113
$(Fe,Ni)_9S_8 + 16CaO + 8CO_{(g)}$	833	0.054	90	0.0900	0.0823	0.051
$(Fe,Ni)_9S_8 + 32CaO + 8CO_{(g)}$	833	0.021	89	0.0510	0.0433	0.098
$(Fe,Ni)_9S_8 + 8CaCO_3 + 8CO_{(g)}$	828	0.035	99	0.0423	0.0248	0.067
$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(g)}$	574	0.002	7	0.0021	0.0124	0.002
$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(g)}$	664	0.011	15	0.0118	0.0651	0.005
$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(g)}$	770	0.080	80	0.0446	0.0383	0.063
$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(g)}$	848	0.120	58	0.2654	0.4470	0.218
$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(g)}$	934	0.171	54	0.4480	0.7952	0.101
$(Fe,Ni)_9S_8 + 8CaO + 8C + 8CO_{(g)}$	808	0.065	38	0.3195	0.8062	0.079
$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(g)} + 8CO_{2(g)}$	809	0.035	53	0.0503	0.0785	0.030

calculated constants and the standard deviation of the experimental values from the calculated equations are listed in Table 2.

(a) Compositional Effects

The direct reduction of iron and nickel sulphides was much more rapid in the presence of CO and either CaO or $CaCO_3$ (decomposes to CaO at reaction temperatures) than in the presence of carbon and either CaO or $CaCO_3$. One exception was the reduction of pyrite (FeS_2) with CO and $CaCO_3$, where almost no reaction occurred. The pyrite decomposed to pyrrhotite (Fe_xS) before the reaction temperature was reached, and the resultant sulphur vapour may have affected the CaO formed from the $CaCO_3$.

The use of both carbon and carbon monoxide gas for reducing agents in the same mixture resulted in sulphide reduction rates between the slower rates found while carbon was the reductant and the faster rates while CO was the reductant. The greater reduction rate for CO and carbon than for carbon alone agrees with a previous study of the reduction of FeS and Ni_3S_2 (3). However, a 1:1 gas mixture of CO and CO_2 retards the reduction reaction.

The reduction reactions were also analyzed by a combination of differential thermal analysis and mass spectrometric analysis. If carbon was used as a reductant, CO was the principal product gas, and if CO was used, CO_2 was the principal product gas. All reactions were exothermic, in agreement with the calculations of Appendix 1.

Carbon, CaO, and $CaCO_3$ were added to the iron and nickel sulphides in the stoichiometric reaction ratios of 1:1, 2:1 and 3:1. The effect of excess reactants on the reduction rate varied with the metal sulphides used and the conditions present (Table 2). The results also indicate that the sulphide concentrates, particularly pyrrhotite, show some variation in reduction behaviour under similar conditions; this indicates that the impurities and gangue material present in the concentrates as well as the metal sulphide composition, may have an important effect on the reduction rates.

(b) Temperature Effects

The effect of temperature on the reduction rates of several sulphide mixtures was also studied. For the reduction of pyrrhotite concentrate in the presence of carbon and CaO, an Arrhenius plot of the rate data yielded an activation energy of 60 kcal/mole. For pentlandite concentrate reduction in the presence of CaO and CO gas, an activation energy of 37 kcal/mole was found for temperatures less than 700°C and 14 kcal/mole for temperatures greater than 740°C. The change in activation energy is probably associated with the decomposition of pentlandite ($(Fe,Ni)_9S_8$) to form pyrrhotite (Fe_xS) and heazlewoodite (Ni_3S_2) at temperatures above 610°C(25). A previous study found that the activation energy for FeS and Ni_3S_2 reduction in the presence of carbon and CaO was 84 and 67 kcal/mole, respectively(3).

Kinetic Analysis of the Calcium Sulphide Carbonation Reaction

The results of the carbonation tests for calcium sulphide are listed in Table 3. The rates of carbonation were very slow when gas mixtures of carbon dioxide and water vapour were passed over the calcium sulphide at atmospheric pressure. The water vapour partial pressure had some effect on the carbonation rate, with a maximum rate occurring at a partial pressure

TABLE 3

Rates of Carbonation of Calcium Sulphide

Partial Pressures (atm)		Temp. (°C)	Initial Reaction Rate (min^{-1})	% reduction in two hours	b	c	Std
H_2O	CO_2						
0.018	0.982	626	0.001	4	0.0008	0.0148	0.001
0.038	0.962	625	0.006	8	0.0077	0.0880	0.016
0.064	0.936	614	0.003	5	0.0019	0.0303	0.008
0.097	0.903	620	0.003	5	0.0038	0.0640	0.007

of 0.04 atm. The carbonation rate did not vary for reactive-gas flows between 50 and 100 cc/min. The low carbonation rates agree with previous studies[17,18], which showed that reasonable carbonation rates were obtained only at gas pressures between 200 and 250 psia. Pressurized studies of the carbonation reaction were not possible with the equipment available in this laboratory.

Kinetic Analysis of the Carbonyl Separation of Nickel from Reduced Sulphide Products

The removal of nickel by the formation of a volatile nickel carbonyl ($Ni(CO)_4$) at 60°C was attempted for several nickel-containing materials, including the reduction roast products which contained reduced metal and calcium sulphide, the nickel-iron powder obtained from the magnetic separation of the reduction roast products, and nickel powder which was used either unactivated or activated by hydrogen at 1000°C. In all cases, the rates were too slow for proper kinetic analysis of the reactions.

Lab-Scale Studies of the Reduction Roast of Metal Sulphides

In these studies, 100-gram mixtures of metal sulphides, calcium oxide, calcium carbonate, and carbon and/or carbon monoxide (50 cc/min unless otherwise stated) were roasted at 830°C and at 960°C in a horizontal tube furnace. The percentage reduction obtained is given in Table 4, and the chemical analyses of the reaction products are listed in Table 5. The molar ratios of the various components are also given in the tables. The percentage reduction of the metal sulphides was calculated both on the basis of weight loss and from the results of the chemical analyses, using the metallic and the total iron and nickel analyses.

TABLE 4

Lab-Scale Reduction of Metal Sulphides

Test. No.	Reaction Stoichiometry	Temp. (°C)	Duration of Test (hours)	% Reduction Calculated from	
				Chemical Analysis	Weight Loss
	Pentlandite Concentrate No. 5				
1	$(Fe,Ni)_9S_8 + 8CaO + 8C$	960	2	21	57
2	$(Fe,Ni)_9S_8 + 16CaO + 16C$	960	2	46	67
3	$(Fe,Ni)_9S_8 + 32CaO + 32C$	960	2	52	44
4	$(Fe,Ni)_9S_8 + 48CaO + 48C$	960	2	55	45
5	$(Fe,Ni)_9S_8 + 16CaCO_3 + 16C$	960	2	41	59
6	$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(g)}$	960	2	14	28
7	$(Fe,Ni)_9S_8 + 16CaO + 8CO_{(g)}$	960	2	26	41
8	$(Fe,Ni)_9S_8 + 32CaO + 8CO_{(g)}$	960	2	22	40
9	$(Fe,Ni)_9S_8 + 8CaCO_3 + 8CO_{(g)}$	960	2	15	32
10	$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(50\ cc/min)}$	850	1	6	28
10a	$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(100\ cc/min)}$	850	1	29	42
10b	$(Fe,Ni)_9S_8 + 8CaO + 8CO_{(150\ cc/min)}$	850	1	24	32

...cont'd

TABLE 4 (cont'd)

Test No.	Reaction Stoichiometry	Temp. (°C)	Duration of Test (hours)	% Reduction Calculated from	
				Chemical Analysis	Weight Loss
	Pyrrhotite Conc. No. 1A				
11	$Fe_xS + CaO + C$	960	2	50	43
12	$Fe_xS + 2CaO + 2C$	960	2	57	62
13	$Fe_xS + 3CaO + 3C$	960	2	57	79
14	$Fe_xS + CaCO_3 + C$	960	2	52	87
15	$Fe_xS + CaO + CO_{(g)}$	960	2	7	50
16	$Fe_xS + 2CaO + CO_{(g)}$	960	2	5	44
17	$Fe_xS + 3CaO + CO_{(g)}$	960	2	7	61
18	$Fe_xS + CaCO_3 + CO_{(g)}$	960	2	8	27
19	$Fe_xS + CaO + CO_{(g)}$	850	1	3	22
20	$Fe_xS + CaCO_3 + CO_{(g)}$	850	1	6	23

...cont'd

TABLE 4 (cont'd)

Test No.	Reaction Stoichiometry	Temp. (°C)	Duration of Test (hours)	% Reduction Calculated from	
				Chemical Analysis	Weight Loss
	Pyrrhotite Conc. No. 1B				
21	$Fe_xS + CaO + C$	960	2	80	92
22	$Fe_xS + 2CaO + 2C$	960	2	76	93.5
23	$Fe_xS + 3CaO + 3C$	960	2	51	75
24	$Fe_xS + CaCO_3 + C$	960	2	56	61
25	$Fe_xS + CaO + CO_{(g)}$	960	2	7	34
26	$Fe_xS + 2CaO + CO_{(g)}$	960	2	5	27
27	$Fe_xS + 3CaO + CO_{(g)}$	960	2	10	40
28	$Fe_xS + CaCO_3 + CO_{(g)}$	960	2	36	37

...cont'd

TABLE 4 (cont'd)

Test No.	Reaction Stoichiometry	Temp. (°C)	Duration of Test (hours)	% Reduction Calculated from	
				Chemical Analysis	Weight Loss
	Pyrrhotite Conc. No. 1C				
29	$Fe_xS + CaO + C$	960	2	42	54
30	$Fe_xS + 2CaO + 2C$	960	2	45	61
31	$Fe_xS + 3CaO + 3C$	960	2	57	72
32	$Fe_xS + CaO + CO_{(g)}$	960	2	8	27
33	$Fe_xS + 2CaO + CO_{(g)}$	960	2	5	27
34	$Fe_xS + 3CaO + CO_{(g)}$	960	2	9	35
35	$Fe_xS + CaCO_3 + CO_{(g)}$	960	2	24	32
	Pyrite Crystal (crushed) No. 2				
36	$FeS_2 + 2CaCO_3 + 2C$	960	2	48	46

...cont'd

TABLE 4 (cont'd)

Test No.	Reaction Stoichiometry	Temp. (°C)	Duration of Test (hours)	% Reduction Calculated from	
				Chemical Analysis	Weight Loss
	Pyrite Concentrate No. 3				
37	$FeS_2 + 2CaO + 2C$	960	2	45	53
38	$FeS_2 + 4CaO + 4C$	960	2	58	59
39	$FeS_2 + 6CaO + 6C$	960	2	65	61
40	$FeS_2 + 2CaCO_3 + 2C$	960	2	49	59
41	$FeS_2 + 2CaO + 2CO_{(g)}$	960	2	1	22
42	$FeS_2 + 4CaO + 2CO_{(g)}$	960	2	14	18
43	$FeS_2 + 6CaO + 2CO_{(g)}$	960	2	11	20
44	$FeS_2 + 2CaCO_3 + 2CO_{(g)}$	960	2	19	80

...cont'd

TABLE 4 (cont'd)

Test No.	Reaction Stoichiometry	Temp. (°C)	Duration of Test (hours)	% Reduction Calculated from	
				Chemical Analysis	Weight Loss
	Synthetic Ni_3S_2 No. 4				
45	$Ni_3S_2 + 2CaO + 2C$	960	2	5	30
46	$Ni_3S_2 + 4CaO + 4C$	960	2	6	53
47	$Ni_3S_2 + 6CaO + 6C$	960	2	1	24
48	$Ni_3S_2 + 4CaO + 2C$	960	2	11	84
49	$Ni_3S_2 + 2CaCO_3 + 2C$	960	2	63	62
50	$Ni_3S_2 + 2CaO + 2CO_{(g)}$	960	2	22	20
51	$Ni_3S_2 + 4CaO + 2CO_{(g)}$	960	2	26	18
52	$Ni_3S_2 + 6CaO + 2CO_{(g)}$	960	2	31	23
53	$Ni_3S_2 + 2CaCO_3 + 2CO_{(g)}$	960	2	24	30

TABLE 5

Chemical Analysis of Reaction Products from the Lab-Scale Reduction Roast Experiments (Table 4)

Test Number (taken from Table 4)	Total Fe	Met. Fe	Total Ni	Met. Ni	S	Ca	C	O	SO_4 /S	CO_2	X-Ray Analysis	
											Major	Minor
Pentlandite Conc. No. 5												
1	14.7	0.79	13.3	5.0	11.3	15.4	3.17	21.0	0.04	0.04		
2	11.4	3.6	10.1	6.3	10.9	26.6	5.19	18.4	0.08	0.1	CaS, CaO	Ni-Fe
3	7.7	2.4	7.0	5.3	7.4	37.7	8.05	21.3	0.05	0.07	CaS, CaO	Ni-Fe
4	6.32	2.0	5.8	4.7	5.82	45.3	9.12	22.4	0.11	0.19		
5	18.3	4.0	10.4	7.69	10.3	27.8		21.9	0.10	0.60		
6	16.7	2.0	15.1	2.4	13.1	--	--	--	0.01	0.29		
7	11.2	1.4	10.7	4.37	11.0	--	--	--	0.004	0.82		
8	8.24	1.8	7.6	5.3	7.56	--	--	--	0.02	1.04		
9	14.7	1.2	13.7	3.1	13.0	--	--	--	0.03	0.25		
10	11.5	0.28	11.1	1.0	10.0	--	--	--	0.46	1.06		
10 a	11.9	2.38	11.9	4.4	10.4	--	--	--	0.06	1.56		
10 b	11.9	1.3	12.0	4.5	10.5	--	--	--	0.03	0.92		

...cont'd

TABLE 5 (cont'd)

Test Number (taken from Table 4)	Total Fe	Met. Fe	Total Ni	Met. Ni	S	Ca	C	O	SO_4/S	CO_2	X-Ray Analysis	
											Major	Minor
Pyrrhotite Conc. No. 1A												
11	34.4	17.3	0.65	0.55	22.2	22.6	5.19	7.4	0.03	0.1		
12	23.7	13.5	0.40	0.25	15.3	37.3	9.5	12.2	0.08	0.39		
13	17.1	9.8	0.34	0.01	11.8	44.8	10.9	15.3	0.07	0.31		
14	35.3	18.2	0.73	0.58	22.0	31.2	--	8.1	0.06	0.38		
15	35.7	2.62	0.60	0.037	22.5	26.9	--	11.6	< 0.01	0.11		
16	25.2	1.22	0.42	0.017	15.9	38.9	--	18.1	0.07	0.25		
17	20.0	1.47	0.35	0.005	12.3	45.9	--	20.6	0.05	0.84		
18	33.6	2.65	0.59	0.40	21.0	--	--	--	0.02	0.09		
19	28.3	0.07	0.57	0.064	17.2	--	--	--	0.44	1.48		
20	33.5	1.8	0.59	0.034	21.1	--	--	--	0.58	0.70		

...cont'd

TABLE 5 (cont'd)

Test Number (taken from Table 4)	Total Fe	Met. Fe	Total Ni	Met. Ni	S	Ca	C	O	SO_4/S	CO_2	X-Ray Analysis	
											Major	Minor
<u>Pyrrhotite Conc. No. 1B</u>												
21	34.0	27.2	0.76	0.38	24.9	29.9	1.78	4.5	0.05	0.09	CaS	Fe
22	22.2	16.8	0.13	0.004	15.5	37.8	10.2	12.5	0.08	0.12	CaS	CaO
23	16.1	8.2	0.07	0.002	5.45	42.7	9.4	15.8	0.17	0.23	CaS, CaO	
24	30.2	16.9	0.45	0.41	19.9	32.0	--	10.7	0.07	0.38		
25	30.7	2.14	0.03	--	20.3	--	--	--	0.09	0.14		
26	20.6	1.05	0.023	0.003	14.0	42.1	--	20.2	0.08	0.74		
27	17.0	1.62	0.017	0.004	11.4	47.1	--	22.6	0.07	0.78		
28	21.5	7.70	0.015	0.027	16.6	--	--	--	0.35	0.08		

...cont'd

TABLE 5 (cont'd)

Test Number (taken from Table 4)	Total Fe	Met. Fe	Total Ni	Met. Ni	S	Ca	C	O	SO_4/S	CO_2	X-Ray Analysis	
											Major	Minor
<u>Pyrrhotite Conc. No. 1C</u>												
29	37.9	16.0	0.54	0.37	17.7	34.6	6.07	10.6	0.01	0.24		
30	23.7	10.7	0.48	0.29	14.5	36.6	8.07	13.0	0.01	0.35		
31	18.3	10.5	0.55	0.04	12.3	42.1	9.85	14.6	0.01	0.30		
32	34.4	2.89	0.62	--	21.5	--	--	--	0.01	0.08		
33	23.9	1.28	0.44	--	15.0	--	--	--	0.11	0.64		
34	19.9	1.70	0.36	--	12.5	--	--	--	0.12	0.68		
35	33.6	8.0	0.63	0.007	20.1	--	--	--	0.01	0.01		
<u>Pyrite Crystal (crushed) No. 2</u>												
36	22.5	10.7	0.033	0.019	26.1	34.4	--	7.13	0.07	0.16		

...cont'd

TABLE 5 (cont'd)

Test Number (taken from Table 4)	Total Fe	Met. Fe	Total Ni	Met. Ni	S	Ca	C	O	SO_4/S	CO_2	X-Ray Analysis	
											Major	Minor
Pyrite Conc. No. 3												
37	24.0	10.7	0.009	0.006	25.6	32.2	5.3	7.8	0.04	0.08		
38	15.1	8.7	0.012	0.002	16.7	42.2	9.1	12.7	0.08			
39	11.0	7.1	0.098	0.003	12.3	45.8	12.1	15.3	0.10	0.21		
40	24.5	12.1	0.20	0.11	21.7	37.8	5.26	9.2	0.01	0.34		
41	24.7	0.26	0.011	--	23.0	--	--	--	0.45	0.26		
42	16.3	1.77	0.008	0.014	16.3	--	--	--	0.66	0.47		
43	12.6	1.37	0.008	0.002	12.9	--	--	--	0.35	0.65		
44	24.7	4.6	0.11	0.03	20.9	--	--	--	0.38	0.21		

...cont'd

TABLE 5 (cont'd)

Test Number (taken from Table 4)	Total Fe	Met. Fe	Total Ni	Met. Ni	S	Ca	C	O	SO_4 /S	CO_2	X-Ray Analysis Major	X-Ray Analysis Minor
Synthetic Ni_3S_2 No. 4												
45	0.073	< 0.1	47.8	2.65	17.5	23.6	5.14	6.08	0.01	0.30		
46	0.088	< 0.1	36.9	2.05	13.2	32.2	7.77	9.33	0.01	0.35		
47	0.20	< 0.1	24.3	0.34	9.0	43.9	10.1	14.5	0.01	0.31		
48	0.083	< 0.1	40.6	5.58	14.3	31.9	--	8.64	0.10	0.55		
49	0.14	< 0.1	52.9	35.8	19.0	24.1	--	3.27	0.10	0.47		
50	0.16	0.017	49.2	10.7	18.0	--	--	--	0.10	0.83		
51	0.10	0.006	39.0	10.0	13.9	--	--	--	0.17	0.75		
52	0.09	0.004	32.3	10.0	11.5	--	--	--	0.16	0.85		
53	0.13	0.08	49.5	12.3	17.6	--	--	--	0.86	0.01		

The reduction roast products obtained from these tests were porous, compact lumps which could be easily crushed to minus 100 mesh. Selected samples were mounted, polished, and the constituents identified by electronprobe analysis. Photomicrographs of two samples are shown in Figure 3. The first photomicrograph is of pyrrhotite concentrate (No. 1B) reduced in the presence of CaO and C. The reduced iron appears as light-coloured, irregular-shaped particles, and the dark-grey phases are CaS. The second photomicrograph is of pyrrhotite concentrate (No. 1B) reduced in the presence of CaO and CO. Much of the iron is present in the medium-grey phase, probably as a solid solution with CaS and CaO. (Fe = 42, Ca = 26, S = 19 wt %); whereas the dark particles consist of CaS, and the light-grey phases are unreacted pyrrhotite and the small white phases are iron-nickel metal grains.

The reduction of metal sulphides in the lab-scale tests was not as complete as in the 1 gram samples used for the TGA. This indicates that the use of loaded boats in tube furnaces is not entirely satisfactory in reducing the metal sulphide mixtures. It would be necessary to optimize the reduction roast step by using a furnace which provides good contact between all of the reacting constituents, including the gas phase. In the case of CO reduction, better results were obtained at 850°C than at 960°C. The use of an excess of CaO, $CaCO_3$, and C did not affect the results greatly. Increasing the flow rate of CO from 50 ml/min to 150 ml/min increased the proportion reacted in one hour. The chemical analyses showed that, in the case of the pentlandite

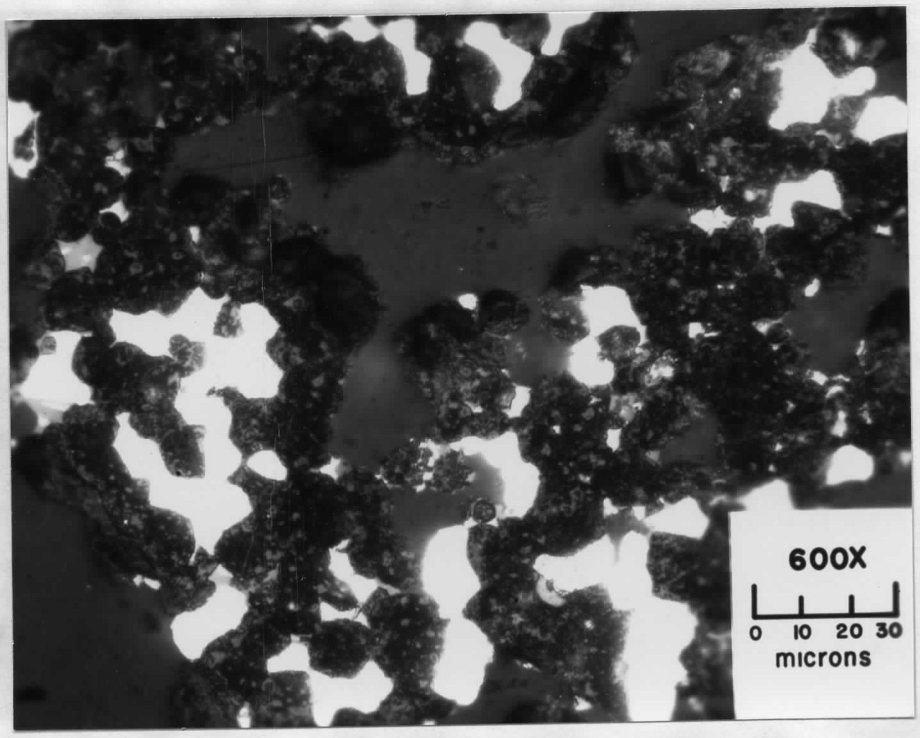

Figure 3(a): Photomicrograph (X600) of product obtained from the reduction of pyrrhotite concentrate (No. 1B) in the presence of CaO and C at 960°C.

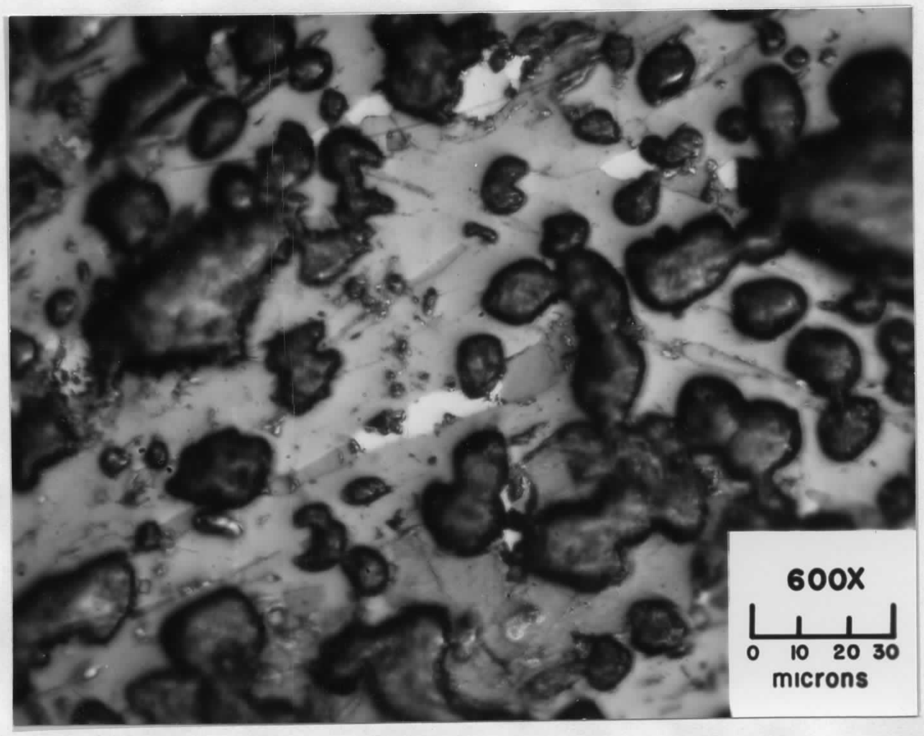

Figure 3(b): Photomicrograph (X600) of product obtained from the reduction of pyrrhotite concentrate (No. 1B) in the presence of CaO and CO at 960°C.

concentrate (which decomposed to FeS and Ni_3S_2 at reaction temperature), proportionally more of the nickel content than the iron content was reduced. The analyses also showed that none of the sulphur was being lost during the reduction roast.

Magnetic Separation of the Reduction Roast Products

The results of the magnetic separation of the reduction roast products are shown in Table 6. Approximately 70 % of the reduced metals were concentrated in the magnetic portion after one pass through the magnetic/density separator. Repeated passes would likely further separate the metallic content from the remaining reduction roast products. Some accumulation of unreacted magnetic Fe_xS would be expected in the magnetic portion.

DISCUSSION

The direct reduction process for nickel and iron sulphides which was described in the Process Outline depends on the development of several key steps. The reduction roast step, in which the sulphide concentrates are reduced at 830°C in the presence of calcium oxide and carbon monoxide, was shown by kinetic and lab-scale studies to be a relatively rapid reaction with almost complete conversion, provided good contact is maintained between all the reacting constituents. Unimpeded diffusion of CO into the reaction mixture is particularly important. A furnace such as a rotating kiln would probably be most suitable for provided good contact between the constituents. The product recovered from the reduction roast step would have to be ground to minus 300 mesh before the magnetic/density separation step.

TABLE 6

Magnetic Separation of Iron and Nickel from Reduced Sulphide Mixtures

Test Number (taken from Table 4)	Magnetic Portion				Non-Magnetic Portion			
	Met. Fe%	Met. Ni%	S%	Ca%	Met. Fe%	Met. Ni%	S%	Ca%
2	3.36	6.92	8.8	13.3	2.5	2.4	15.3	19.3
6	1.3	2.5	12.0	17.6	0.9	1.2	12.7	--
15	2.90	--	22.1	15.2	1.62	--	22.2	16.7
22	18.1	--	14.1	19.8	9.14	--	18.3	24.2
37	10.8	--	25.1		6.90	--	26.8	--
41	0.09	--	22.2	18.8	0.13	--	24.0	36.9
45	--	19.9	17.3	9.05	--	7.45	18.1	24.0
50	--	12.3	14.5	19.5	--	1.9	18.3	--

The reactions involved in the reduction process were not clearly defined in this study. However, they probably proceed according to the following equations:

$$MS_{(s)} + CaO_{(s)} \rightarrow MO_{(s)} + CaS_{(s)} \qquad [6]$$

$$MO_{(s)} + C_{(s)} \rightarrow M_{(s)} + CO_{(g)} \qquad [7]$$

$$MO_{(s)} + CO_{(g)} \rightarrow M_{(s)} + CO_{2\,(g)} \qquad [8]$$

where M represents Ni or Fe. Small amounts of metal oxides were found by X-ray diffraction and electron-probe analyses in the reaction products for the lab-scale studies of the reduction of nickel and iron sulphides in the presence of CaO and CO, but none were found either where carbon was present or in the TGA studies. The incomplete reduction, found for the sulphides in the presence of CaO and CO at temperatures above 850°C, may be due to the formation of a (Fe, Ca, S) solid solution with some CaO present, as shown by electronprobe analyses. This possibility should be checked in greater detail because it will affect the rates of reduction.

The separation of iron and nickel powder from the reduction roast products was only partially successful in this study. The magnetic/density separation technique concentrated 70% of the reduced metals into the magnetic portion of the separated reduction products. However, a greater degree of separation would be required in a commercial process. As indicated in the photomicrographs of Figure 3, the metallic particles are sufficiently irregular to make it difficult to completely separate CaS from the metallic particles even with fine grinding. A possible alternative would be to provide a heat treatment of some sort to the reduction roast products in order to allow the metallic particles to coalesce. There is also the problem of the formation of solid phase which would tie-up the reduced metals with the sulphides and the problem of the separation of unreacted magnetic pyrrhotite along with the reduced metals.

The carbonyl separation(10) of nickel either from the magnetically separated iron-nickel powders or from the reduction roast products before magnetic separation would result in a high-purity product. However, attempts to separate the nickel as a carbonyl gas from the reaction products with the equipment available were unsuccessful even when pure activated nickel was used. The reaction is apparently not kinetically favourable except under a closely controlled set of conditions which were not attained in this study. However, the method should be studied further as a means of recovering both nickel and iron from the reaction products. Careful experimental procedures are required in this study because nickel and iron tetracarbonyl are extremely poisonous.

The solid-state carbonation of calcium sulphide was found to proceed too slowly at atmospheric pressure to be of interest in a commercial process. Studies done elsewhere have shown that favourable reaction rates are attained only when the reaction is done under pressure(17,18). These studies indicate that the presence of impurities such as CaO and unreacted sulphides in the CaS, after it has been removed from the reduction roast product by magnetic/density separation, did not affect the rate of carbonation. Additional studies are needed to determine the rate of carbonation of impure CaS under pressure in a reactor.

The other two major steps, the calcination of $CaCO_3$ and the conversion of H_2S to sulphur in a Claus reactor, present no problems in a commercial process because of the available technology.

SUMMARY

Several aspects of the direct reduction of nickel and iron sulphide concentrates to nickel, iron, and elemental sulphur have been studied. The direct reduction takes place at 830°C in the presence of CaO and carbon monoxide gas both of which are relatively inexpensive and readily obtainable. The process is essentially non-polluting because the CaO is recycled and CO_2, rather than sulphur oxides, is released.

SUGGESTIONS FOR FUTURE STUDIES

1. The proposed process described in this report would be of particular interest to companies processing sulphide nickel ores if the nickel sulphides could be reduced in preference to the iron sulphides. The thermochemical analysis given in Appendix 1 indicates that Ni_3S_2 can be reduced in the presence of CaO in preference to Fe_xS, provided certain P_{CO_2}/P_{CO} ratios are maintained (Figure 4). For example at the proposed reaction temperature of 830°C, P_{CO_2}/P_{CO} ratios between 2.5 and 12 would be necessary to reduce Ni_3S_2 instead of Fe_xS. This study has indicated that, though some selective reduction of Ni_3S_2 to Ni occurs even at low P_{CO_2}/P_{CO} ratios, the presence of CO_2 in the reaction gas stream retards the reaction. This would off-set the advantages obtained by the selective reduction of Ni_3S_2.

2. The recovery of precious metals is important in all ore treatment. Likely, in the process described, the precious metals would accumulate in the reduced metal phase and would be recovered in the separation step. The accumulation of precious metals in the reduced metal phase was not determined in this study but it should be determined in future studies when possible.

3. This study showed that although the reduction roast of the nickel and iron sulphide concentrates can proceed efficiently, the difficulties encountered in making a clean separation of the nickel and iron powders from the reduction roast products will have to be overcome before the process is scaled up. The carbonyl process shows the most potential for clean separation of the iron and nickel powders, providing the reaction rates are fast enough. Probably a combination of magnetic/density separation followed by carbonyl separation would be most successful. This method would also yield an unreacted, magnetic pyrrhotite residue for either discard or further processing.

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APPENDIX 1

A negative free energy change (ΔG°) for a reaction at constant temperature is an indication that the reaction will proceed spontaneously under equilibrium conditions. The free energies, for the sulphide reactions shown in Appendix Table 7, were calculated assuming unit activity for the various components(27,28). Several sulphides of interest are not shown in the table because they decompose into simpler sulphides before the reaction temperatures of interest is reached. For example, pentlandite $(Fe,Ni)_9S_8$ decomposes into pyrrhotite (Fe_xS) and heazlewoodite (Ni_3S_2) at 610°C(25), pyrite (Fe_2S) decomposes into pyrrhotite and sulphur at temperatures above 550°C(29), covellite (CuS) decomposes above 510°C to form chalcocite (Cu_2S) and sulphur(30), and chalcopyrite ($CuFeS_2$) decomposes above 750°C to form pyrrhotite, bornite (Cu_5FeS_4), and sulphur(30).

If carbon is present in the reaction mixtures, carbon monoxide will be the principal gas product because of the equilibrium established by the reaction $C + CO_2 = CO$. However, if only carbon monoxide is present in the reaction mixture, carbon dioxide will be the principal gas product. If sulphur is evolved from the sulphides before the reaction temperature (> 700°C) is reached, as would occur with the thermal decomposition of pyrite(29), the presence of carbon monoxide would likely result in the formation of carbonyl sulphide (COS). However, once reduced metal is present in the mixture, only trace amounts of COS are formed(31).

TABLE 7

Free Energies of Process Reactions at Different Temperatures

Reaction	ΔG°, cal per mole		
	600°C	800°C	1000°C
$FeS + CaO + C = Fe + CaS + CO$	60	- 5,900	-12,800
$FeS + CaO + CO = Fe + CaS + CO_2$	- 3,100	- 1,900	- 440
$Ni_3S_2 + 2CaO + 2C = 3Ni + 2CaS + 2CO$	- 3,000	-19,500	-35,580
$Ni_3S_2 + 2CaO + 2CO = 3Ni + 2CaS + 2CO_2$	-11,100	-11,000	-10,900
$Cu_2S + CaO + C = 2Cu + CaS + CO$	3,500	- 6,210	-15,860
$Cu_2S + CaO + CO = 2Cu + CaS + CO_2$	- 1,860	- 3,110	- 4,440
$PbS + CaO + C = Pb + CaS + CO$	- 5,300	-10,800	-16,300
$PbS + CaO + CO = Pb + CaS + CO_2$	- 7,400	- 7,100	- 6,800
$ZnS + CaO + C = Zn + CaS + CO$	19,600	11,200	2,800
$ZnS + CaO + CO = Zn + CaS + CO_2$	16,000	15,300	14,600
$2CO + S_2 = 2COS$	-13,070	- 5,520	1,880
$CaS + H_2O + CO_2 = CaCO_3 + H_2S$	- 6,030	3,220	12,520

As indicated by the differences in free energies associated with the reductions of Ni_3S_2 and FeS in the presence of CaO and CO, it should be possible to selectively reduce Ni_3S_2 to Ni while leaving FeS in an unreduced state. A predominance area-reciprocal temperature diagram (Figure 4) was constructed using the relationship $\Delta G = RT \ln Kp$ and the free energy values listed in Table 7. Unit activities were assumed for the solid components and ideal gas behaviour at a total pressure of one atmosphere was assumed for CO and CO_2. As shown on the diagram, there is a limited range of P_{CO_2}/P_{CO} values in which the selective reduction of Ni_3S_2 can occur in the presence of CaO.

The heats of reaction, for the reduction of FeS and Ni_3S_2, as calculated from data listed for 298°K$^{(27)}$, are shown below. The negative signs indicated exothermic reactions.

$$FeS + CaO + CO \rightarrow Fe + CaS + CO_2 \qquad \Delta H_{298} = -\ 3{,}200 \text{ cal/mole} \tag{1}$$

$$Ni_3S_2 + 2CaO + 2CO \rightarrow 3Ni + 2CaS + 2CO_2 \qquad \Delta H_{298} = -\ 2{,}500 \text{ cal/mole} \tag{2}$$

The amount of heat required to decompose $CaCO_3$ is 42,000 cal/mole at 750°C$^{(21)}$.

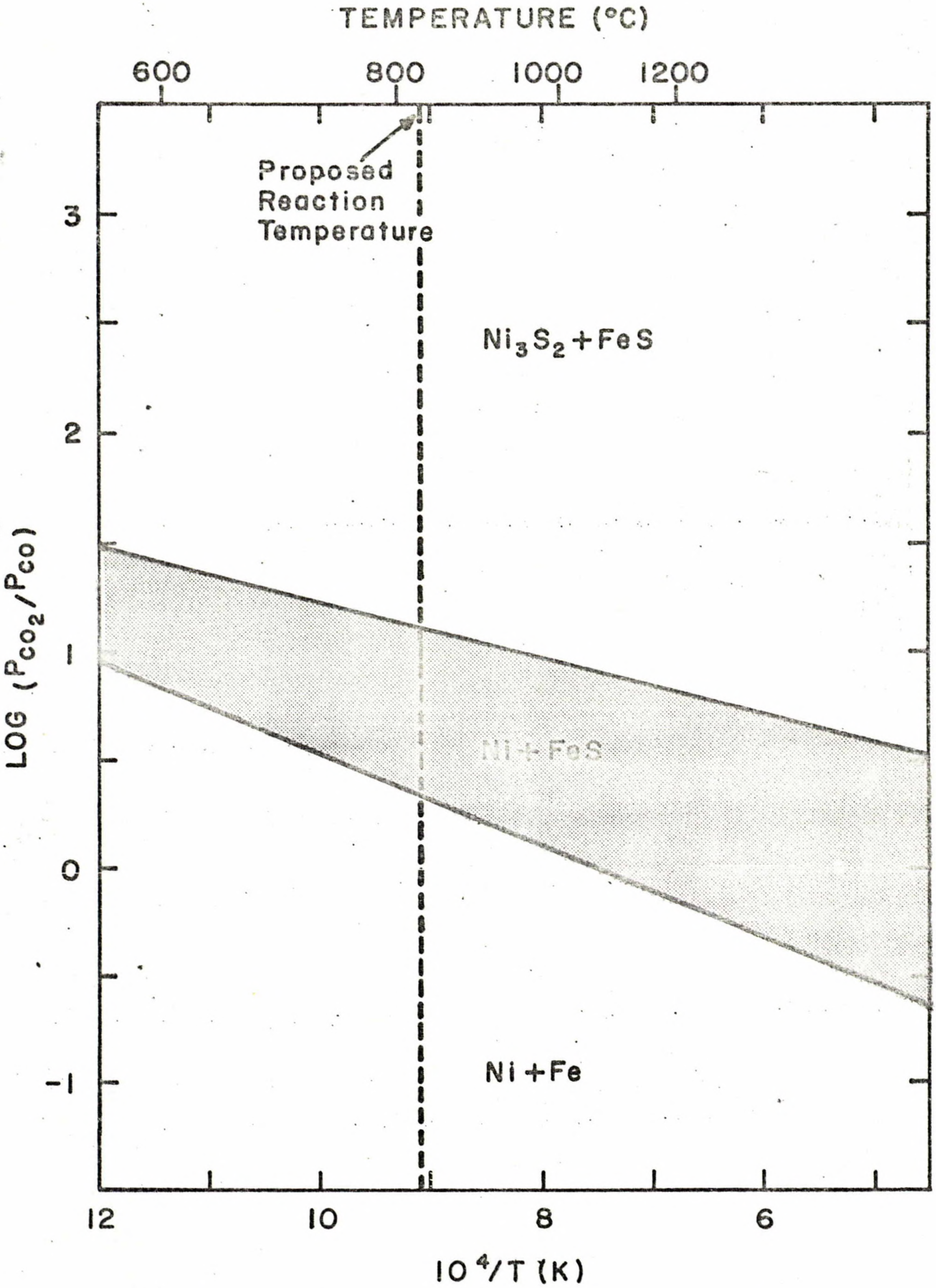

Figure 4: Predominance Area - Reciprocal Temperature Diagram showing the reaction products obtained from the reduction of Ni_3S_2 and FeS in the presence of CaO and CO_2/ CO gas