

THE DECOMPOSITION OF PYRITE AND OTHER
SULPHIDE MINERALS BY SULPHUR CHLORIDE

BY

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ABSTRACT

The reactions of pyrite (FeS_2) and other sulphide minerals with liquid sulphur chloride (S_2Cl_2) have been investigated in an attempt to develop a process for the extraction of metals such as Fe, Pb, Cu, Mo, etc. from sulphide minerals using S_2Cl_2 (with or without dissolved sulphur) as both the solvent and reactant. For this purpose, flotation concentrates and synthetic mineral powders of various particle sizes were reacted at temperatures in the range 40-150°C with S_2Cl_2 containing 0-40 weight percent dissolved sulphur.

Pyrite, chalcopyrite (CuFeS_2) and galena (PbS) reacted with excess S_2Cl_2 to form solid metal chlorides (FeCl_3 , CuCl_2 , PbCl_2) and dissolved sulphur. Pyrite reacts completely with S_2Cl_2 containing 25-40 wt % dissolved sulphur, but only partially with S_2Cl_2 or S_2Cl_2 containing 10 wt % or less of dissolved sulphur. Chalcopyrite was found to react completely with S_2Cl_2 solutions containing 40 wt % S. Galena (PbS) reacts completely with distilled S_2Cl_2 or S_2Cl_2 containing 10 wt % S, and this reaction was found to be catalyzed by the natural impurities silver, antimony, and bismuth. Pyrrhotite (FeS) and a marmatitic zinc concentrate were only partially decomposed by S_2Cl_2 . A series of investigations with sphalerite (ZnS) and molybdenite (MoS_2) indicated that these minerals could not be significantly attacked by S_2Cl_2 .

In all cases, sulphur produced in these reactions can be crystallized in stoichiometric yield by cooling the solvent.

A geometric model for the reactions of pyrite, galena, and chalcopyrite with sulphur chloride has been used to interpret the reaction data and to calculate specific rates and activation energies for the reactions concerned.

On the basis of this investigation, potential processes for the treatment of pyrite, galena and molybdenite are proposed.

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1. INTRODUCTION

1.1 General

Pyrite (FeS_2) ores and concentrates frequently contain significant quantities of non-ferrous metals (e.g. Cu, Pb, Zn, Co, Au, Ag) in forms not amenable to physical concentration (1). Recovery of these metals requires chemical treatment of the entire pyrite concentrate.

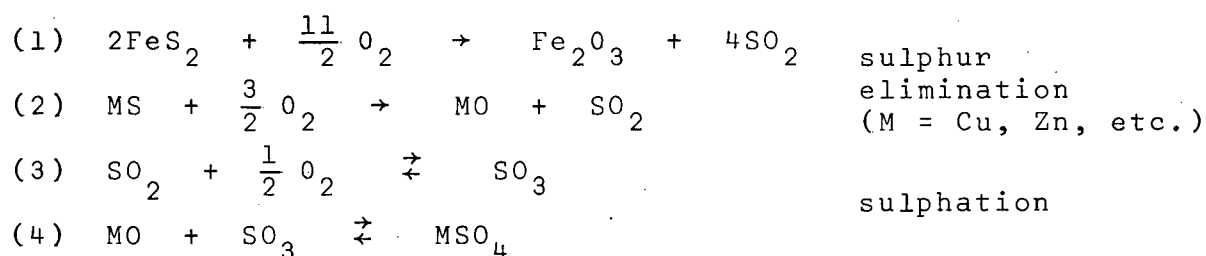
Pyrite is a common mineral, frequently found by itself (2) and adjacent to or interspersed with more valuable sulphides (3) so it is readily available in large quantities. Pyrite is treated in large quantities (4) to produce sulphur dioxide (SO_2) and iron oxide which is used in iron production. Non-ferrous metals associated with pyrite have been recovered by leaching before (5) or after (6,7) roasting, or by volatilization (4,8) of non-ferrous metal chlorides from roasted materials.

A considerable amount of research has been directed towards improvement of processes currently used for pyrite treatment and to development of new processes. Production of elemental sulphur from pyrite has been the subject of many of these studies (9-18).

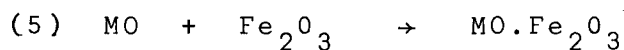
1.2 Methods of Pyrite Treatment

1.21 Roasting

Roasting, followed by acid leaching, is used to treat large amounts of pyritic material. Roasting decomposes sulphides by oxidation to form sulphur dioxide and metal oxides (or sulphates) in the overall reactions:



Dead roasting for complete elimination of sulphur leads to ferrite formation (19) by the reaction:



Ferrites - compounds of the form $\text{MO} \cdot \text{Fe}_2\text{O}_3$ where $\text{M} = \text{Cu, Zn, etc.}$, and usually having a spinel structure - are conventionally termed acid insoluble (more correctly they are very difficult to dissolve) and are an undesirable product of roasting since any non-ferrous metal in the form of ferrite is not recoverable by conventional acid leaching and may make the leached residue unsuitable for use as a raw material in iron production.

Sulphating roasting - selectively sulphatizing non-ferrous metals while retaining iron as the form of ferric oxide - solubilizes more of the non-ferrous metals than dead roasting but also solubilizes some of the iron and frequently leaves some sulphide sulphur in the calcine. Thus, extensive purification of the leach liquor may be required, and the iron oxide residue may be contaminated with sulphur.

To prevent agglomeration, roasting reactions are normally carried out at temperatures below the melting points of the (solid) reactants or products. Thus, protective oxide films may be formed and in some cases (20) roasting reactions proceed slowly, so large capacity reactors are required. Also, material which has been roasted and leached in a finely divided form must be agglomerated (by sintering or pelletizing) before use in conventional iron production.

1.22 Chloridizing Roasting

Chloridizing roasting (6,13,14) is also used in the treatment of pyrite. In this process, pyrite is roasted for sulphur elimination and the calcine is then roasted in the presence of sodium chloride or other low cost source of chlorine. Non-ferrous metal oxides are converted to chlorides and recovered by leaching the chloridized calcine. However, leaching of these calcines has proven difficult (4),

agglomeration of the fine leach residues is required if the residue is to be used for conventional iron production, and a complex leach liquor containing a mixture of metal chlorides and sodium sulphate is produced.

1.23 Chloridizing Volatilization

Chloridizing volatilization (4,8,21) is another method used in the treatment of pyrite calcine. In a process of this type used in Japan (8), pyrite calcine is mixed with calcium chloride, pelletized, dried, and heated in a kiln to chlorinate and volatilize the non-ferrous metal content of the material. This process requires a heating gas low in hydrogen to minimize hydrolysis of calcium chloride at low temperatures where chlorination and volatilization of non-ferrous metals will not occur. Also, this process is best suited to calcines low in sulphur and arsenic since these elements are only partially eliminated.

A substantially different method of chlorinating and volatilizing non-ferrous metals from pyrite calcine is in use in Germany (4). This process uses chlorine gas (Cl_2) to remove non-ferrous metals from pelletized pyrite calcine. In the most recent modification of this process, a shaft furnace with three reaction zones is used. In the first zone, green pellets are dried and indurated by hot combustion gases. In the second zone, non-ferrous metals are removed by a stream of air and chlorine, and in the final

zone the pellets are air cooled. Thus the non-ferrous metals are eliminated in a small, easily treatable volume of gas, green pellets can be charged to the furnace, and sulphur and arsenic removal is not inhibited by addition of calcium to the pellets.

All roasting procedures have a common feature - they convert the pyritic sulphur to sulphur dioxide (SO_2). This product is useful where a local market for sulphuric acid (H_2SO_4) exists. However, where markets for the sulphur product of pyrite processing are far from the processing site, a more desirable product would be elemental sulphur which is more easily transported than sulphur dioxide or sulphuric acid, and is readily converted to other sulphur compounds.

1.24 Hydrometallurgy of Pyrite

1.241 Hydrometallurgical Treatment of Pyritic Material

Hydrometallurgical methods have been used to leach non-ferrous sulphide minerals in the presence of pyrite. Cupriferous pyrites have been heap leached (5) for copper extraction, and copper-, lead-, and zinc sulphides have been leached by aqueous ferric chloride solutions without significant attack on the pyrite present (23,24).

Pyrite can be decomposed in an aqueous environment by leaching under oxygen pressure (18), with chlorine (25,26,27), by bacterial action (28), or electrolytic oxidation (29).

Up to 50% of the sulphur content of pyrite can be converted to the elemental form by leaching in acid under oxygen pressures, but anodic oxidation and bacterial or chlorine leaching converts pyritic sulphur entirely to sulphur (VI) (sulphate or bisulphate). Thus, pyrite can be decomposed in aqueous systems.

Ferric sulphate solutions resulting from oxidizing leaching of pyrite are used in dump or in-situ leaching (28) but otherwise the iron and sulphur products of pyrite leaching are difficult to convert to commercially useful forms.

The difficulty in oxidizing pyritic sulphur to the elemental form in an aqueous system makes pyrite almost unique, since the sulphur content of other sulphide minerals such as pyrrhotite (FeS), chalcopyrite (CuFeS_2), sphalerite (ZnS), galena (PbS) and nickel-cobalt sulphides can be converted to elemental sulphur by aqueous oxidation with solutions containing ferric ion or chlorine (24,26). In contrast, pyritic sulphur apparently cannot be completely converted to the elemental form in aqueous systems.

1.242 Rate Control in Hydrometallurgical Decomposition of Sulphides

The rate controlling steps for aqueous decomposition of sulphides can be grouped into five general classes (30): transfer of oxidant from the gas to the liquid phase,

transport of reactants or products across a diffusion layer, transport of reactants or products through an insoluble film, heterogeneous reaction at the surface, or a combination of these.

When the rate of oxygen transfer from the gas phase into a leaching mixture is rate controlling (i.e. oxygen is consumed as fast as it can be taken into solution) then the rate of the leaching reaction is constant (31).

When transport of a reactant or product across a liquid diffusion layer (Nernst layer) is rate controlling, linear kinetics are observed (26) and the reaction is usually characterized by a low (~ 5 Kcal/mole) activation energy, and a strong dependence of reaction rate on stirring (30). An example of this type of control is the aqueous chlorination of pyrite (25).

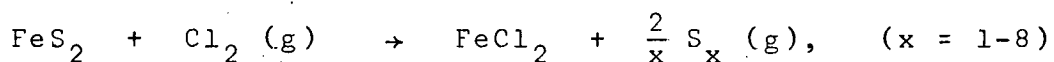
When a reaction product is insoluble in the leaching solution, a protective layer of this insoluble product may be formed on the reacting surface. When this occurs, the reaction can only proceed by diffusion through this layer. Such a diffusion layer has been reported (32) to be the rate controlling mechanism for the decomposition of chalcopyrite in aqueous ferric sulphate solutions. Under these conditions the reaction displays parabolic kinetics, and the rate is insensitive to stirring.

Reactions in which the rate determining step is a heterogeneous surface reaction exhibit high apparent activation energies and are insensitive to stirring (30).

Mixed reaction control occurs when two steps of a reaction proceed at comparable rates at a particular temperature. In this case, a change in temperature can cause a change in the rate determining step. For example, in the aqueous chlorination of galena (33) the reaction rate is transport controlled above 45°C, but at 20°C mixed chemical and transport control is observed.

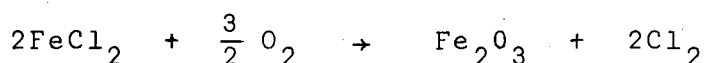
1.25 Chlorination Processes

A direct chlorination process for pyrite treatment has been developed by Hohn et al. (9). In this process, pyrite is reacted with chlorine gas in a fluid bed at a temperature above the boiling point of sulphur. Sulphur is eliminated by the reaction:



Chlorination above the boiling point of sulphur and removal of sulphur from the system as a gas ensures that the reaction cannot be stopped by a layer of solid or liquid sulphur on the surface of the reacting sulphide.

The metal chloride product of this reaction is then oxidized:



to regenerate chlorine and produce a mixture of iron oxide

(Fe_2O_3) and soluble non-ferrous metal chlorides. The only chlorine consumed by the process is that associated with the non-ferrous metals - the remainder recycles within the system.

Problems in this process include the handling of high temperature sulphur vapour, prevention of back mixing through the system, and dust control.

Thermodynamic studies by Pilgrim and Ingraham (34,35) have shown that chlorination of iron-, cobalt-, nickel-, manganese-, lead-, and zinc sulphides by chlorine gas or ferric chloride is thermodynamically favoured and that selective oxidation of iron chlorides to iron oxide and chlorine is thermodynamically feasible.

References to other processes involving chlorination of pyrite or other sulphides with chlorine gas or ferric chloride at temperatures below the boiling point of sulphur are found in the literature (10-18,25,27,36-41), but the problem of separation of the various reaction products appears to be unresolved in many cases. Suggested methods of separation include distillation of product sulphur (36) or ferric chloride (14) from a solid or fused mass of metal chlorides, and combustion of product sulphur (40). Distillation methods require significant amounts of heat input and may pose problems in heat transfer or containment, and combustion of product sulphur produces sulphur dioxide rather than elemental sulphur.

Where an anhydrous metal chloride product is not required, aqueous leaching of the sulphur-metal chloride products of chlorination reactions has been suggested (15) and chlorination of metal sulphides in aqueous solution has been demonstrated (25-27,33,38,39). Anhydrous lead chloride can be produced by chlorination of lead sulphide in hot acid chloride solutions followed by cooling to crystallize lead chloride (33).

However in the chlorination of pyrite, where the recovery of sulphur, iron oxide, and chlorine is desirable, the high temperature process proposed by Hohn et al. appears to present the most practical approach to the problem of separation of products.

1.26 Summary

In general, processes for treatment of pyrite are designed to recover all the valuable components of the mineral in commercially useful forms. The desired products are: iron oxide (free from harmful impurities), a concentrate of non-ferrous metals in a form suitable for further processing, and sulphur in an economically useful form.

For future pyrite processing plants, production of elemental sulphur (from pyrite) may be desirable, since elemental sulphur is easily transportable and can be readily converted into other forms. Decomposition of pyrite (or solubilization of non-ferrous metals) at a faster rate than

that attainable with present roasting methods would also be desirable.

All the processes described above are useful in the production of sulphur (or its derivatives) and metals from pyrite. However, most of these processes have problems associated with them.

1.3 Background to the Present Investigation

1.31 Low Temperature Chlorination of Pyrite

An appealing route to the production of elemental sulphur, iron oxide, and a non-ferrous metal concentrate from pyrite seemed to be via low temperature chlorination of pyrite to metal chlorides and (low temperature) separation of sulphur. The second stage of such a process would be selective oxidation of iron chlorides to iron oxide and chlorine for recycle. Non-ferrous metal chlorides would not be oxidized and could be separated from iron oxide by volatilization or leaching. Chlorination of pyrite in aqueous solution converts the entire sulphur content of the mineral to sulphur (VI) (26) so use of a non-aqueous solvent seemed appropriate.

Initially, samples of a pyrite flotation concentrate were reacted with chlorine dissolved in carbon tetrachloride (CCl_4). This work showed that pyrite is reactive to chlorine at low temperatures in a non-aqueous environment, but the pyritic sulphur was converted to sulphur chloride

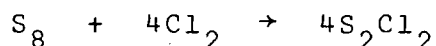
(S₂Cl₂) rather than elemental sulphur.

The properties of sulphur chloride (cf. next section) suggested that this material might be a good solvent and reactant for the desired reaction - conversion of pyrite into metal chlorides and elemental sulphur.

1.32 Properties of Sulphur Chlorides

1.321 Chemical and Physical Properties of Sulphur Chlorides

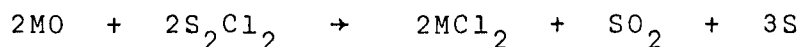
Sulphur Chloride (S₂Cl₂) is conveniently prepared by contacting chlorine gas and elemental sulphur:



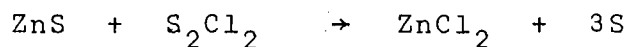
and may be purified by fractional distillation (42). Some physical properties of sulphur chloride (42,43) are: melting point -82°C, boiling point 138°C, specific gravity (20°C) 1.6733, heat of vaporization 64.6 cal/g, surface tension (22°C) 40.78 dynes/cm, viscosity (18°C) 2.015 cps.

In the vapour phase, sulphur chloride has the structure Cl-S-S-Cl (44). The S-S and S-Cl bond lengths are 2.5A., and 1.99A. The S-S-Cl angle is 103° and the molecule is twisted out of plane giving it a structure similar to that of hydrogen peroxide.

Sulphur Chloride is reported (45) to react with metal oxides:



and sulphides:



and is readily hydrolyzed (44) to sulphur, sulphur dioxide, and hydrogen chloride, but is miscible with nonpolar solvents such as carbon tetrachloride and ethylene chloride. Sulphur chloride forms at least one adduct with a Lewis acid - $\text{AlCl}_3 \cdot 2\text{S}_2\text{Cl}_2$ but this material decomposes on heating to $\text{AlCl}_3 \cdot \text{S}_2\text{Cl}_2$ (46). Reaction of sulfanes (HS_nH) with sulphur chloride (42) produces chlorosulphanes (S_nCl_2 , $n = 3-8$) by reactions of the form:



These chlorosulphanes are unstable and sensitive to impurities.

Chlorination of sulphur chloride produces sulphur dichloride - S_2Cl_2 . Impure sulphur dichloride is unstable even at room temperature with respect to decomposition to sulphur chloride and chlorine but it can be distilled at 59.5°C (760mm Hg) after adding 0.5% phosphorus pentachloride to the impure mixture (42).

Sulphur dichloride forms a variety of compounds with

Lewis acids - e.g. $\text{AlCl}_3 \cdot \text{SCl}_2$, $\text{FeCl}_3 \cdot \text{SCl}_2$, $\text{SbCl}_5 \cdot \text{SCl}_2$ (46).

The suggested structure of these compounds is of the type $\text{SCl}^+ \text{AlCl}_4^-$.

Addition of chlorine to sulphur dichloride at low temperature produces yellow crystals of sulphur tetrachloride (SCl_4) which decompose dissociatively above -31°C (44).

1.322 Sulphur - Sulphur Chloride Solutions

Sulphur is miscible with sulphur chloride at temperatures above the melting point of sulphur and extensively soluble below this temperature. The solubility of sulphur in sulphur chloride in the temperature range 0°C - 119.5°C (determined by Aten(47)) is shown in Appendix H. Experiments using labelled (radioactive) sulphur (48) have shown that above 100°C there is a significant amount of exchange of sulphur between dissolved sulphur and sulphur chloride. However, the instability of chlorosulphanes (42) (cf. previous section) suggests that the species in solution are primarily molecules of sulphur (S_8) and sulphur chloride.

Also, from the ideal solution model of Glasstone (49) when the solution is treated as consisting only of S_2Cl_2 and S_8 molecules the predicted solubility (Appendix H) is sufficiently close to the experimental values to justify treating the system as essentially ideal. In calculating the ideal solubility of sulphur in sulphur chloride the thermodynamic data of Meyer (50) were used. The

physical properties of the various forms of elemental sulphur are quite complex and are fully discussed by Meyer (50).

1.323 Physiological Properties of Sulphur Chloride

Sulphur chloride and sulphur dichloride both have revolting odours and are classified as acute respiratory irritants (51). The maximum permissible level of exposure to sulphur chloride vapour is 1 ppm over eight hours.

1.33 Thermodynamics of Chlorination of Metal Sulphides

Table 1 summarizes the calculated enthalpy and free energy changes (at 25°C) for the reactions of common sulphide minerals with sulphur chloride.

1.34 Thermodynamics of Oxidation of Metal Chlorides

Selective oxidation of iron chlorides to iron oxide and chlorine (without conversion of non-ferrous metal chlorides to oxides) is an integral part of the scheme proposed in 1.31.

Table 1: Enthalpy and Free Energy Values for Reactions of
Selected Metal Sulphides with S_2Cl_2 *

Reaction	ΔH° (Kcal)	ΔF° (Kcal)
$FeS_2 + \frac{3}{2} S_2Cl_2 \rightarrow FeCl_3 + 5S$	-32.7	-31.7
$FeS + \frac{3}{2} S_2Cl_2 \rightarrow FeCl_3 + 4S$	-52.5	-58.5
$CuS + S_2Cl_2 \rightarrow CuCl_2 + 3S$	-26.3	-24.4
$PbS + S_2Cl_2 \rightarrow PbCl_2 + 3S$	-48.9	-47.0
$ZnS + S_2Cl_2 \rightarrow ZnCl_2 + 3S$	-36.5	-35.0
$Ag_2S + S_2Cl_2 \rightarrow 2AgCl + 3S$	-38.7	-36.9
$MoS_2 + \frac{5}{2} S_2Cl_2 \rightarrow MoCl_5 + 7S$	+ 0.7	+ 4.0

*Values calculated from data of Latimer (52) at 25°C.

Free energy values and equilibrium constants for the reactions of ferric chloride and other metal chlorides with oxygen at 700°K have been calculated using the data of Glassner (53). (Note that at temperatures up to about 900°K ferric chloride vapour consists predominantly of the dimer Fe_2Cl_6 (54)). The calculated values are presented in Table 2.

Table 2: Calculated Free Energy of Oxidation for Selected Metal Chlorides at 700°K*

Reaction	ΔF_{700}° (Kcal)	$\log_{10} K$
$\text{Fe}_2\text{Cl}_6 \text{ (g)} + \frac{3}{2} \text{O}_2 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{Cl}_2$	-31	+9.6
$\text{CuCl}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CuO} + \text{Cl}_2$	+ 5	-1.55
$\text{PbCl}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{PbO} + \text{Cl}_2$	+28	-8.7
$\text{ZnCl}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{ZnO} + \text{Cl}_2$	+ 9	-2.8
$\text{NiCl}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NiO} + \text{Cl}_2$	+ 3	-0.9

*Values calculated from the data of Glassner (53) at 700°K.

For the reaction of ferric chloride,

$$K = \frac{a_{\text{Fe}_2\text{O}_3} P_{\text{Cl}_2}^3}{P_{\text{Fe}_2\text{Cl}_6} P_{\text{O}_2}^{3/2}} = 10^{9.6}$$

If $P_{\text{Fe}_2\text{Cl}_6}$ is arbitrarily set at 0.01 (corresponding to 1% carryover of ferric chloride in a continuous process), the calculated equilibrium P_{O_2} (at $P_{\text{Cl}_2} = 1$ atmosphere) is $10^{-5.07}$. Thus very little oxygen will be introduced into the chlorination reactions, and the high P_{Cl_2} value will suppress oxidation of non-ferrous metal chlorides.

Experiments performed by Hohn et al. (9) have

qualitatively confirmed the predicted equilibrium in the oxidation of ferric chloride and shown the reaction to be fast at 700°K-800°K.

1.4 Objectives

Liquid sulphur chloride has never been seriously investigated as a process reagent for extractive metallurgy. The main purpose of this study was to determine conditions under which the properties of sulphur chloride as a sulphur solvent and chlorinating agent could be used in processing sulphide concentrates for the extraction of metals and sulphur. In particular, it was desired to find conditions under which specific minerals could be completely decomposed by sulphur chloride, to collect and interpret reaction rate data, and to determine the nature of the metal chloride and sulphur products of such reactions. Other specific objectives were: to determine the effect of particle size on reaction rates, the effect (if any) of mineral impurities on the rate and extent of reaction, the relative reactivities of minerals of different geographical origin and/or chemical composition, and the effect of reaction products on the rate and extent of reaction.

The determination of reaction paths was not a primary aim of this study.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Natural Sulphide Minerals

With a few exceptions, the experiments to be described were done on natural sulphide minerals in the form of flotation concentrates. The natural minerals which have been studied are pyrite (FeS_2), pyrrhotite (FeS), chalcopyrite (CuFeS_2), galena (PbS), sphalerite (ZnS) and molybdenite (MoS_2). The sources and chemical analyses of these minerals are presented in Appendix A.

Natural minerals were used for two reasons: any industrial application of the methods developed in this study would involve treatment of natural minerals (probably in the form of flotation concentrates), and natural minerals frequently differ in reactivity from synthetics since the latter have not been annealed over geologic time periods (32).

2.1.2 Synthesis of Minerals and Chemicals

In the course of this study some chemicals (sulphur chloride and anhydrous ferrous chloride) and synthetic

minerals (lead sulphide and low-sulphur pyrrhotite) were prepared in the laboratory. The methods of preparation and chemical analyses of these materials are discussed below.

The sulphur chloride used in this study was prepared by passing chlorine gas through a glass diffuser into sulphur-sulphur chloride mixtures. Purification was done by distillation at $137 (\pm 1)^{\circ}\text{C}$. A small amount of fore-run (at the distillation temperature) was discarded from each batch. The average composition of several lots of this material was 47.5 weight percent (wt %) sulphur and 52.4 wt % chlorine. These results are in good agreement with the theoretical composition of 47.4 wt % S and 52.6 wt % Cl. For experiments using sulphur-sulphur chloride ($\text{S.S}_2\text{Cl}_2$) solutions, weighed quantities of sulphur and sulphur chloride were mixed and heated to dissolve the sulphur.

Anhydrous ferrous chloride (FeCl_2) was used to investigate the possibility that ferrous chloride might be an intermediate product in the reaction of iron sulphide minerals with sulphur chloride. This material (FeCl_2) was prepared by heating reagent grade hydrated ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) to 400°C in a stream of dried hydrogen chloride gas. The product contained 46.0 wt % Fe and 53.8 wt % Cl (vs theoretical values of 46.1 wt % Fe and 53.9 wt % Cl).

Synthetic lead sulphide (PbS) - used to study the reactions of lead sulphide in the absence of impurities found in the natural mineral - was prepared by heating

powdered test lead and excess sulphur at 500°C in a muffle furnace. The covered crucible containing the lead-sulphur mixture was packed with charcoal in a larger crucible to minimize oxidation of the charge. The analysis of the product was 87.0 wt % Pb and 12.9 wt % S (vs theoretical values of 86.7 wt % Pb and 13.3 wt % S).

A low-sulphur artificial pyrrhotite (FeS) was prepared by passing hydrogen gas through a sample of Sullivan pyrite (Appendix A) for two hours at 550°C. The solid residue from this treatment contained 60.5 wt % Fe and 35.7 wt % S (vs theoretical values of 63.5 wt % Fe and 36.5 wt % S in stoichiometric, pure FeS).

2.13 Other Materials

Other materials - chemicals, metals, and solvents - used in this study are listed according to grade in Appendix B.

2.2 Experimental Methods and Apparatus

2.21 Sample Preparation

Mineral concentrates were carefully sized by screening before use. Pyrrhotite (both natural and synthetic) was dry-screened to minimize surface oxidation. All other minerals were screened wet and dry to eliminate fine material. After sizing, the mineral samples were washed in acetone and air dried. To obtain reproducible results with galena, it was necessary to wash each sample with hot sodium

chloride solution (followed by water and acetone) before leaching. Other minerals showed no difference in reactivity after long periods of air exposure.

2.22 Experimental Apparatus and Procedure

Leaching experiments were done in the apparatus shown schematically in Figure 1. A covered 250 cc pyrex electrolytic beaker contained the reaction mixture and a Teflon coated magnetic stirring bar. Agitation and basal heating were provided by a Corning heater-stirrer (model PC 351). Temperature control was maintained by a Thermistemp temperature controller and probe (Yellow Springs Instrument Co. models 71 and 403 respectively). A small indentation was made in the lip of the beaker to allow the probe to be partially immersed in the reaction mixture. Variable heating was done by an infrared lamp connected via a voltage regulator to a relay in the temperature controller.

All leaching experiments were done in a fume hood to prevent sulphur chloride vapour from entering the laboratory area.

For experiments to test the effect of more violent agitation on reaction rates, stirring was done by a 1 1/4 inch diameter stainless steel impeller mounted on a variable speed electric motor, and two 1/2 inch radial baffles were inserted at opposite sides of the beaker.

For an individual experiment, the solvent (usually 300 g) was brought to temperature and a small (usually 1-2 g)

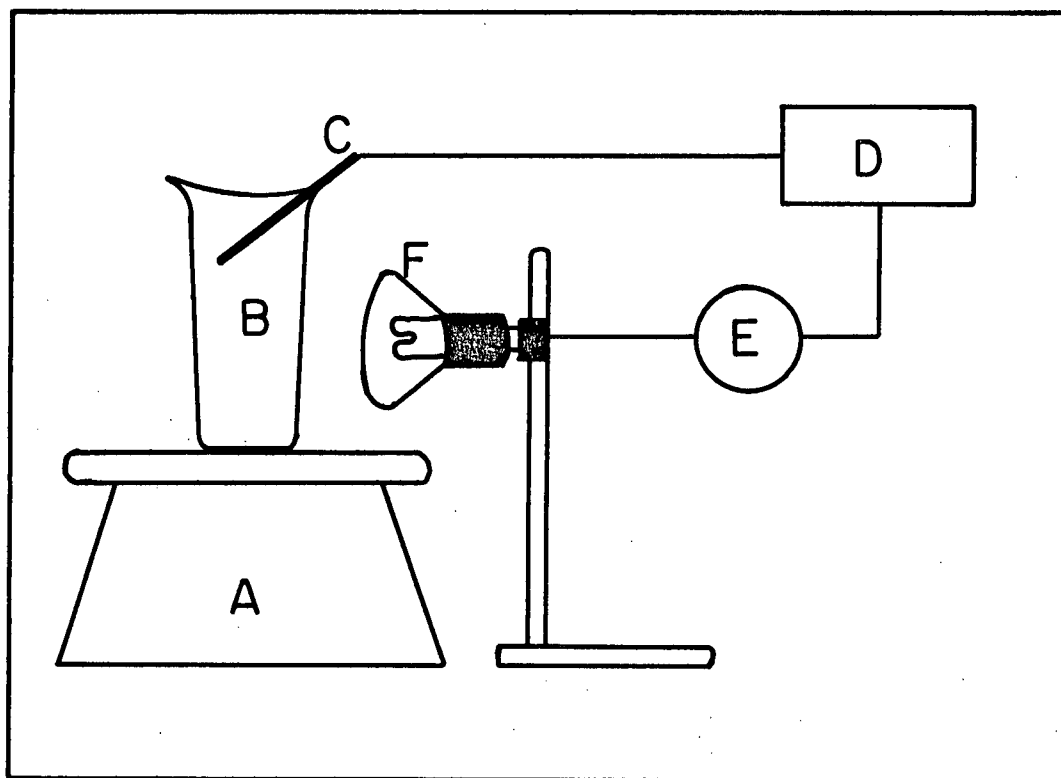


Figure 1: Schematic Diagram of the Experimental Apparatus

- A. Heater -magnetic stirrer.
- B. Covered 250 cc electrolytic beaker containing the reaction mixture and a stirring bar.
- C. Temperature probe.
- D. Temperature controller.
- E. Power supply for heating lamp.
- F. Infrared heating lamp.

sample of solids was added. When the pre-determined time had elapsed, the beaker was lifted off the hotplate and let stand for fifteen seconds to settle the solids. Excess solvent was then decanted (selected samples being retained for analysis) and the residue washed in the beaker with carbon tetrachloride, carbon disulphide, acetone, and water. Finally, the solids were transferred to a sintered glass crucible, rinsed with acetone, dried briefly in an oven at 80°C, and weighed. Galena samples required a double wash with hot salt solution to remove product lead chloride, but all other residues were washed clean by the solvent sequence given. The carbon tetrachloride wash chilled the residue to room temperature and diluted the sulphur chloride in the residue, carbon disulphide removed elemental sulphur and any remaining sulphur chloride; acetone and water removed metal chlorides, and the final acetone rinse facilitated drying of the residues.

Iron metal and monel alloy were treated with sulphur chloride solutions to investigate their reactivities in these solutions. Solid metal specimens were suspended in the solution by a nickel plated test-tube holder or supported on a bent glass rod.

2.3 Analytical Methods

In the course of the investigation it was necessary to develop analytical methods for sulphur and chlorine in

sulphur chloride, and for chlorine in low concentrations in sulphur.

Chlorine in S_2Cl_2 and in sulphur was determined by dissolving a weighed sample of the unknown in CS_2 , adding aqueous sodium acetate (NaOAc) solution and heating to boil off the CS_2 and hasten the hydrolysis of S-Cl compounds. When the CS_2 had evaporated, the mixture was filtered, the sulphur broken up and washed. The cycle was repeated to ensure complete extraction of chloride into the aqueous phase. The resulting solution - buffered by NaOAc at pH 7 - was diluted to volume and aliquots were titrated with 0.1 or 0.001 N silver nitrate solutions using a drop of saturated potassium chromate solution as indicator.

Sulphur in S_2Cl_2 was determined by dissolving a weighed sample of the unknown in chlorine saturated CCl_4 and hydrolyzing this solution with dilute sodium hydroxide. Chlorine was added in excess to ensure complete conversion of sulphur to sulphate. The resulting aqueous solution was acidified and boiled. Sulphate was precipitated with barium chloride solution, filtered, ignited, and weighed as barium sulphate.

Loss of sulphur or chlorine during analysis was found to be negligible since %S + %Cl values totalled $100 \pm 0.4\%$ in all cases where both elements were determined.

Ferrous and total iron determinations were done by titration with standard cerium(IV) sulphate solution using

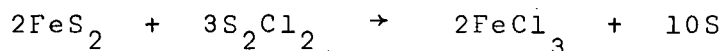
(1,10)-o-phenanthroline indicator. Reduction of ferric iron for total iron determination was done by boiling the sample with test lead in hydrochloric acid solution.

3. RESULTS AND DISCUSSION

3.1 Decomposition of Pyrite and Related Compounds by Sulphur Chloride

3.1.1 Reaction of Pyrite with Sulphur Chloride

The stoichiometry of the reaction of pyrite with distilled sulphur chloride was determined (See Appendix C-1) to be:



However, as shown in Figure 2, this reaction does not go uniformly to completion. The extent to which the reaction occurs (in a constant weight of sulphur chloride) was found to be dependent on the size of the initial pyrite sample at temperatures up to the boiling point of pure sulphur chloride.

A protective layer of product ferric chloride on the mineral surface was suspected to be the cause of the incomplete reaction. The presence of anhydrous ferric chloride (added as reagent or as the product of a previous reaction) was found to decrease the extent of reaction. The results

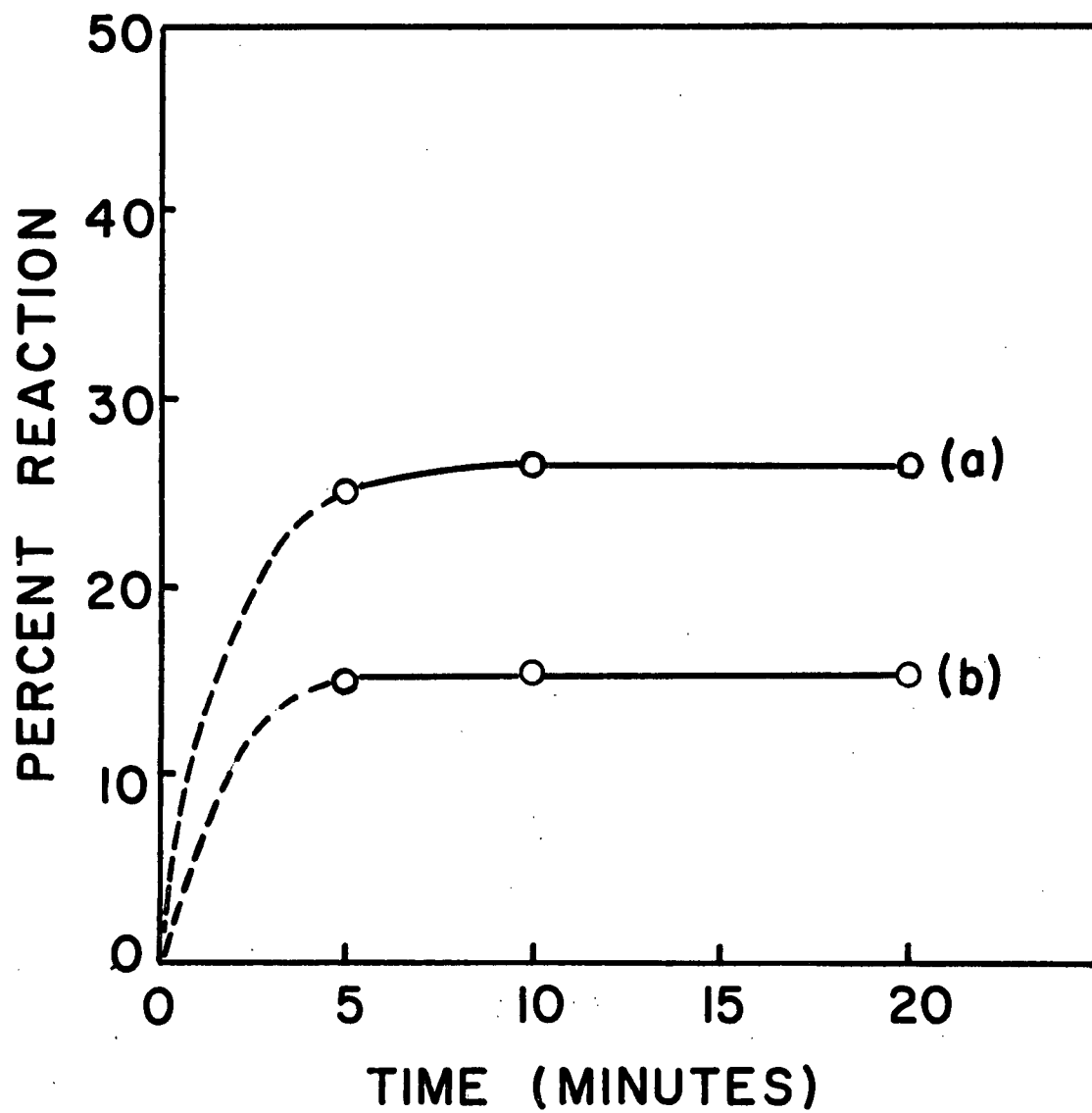


Figure 2: Reaction of Pyrite with Pure Sulphur Chloride at 133°C.

(a) 1 g FeS_2 in 300 g S_2Cl_2

(b) 2 g FeS_2 in 300 g S_2Cl_2

of these experiments were quite non-reproducible, but the extent of reaction when ferric chloride was present in the initial reaction mixture was always less than that with pure sulphur chloride. No ferric chloride film could be visually detected on the surface of massive polished pyrite specimens after reaction in sulphur chloride since any solvent which removed the adhering liquid layer left a clean sulphide surface.

The possibility of a protective layer of ferrous chloride (a possible reaction intermediate) on the sulphide surface was investigated by determining the amount of ferrous iron in the (dilute) acid soluble material associated with the solid reaction residue. No significant amount of iron (II) was found, indicating that no substantial amount of iron (II) chloride is associated with the mineral surface.

The incomplete reaction of pyrite in pure sulphur chloride is discussed in relation to the reactions of other materials in Section 3.162.

Since it was desired to find conditions under which pyrite could be completely decomposed, the reaction conditions were changed by addition of sulphur to the sulphur chloride reactant. The original purpose of this addition was to raise the boiling point of the reaction mixture, thus extending the temperature range available without using a pressurized reactor. However, the presence of dissolved sulphur in sulphur chloride was found to have a strong effect

on the reaction of sulphur chloride with pyrite at all temperatures investigated (110-150°C). This effect is discussed below.

3.12 Reaction of Pyrite with Sulphur-Sulphur Chloride Solutions

3.121 Effect of Dissolved Sulphur

The extent to which pyrite reacts with sulphur chloride was found to be strongly affected by the presence of dissolved sulphur in the sulphur chloride. Experimental results (Figure 3) showed that increasing the dissolved sulphur content of sulphur chloride leads to more complete reaction and that in 25 wt % sulphur-75 wt % sulphur chloride (25 wt % $S.S_2Cl_2$) and 40 wt % $S.S_2Cl_2$ solutions, the reaction goes uniformly to completion. From the results of Figure 3, it appears that there is a critical level (in the range of 10-25 wt %) of dissolved sulphur above which the reaction goes to completion, and that in the composition range 25-40 wt % $S.S_2Cl_2$ the rate and extent of the reaction are not significantly affected by the amount of dissolved sulphur.

The solvent composition chosen for further work on pyrite decomposition was 40 wt % $S.S_2Cl_2$, in which pyrite was found to react uniformly to completion. This solution has a higher boiling point than 25 wt % $S.S_2Cl_2$ (thus extending the temperature range available without pressure above atmospheric), and has a lower vapour pressure than pure

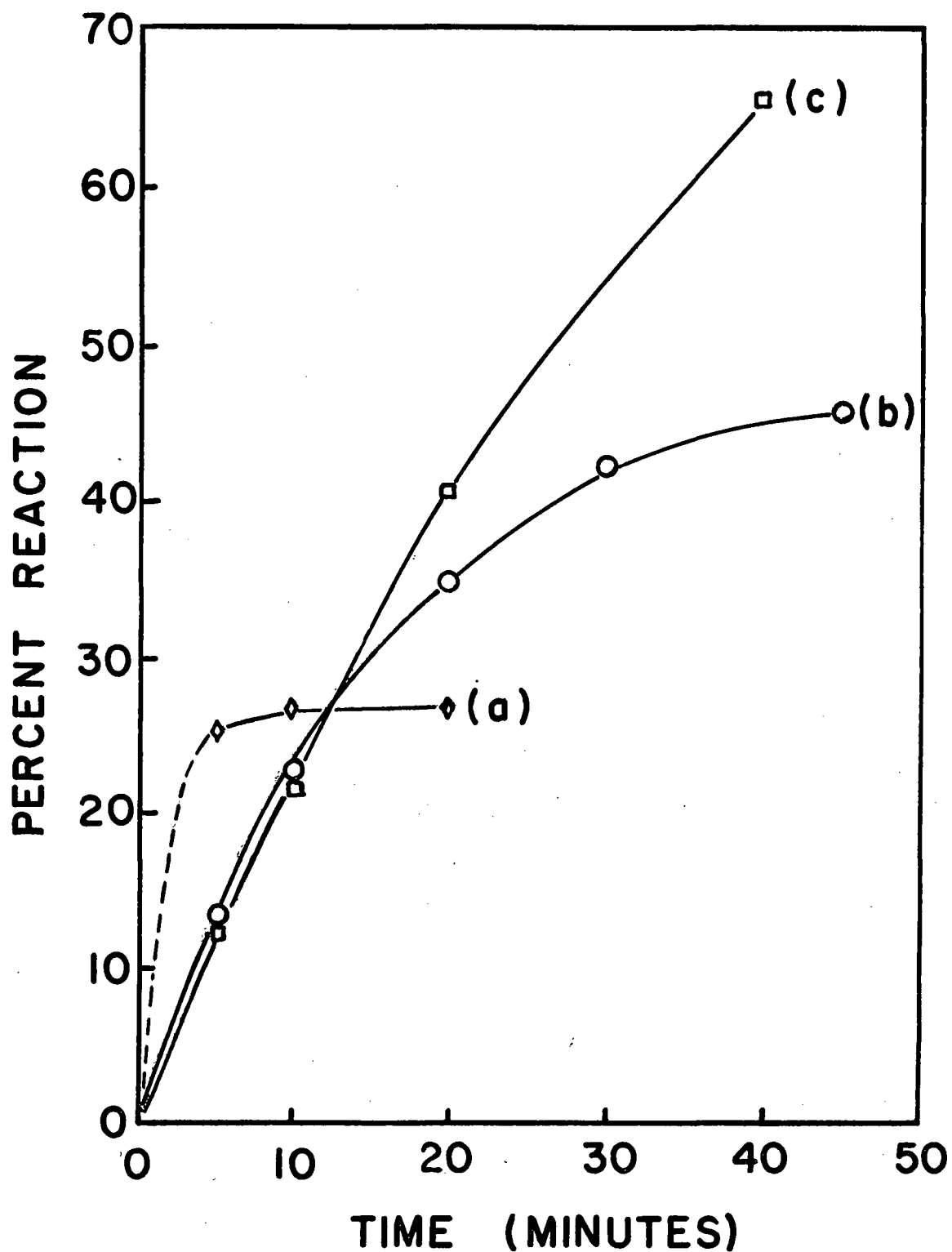


Figure 3: Effect of Dissolved Sulphur on the Reaction of Pyrite with Sulphur Chloride at 133°C (Substrate: -70 + 100 mesh Sullivan FeS₂)

(a) 1 g FeS₂ in 300 g S₂Cl₂

(b) 1 g FeS₂ in 300 g 10 wt % S.S₂Cl₂

(c) 1 g FeS₂ in 300 g 25 or 40 wt % S.S₂Cl₂

sulphur chloride. Also, in an industrial application of sulphur chloride decomposition of sulphides, a high level of dissolved sulphur would be desirable to minimize the amount of cooling necessary to crystallize product sulphur. For the small pyrite samples used in these experiments, the composition (S:Cl ratio) of the solvent is essentially constant since complete reaction of the substrate in the quantity (300 g) of solvent used changed the chlorine content of the solvent by less than 1%.

3.122 Effect of Stirring on the Reaction Rate

Experiments with various rates of stirring in the apparatus shown in Figure 1 showed that the rate of reaction of pyrite in 40 wt % S_2Cl_2 was independent of the stirrer speed once all solids were in suspension. To test the effect of more violent agitation, the apparatus of Figure 1 was modified by the insertion of baffles and the use of a variable speed impeller. The results (Figure 4) show the same limiting rate as with magnetic stirring and the same requirement for complete suspension of the particles to reach this limiting rate.

3.123 A Geometric Model of the Reaction

Microscopic examination of the pyrite concentrate (Figure 8) indicated that the individual particles were (roughly) equiaxed, and the form of the plot of percent

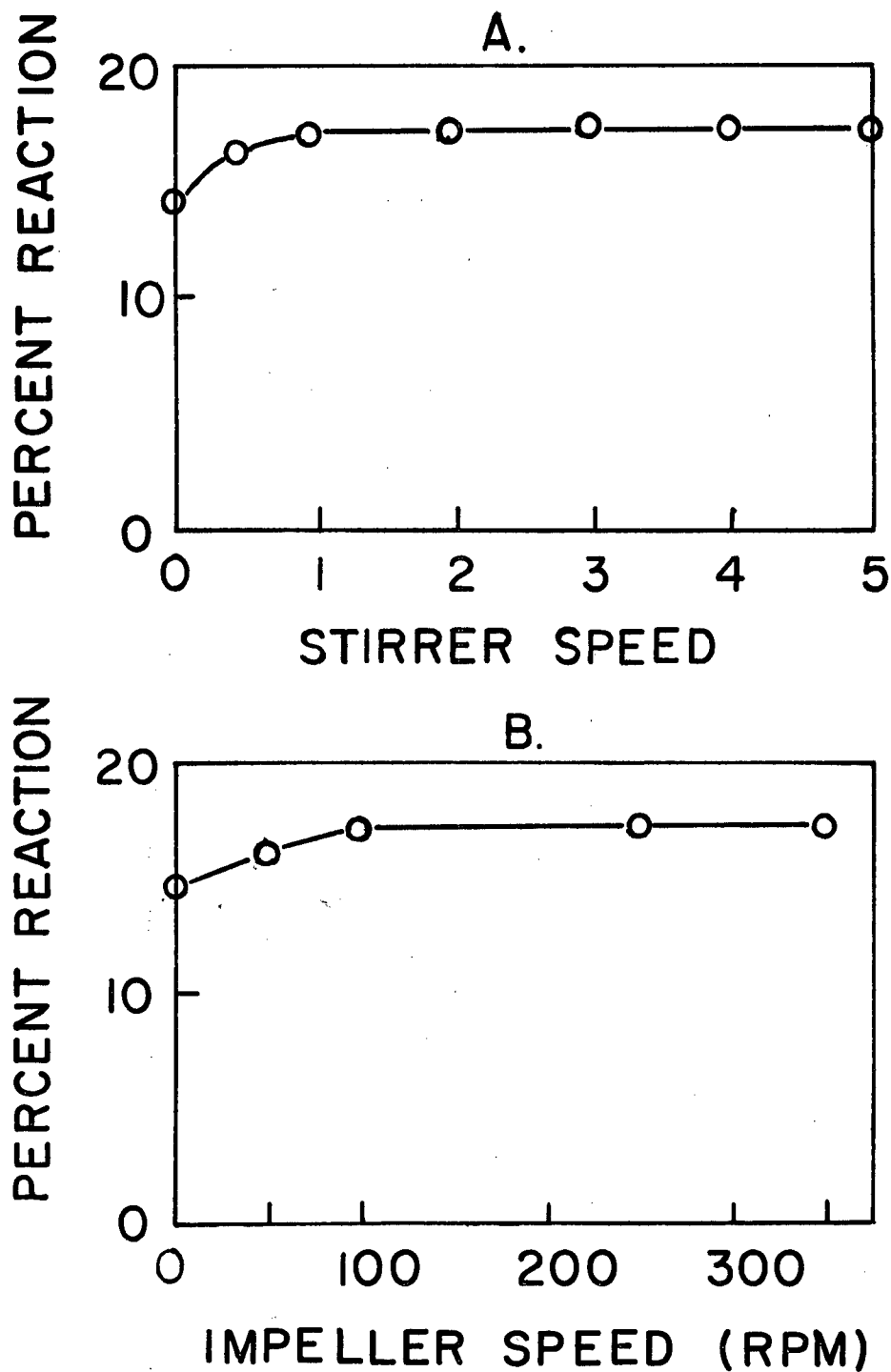


Figure 4: The Effect of Stirring on the Rate of Reaction of FeS_2 with 40 wt. % S_2Cl_2 . ("Stirrer Speed" refers to control dial setting.)

A. Agitation by Magnetic Stirring Pellet. All Solids Suspended at Stirrer Speed = 1.

B. Agitation by Impeller with Baffles. All Solids Suspended at Impeller Speed = 100 rpm.

Conditions: $T = 126.2^\circ\text{C}$, substrate: -70 + 100 m Sullivan FeS_2
Reaction time = 10 minutes in all cases

reaction vs. time appeared to be consistent with a constant rate of decomposition (per unit area) of the particles. An equation describing the reaction of an equiaxed particle when the interface velocity of the reacting surfaces is constant can be derived as follows:

Consider a roughly equiaxed particle having a volume αr_o^3 where r_o is the initial radius and α is a constant. If the particle reacts at a rate which is constant per unit of surface area, then

$$\frac{-dr}{dt} = k \quad \text{or} \quad r = r_o - kt$$

if the fraction of the particle reacted at time t is R then

$$(1-R) = (\text{fraction unreacted}) = \frac{\alpha r^3}{\alpha r_o^3} = \left(\frac{r_o - kt}{r_o}\right)^3 = \left(1 - \frac{kt}{r_o}\right)^3$$

therefore

$$(1-R)^{1/3} = 1 - \frac{kt}{r_o} \quad \text{or} \quad r_o[1-(1-R)^{1/3}] = kt.$$

If a plot of the function $r_o[1-(1-R)^{1/3}]$ vs. time is linear, this indicates that the reaction rate is constant per unit of surface area. The function can be used for a single particle or a group of equally sized particles. In this case it is used for a group of narrowly sized particles (between two screen sizes).

Values of r_o were calculated for each screen size

fraction. For a particular size fraction, the value of r_o calculated by several methods (55) varies by < 4%.

The experimental data were then plotted in the form $r_o[1-(1-R)^{1/3}]$ vs t . The values of r_o were calculated from the geometric mean of the screen dimensions. (Appendix D-4)

3.124 Results of Experiments on Sullivan Pyrite

Samples of Sullivan pyrite (Appendix A) of various screen sizes were reacted in 40 wt % $S.S_2Cl_2$ over a range of times and temperatures. Representative plots of percent reaction vs time for these reactions are shown in Figure 5.

The experimental data were then plotted in the form $r_o[1-(1-R)^{1/3}]$ vs time. Figure 6 shows a representative sample of such plots for the reaction of Sullivan pyrite with 40 wt % $S.S_2Cl_2$. Since the starting material had a range of sizes, it is to be expected that after 65 % reaction the smallest of the original particles will have reacted completely. This effect is shown in Figure 5 (plot for 129°C).

No attempt was made to compute a shape factor, so the rates calculated from the slopes of $r_o[1-(1-R)^{1/3}]$ vs time will be subject to some correction factor to be accurate in absolute terms.

Table 3 summarizes the results of these experiments in terms of the calculated interface velocities (rates of

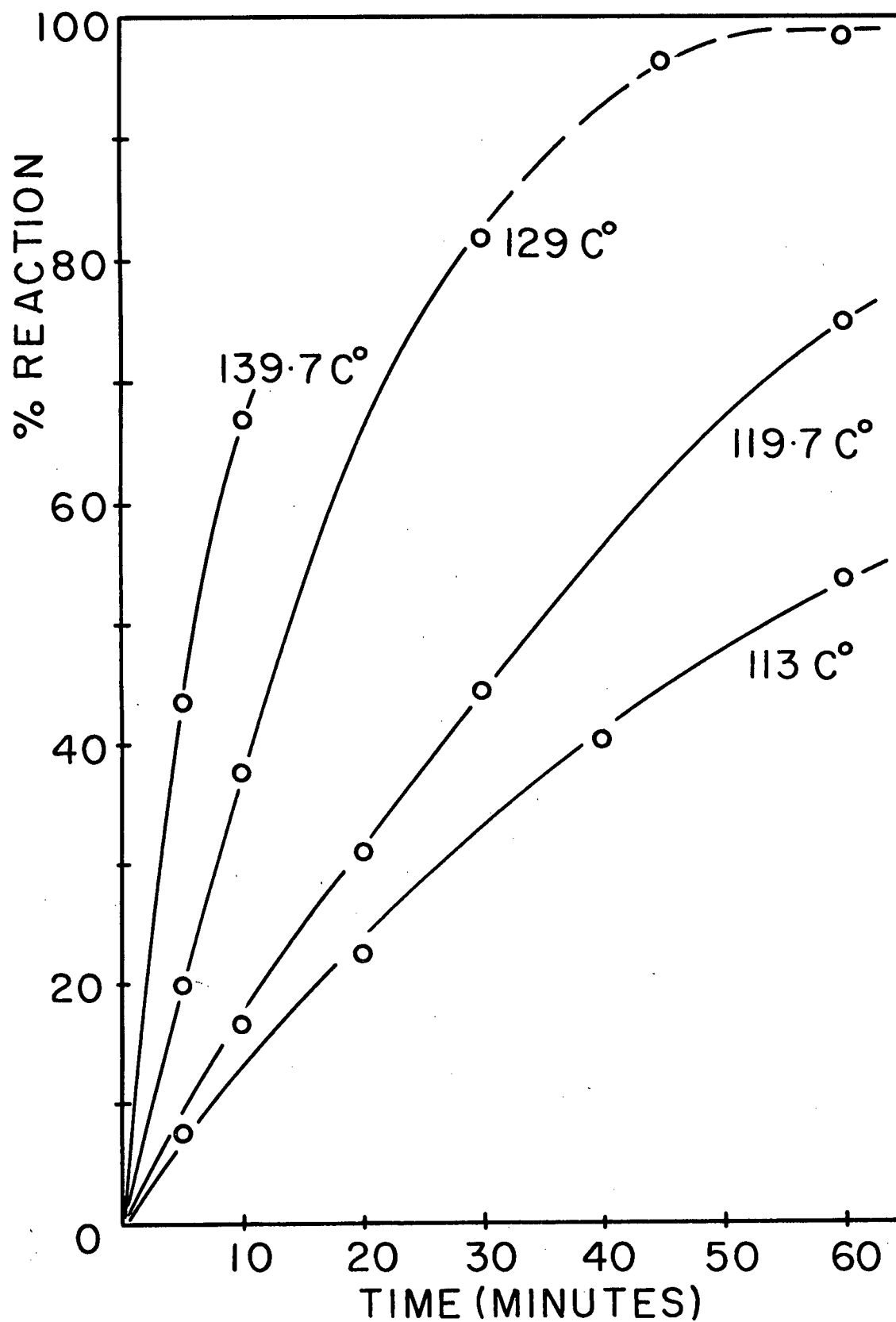


Figure 5: Reaction of -200 + 270 m Sullivan FeS_2 with 40 wt. % $\text{S.S}_2\text{Cl}_2$.

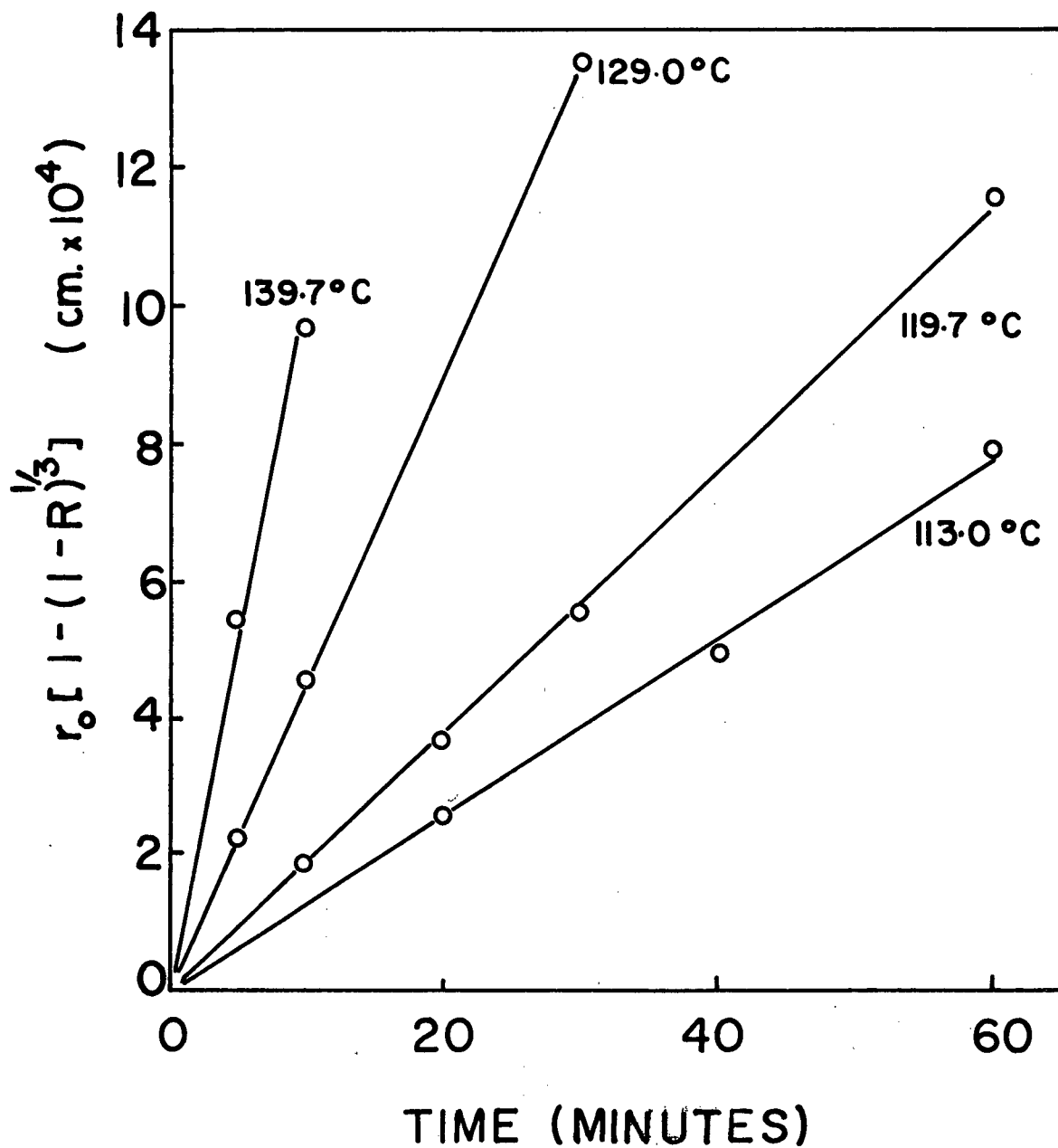


Figure 6: Plot of $r_o[1-(1-R)^{1/3}]$ vs Time for the Reaction of -200 + 270 m Sullivan FeS_2 in 40 wt % S_2Cl_2

Table 3: Rates of Reaction of Sullivan Pyrite with
40 wt % S.S₂Cl₂ (reaction rates expressed as
rate of penetration of the solid (cm min⁻¹ x 10⁵))

Screen Size Fractions	-70 + 100m		-200 + 270m		-270 + 325 m	
	T(°C)*	rate	T(°C)	rate	T(°C)	rate
	113.0	2.01	113.0	1.29		
	120.0	3.14	119.7	1.86	119.9	2.15
	126.2	5.38				
			129.0	4.49		
	133.0	8.70				
	139.7	12.6	139.7	10.2		
	146.9	19.2				

* Small variations in measured temperatures are due to drift of the temperature controller over the period of experimentation.

penetration) for three screen size fractions of the Sullivan pyrite concentrate. These rates were calculated from the slopes of plots of the form of Figure 6.

It is suggested that the different rates for the various size fractions at the same temperature may be due to different shape factors or different particle size distributions within the screen fractions, or to crevice corrosion (Figure 7) which exposes more area to attack and

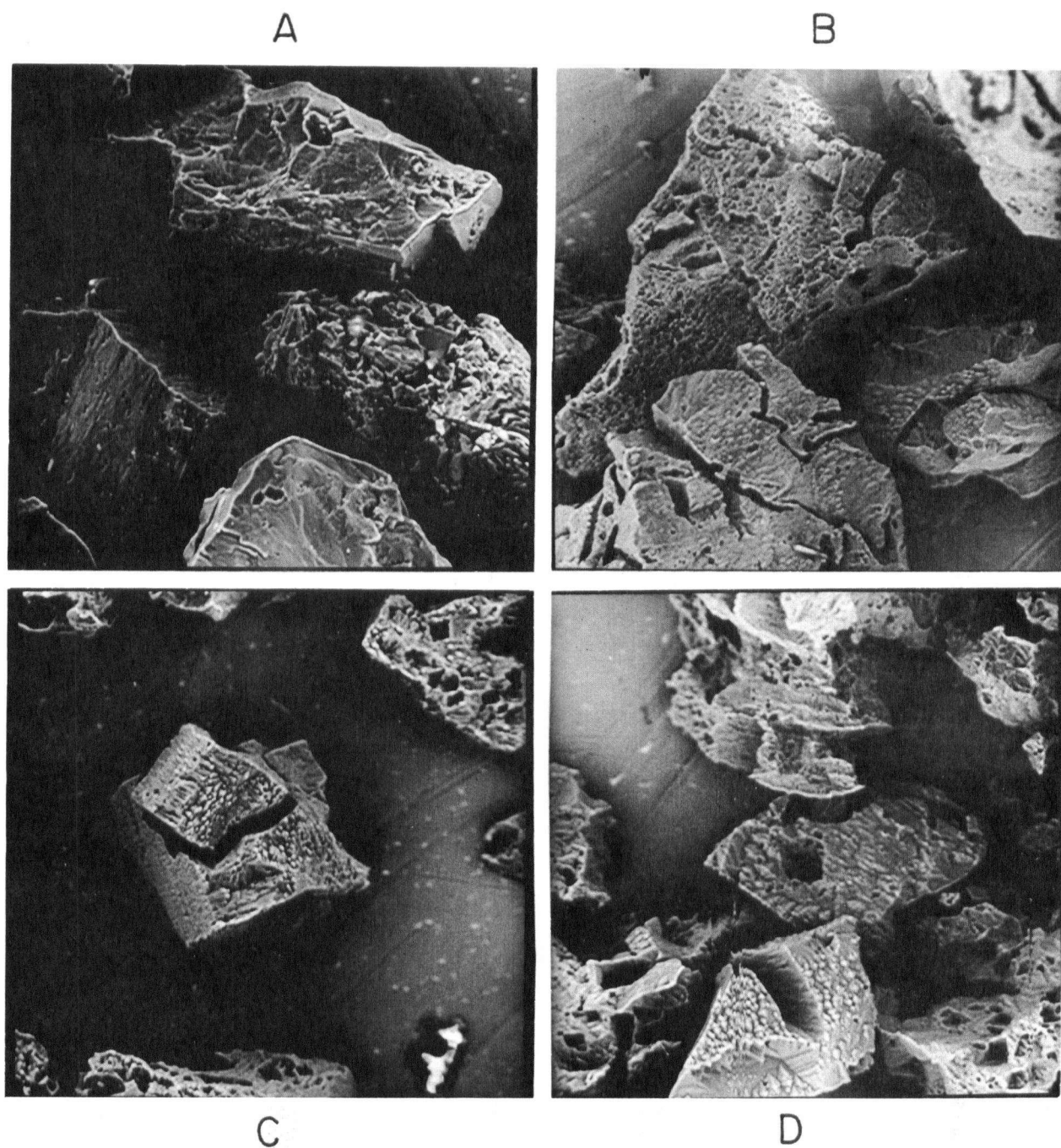


Figure 7: Reaction of -70 + 100 m Sullivan FeS₂ with 40 wt. % S₂Cl₂.

A Unleached FeS₂

B 23.8% Reaction

C 51% Reaction

D 72% Reaction

Absorbed Electron Image Micrographs, 240 x Magnification.

may occur to a greater extent in the coarser particles. In addition it may be possible that in the coarser fraction, individual particles may contain more than one grain, and that intergranular attack exposes more surface area, causing the higher calculated reaction rates. Figure 8 shows unleached samples of -70 + 100 mesh and -200 + 270 mesh Sullivan pyrite.

Figure 7 shows pyrite after various amounts of leaching in 40 wt % $\text{S.S}_2\text{Cl}_2$ solutions. Although etch pits or channels are evident in the leached material, the size of the leached particles decreases without faceting or other evidence of anisotropic dissolution.

To investigate the possibility that any of the common trace impurities in sulphide ores might catalyze or inhibit the reaction of pyrite with 40 wt % $\text{S.S}_2\text{Cl}_2$ solutions, a sample of Pine Point galena concentrate containing a large variety of impurities was completely chlorinated in 40 wt % $\text{S.S}_2\text{Cl}_2$. A sample of -70 + 100 mesh Sullivan pyrite was then introduced into the reaction mixture and treated for 10 minutes at 133°C. The extent of reaction (22%) was the same as with fresh solvent, indicating that at low concentrations in the solvent none of the impurities in this mixture have a significant effect on the rate of reaction of pyrite with 40 wt % $\text{S.S}_2\text{Cl}_2$.

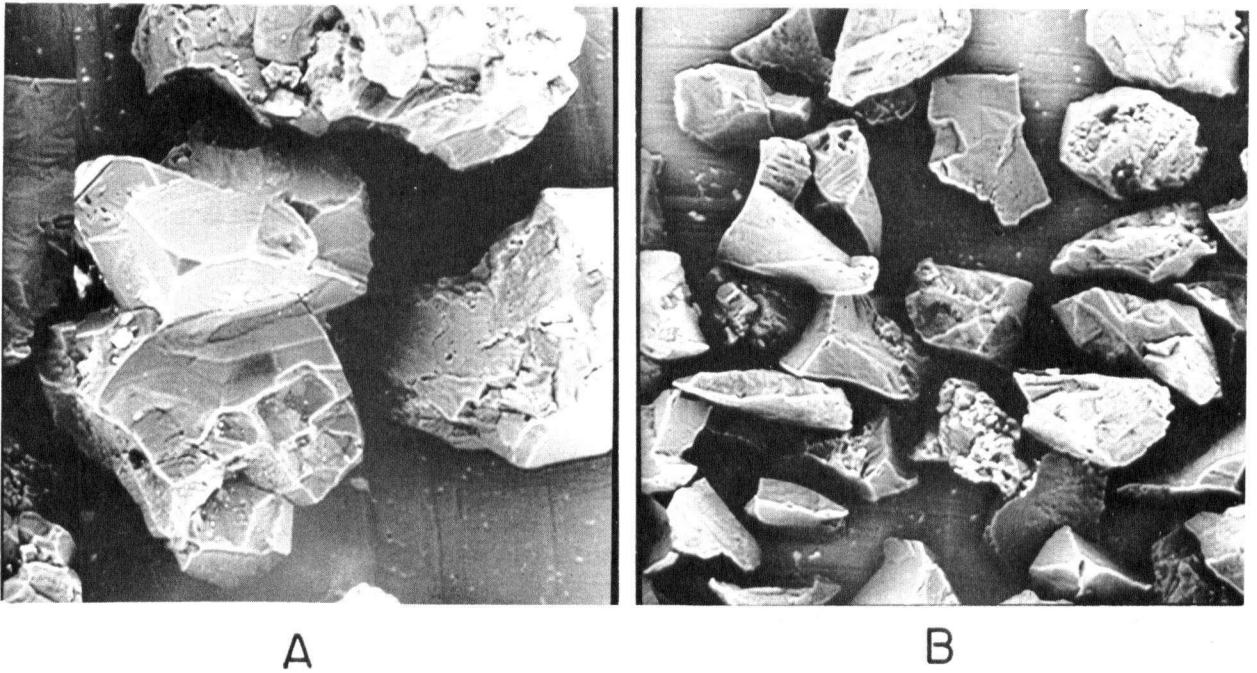


Figure 8: Absorbed Electron Image Micrographs, Magnification = 240 x

A -70 + 100 m Sullivan FeS₂

B -200 + 270 m Sullivan FeS₂.

To investigate the effect of a large variation in the initial ratio of pyrite to $S.S_2Cl_2$ solution on the total reaction, a relatively large scale experiment was done with 40 g of -70 + 200 mesh Sullivan pyrite and 500 g of 25 wt % $S.S_2Cl_2$. The solvent was heated to 130°C and pyrite was added gradually over a period of 5 minutes to avoid boiling due to the heat of the reaction. The mixture was then held for 5 minutes at 150°C, cooled to 100°C, and the solid products allowed to settle. The clear supernatant liquid was decanted and the residue analyzed. Analysis of the reaction products showed that 99% of the pyrite was decomposed. The solid, water insoluble residue consisted of the zinc sulphide (ZnS), silica and magnetite (Fe_3O_4) content of the concentrate (see Appendix C-3).

3.125 The Activation Energy

The rates of reaction of the -70 + 100 mesh fraction of Sullivan pyrite with 40 wt % $S.S_2Cl_2$ were used to construct an Arrhenius plot (Figure 9). This size fraction was used because smaller particles are nearly completely reacted in short times at high temperatures.

The slope of the Arrhenius plot indicates an activation energy of 21.7 ± 2 Kcal/mole.

This activation energy value, the lack of effect of stirring (beyond that necessary to suspend the particles in

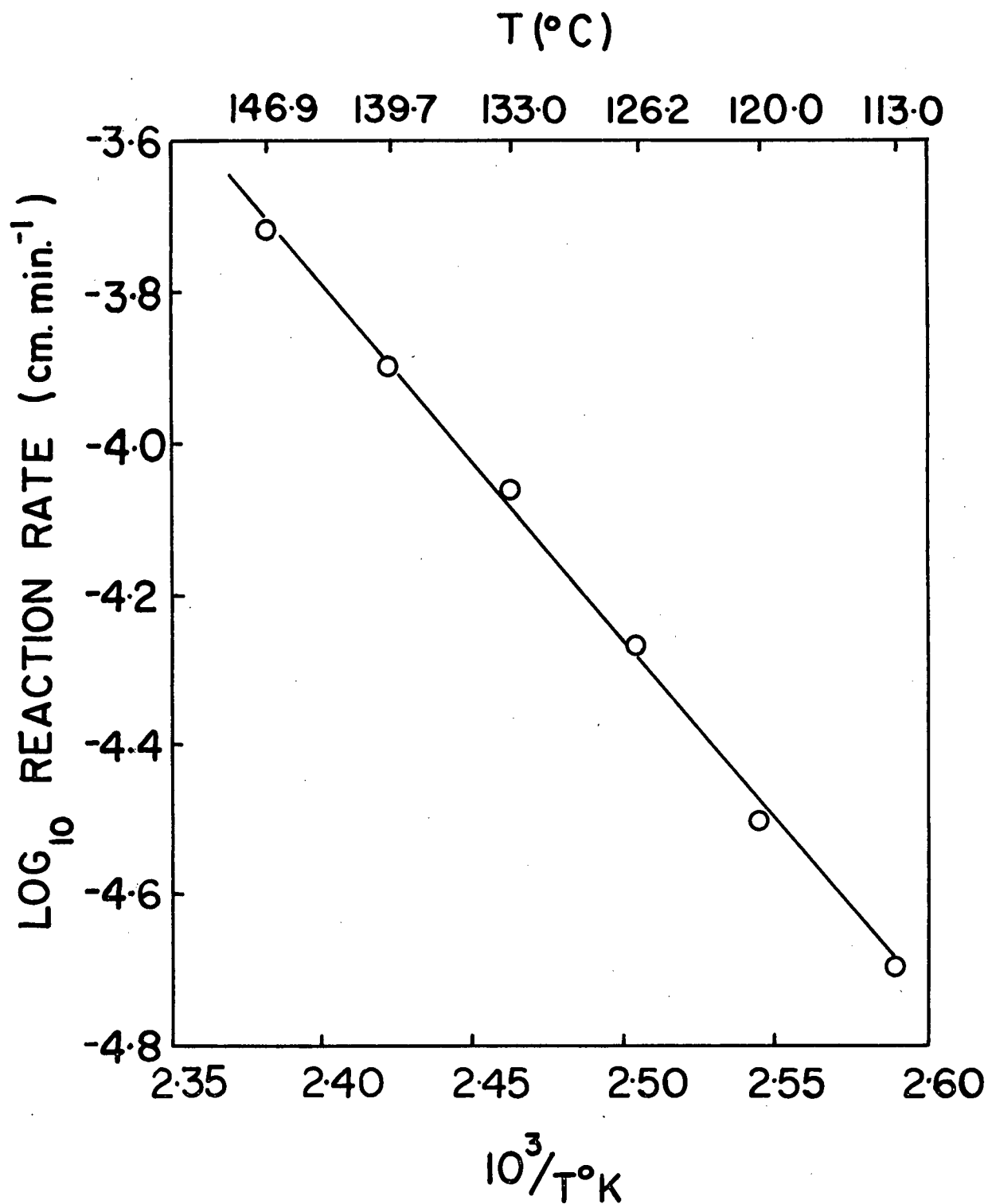


Figure 9: Arrhenius Plot for the Reaction of -70 + 100 m Sullivan Pyrite with 40 wt % $\text{S.S}_2\text{Cl}_2$

the $S.S_2Cl_2$ solution) on the reaction rate, and the linearity of the plots of $r_o[1-(1-R)^{1/3}]$ vs time indicate that the rate limiting factor is a chemical phase boundary reaction (56).

3.126 Reaction of Pyrite from a Different Source

Pyrite samples from Noranda Mines Ltd. (Appendix A) were reacted under the same conditions as Sullivan material to compare the rates of reaction.

The Noranda pyrite reacts ~50% slower than the Sullivan pyrite, but with the same stoichiometry. The results were linear in both cases when plotted in the form $r_o[1-(1-R)^{1/3}]$ vs time (Figure 10). Figure 11 shows samples of -70 + 100 mesh Sullivan and Noranda pyrites before leaching. It appears that the surfaces of the Noranda material are relatively smoother - thus presenting less effective area for chemical attack. It is suggested that this difference in surface roughness is at least partially responsible for the difference in reactivity between the two materials.

3.13 Reaction of Natural and Synthetic Pyrrhotite

The reactions of natural (Sullivan - Appendix A) and low sulphur synthetic pyrrhotite with (initially) pure S_2Cl_2 and 40 wt % $S.S_2Cl_2$ have been studied. The observed stoichiometry of the limited reaction which occurred was found (Appendix C-4) to be:

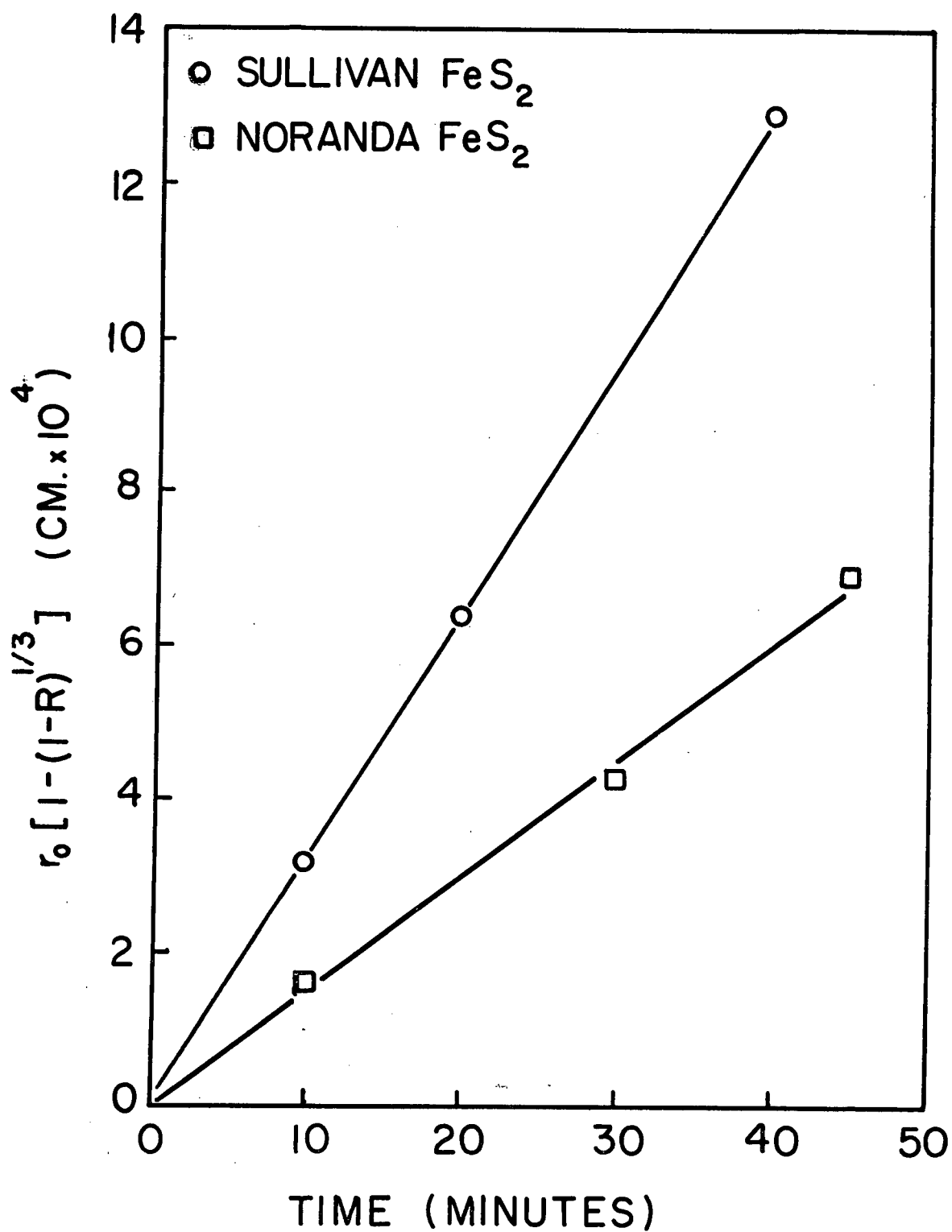


Figure 10: Plot of $r_0[1-(1-R)^{1/3}]$ vs. Time for -70 + 100 m Sullivan and Noranda Pyrites Reacted with 40 wt. % S_2Cl_2 at 119.9°C .

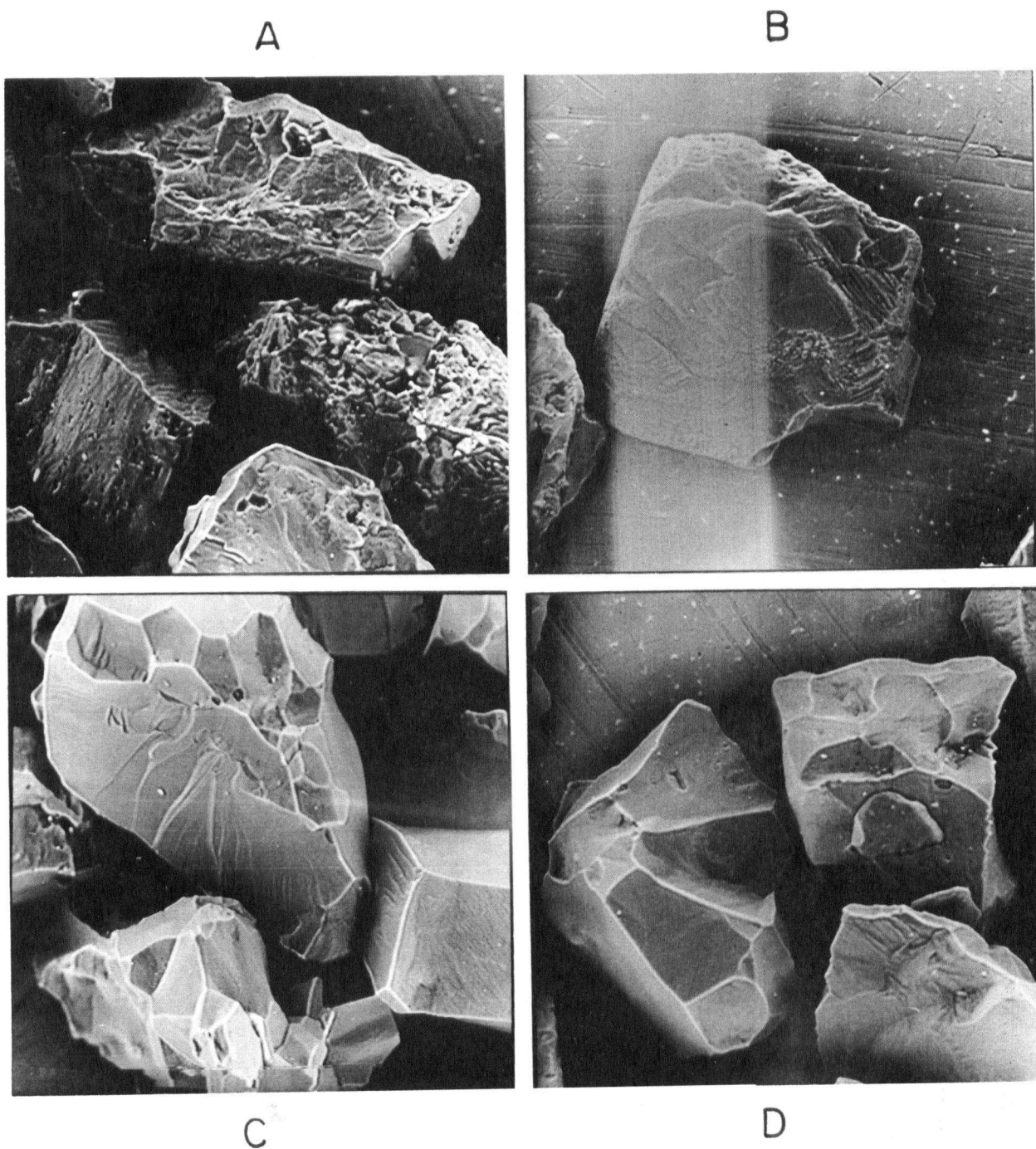
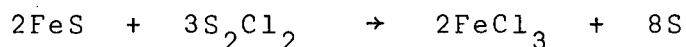


Figure 11: -70 + 100 m Sullivan and Noranda Pyrites Before Leaching.

A, B Kimberley FeS_2 ; C, D Noranda FeS_2

A, C, D Absorbed Electron Image Micrographs, 240 x

B Backscattered Electron Image Micrograph, 240 x.



The effects of temperature, solvent composition, and sample size on the reaction of Sullivan pyrrhotite with sulphur chloride are shown in Figure 12.

The abrupt decrease in reaction rate after partial reaction and the decreased extent of reaction with increased sample size indicate that the reaction is stifled by some product. In contrast to the results of experiments on pyrite, the presence of a large amount (40 wt %) of sulphur in the initial solution had no significant effect on the extent of reaction. Addition of ferric chloride to the initial reaction mixture depressed the extent of reaction of pyrrhotite but, as was found to be the case with pyrite, the results were not reproducible.

Formation of an inhibiting film of ferrous or ferric chloride at the sulphide surface seemed to be a probable cause of the stifling of the reaction, but such a film could not be positively identified. Solvents such as carbon tetrachloride, carbon disulphide, or dichloroethane which removed adhering solvent from the mineral surface also removed ferric chloride, so the extent (if any) to which ferric chloride formed a film on the reacting surface could not be determined. Attempts to detect a film of ferrous chloride on the reacting surface by titration of water soluble iron (II) in the solid reaction product were complicated by the

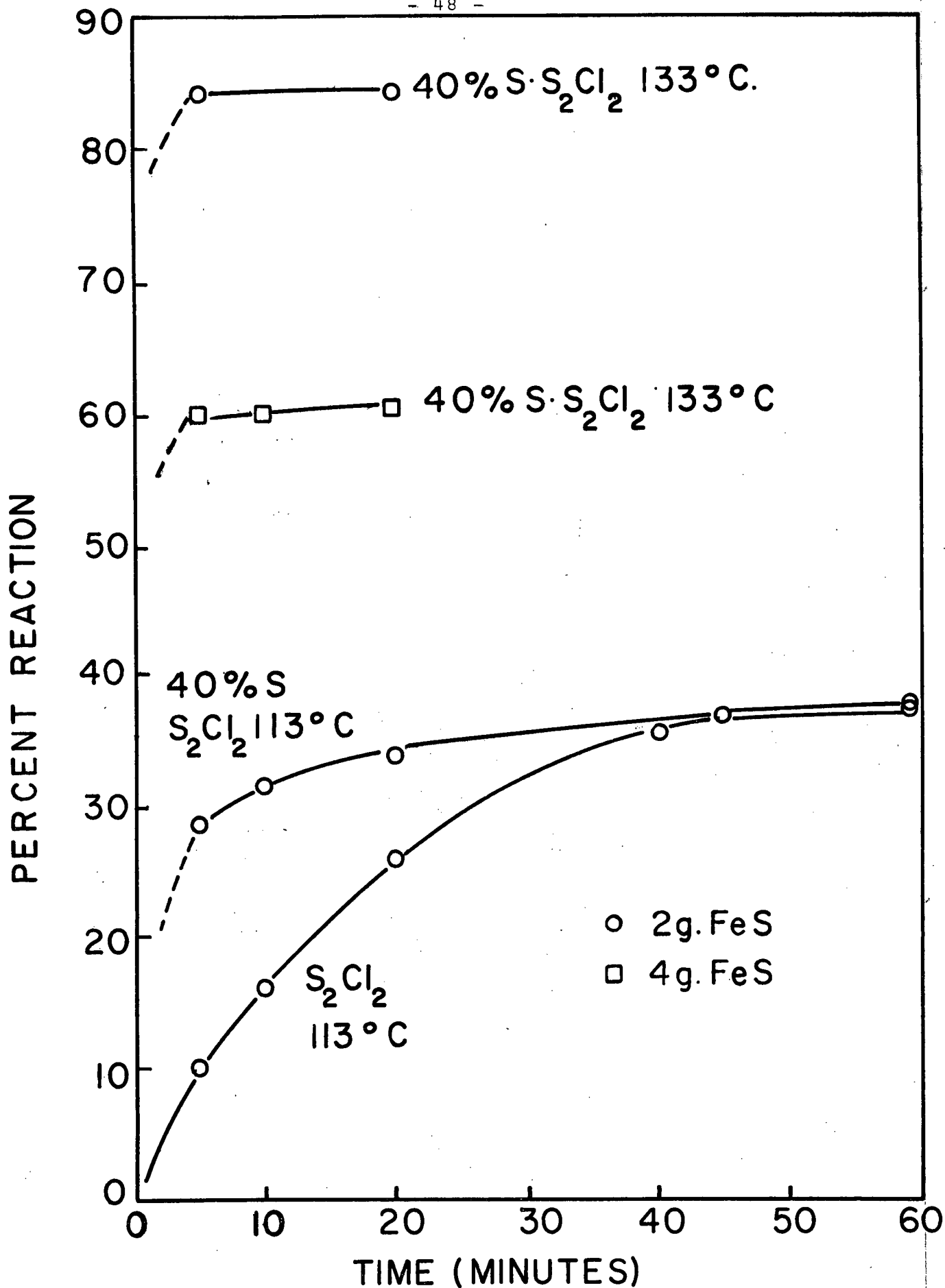


Figure 12: Reaction of -140 + 200 m Sullivan FeS with S₂Cl₂ and 40 wt. % S.S₂Cl₂.

tendency of the sulphide to dissolve in a slightly acid wash solution. High and erratic iron (II) titration blanks (wash solution passed through unleached solids) were obtained, but there was no indication of any substantial ferrous chloride film on the surface of leached material.

To investigate the effect of the mineral composition on the reaction of pyrrhotite, low sulphur synthetic pyrrhotite was also treated with 40 wt % $S.S_2Cl_2$. The experimental results are summarized in Table 4. This material appears to react in the same way as the natural mineral except that the extent of rapid reaction at a particular temperature, e.g. $113^{\circ}C$, was found to be greater with 40 wt % $S.S_2Cl_2$ than with S_2Cl_2 .

These results are difficult to explain in terms of the role of dissolved sulphur in the solvent.

Table 4: Reaction of Synthetic FeS and FeCl₂ with S.S₂Cl₂ Solutions

Solvent	Substrate	Time minutes	T°C	% Reac- tion	mg Fe [*] reacted
40 wt % S.S ₂ Cl ₂	FeS (2 g)	5	113.0	47	284
"	"	10	"	50	302
"	"	20	"	52	314
S ₂ Cl ₂	FeS (2 g)	5	113.0	28	169
"	"	10	"	30	181
"	"	20	"	32.5	193
S ₂ Cl ₂	FeS (1 g)	5	113.0	30	90
"	"	10	"	32	95
40 wt % S.S ₂ Cl ₂	FeCl ₂ (1 g)	5	113.0	95.3	395
"	" (3 g)	5	"	88	1241
S ₂ Cl ₂	FeCl ₂ (1 g)	5	113.0	80.5	358
"	"	60	"	78.7	350

* In 300 g of solvent.

3.14 Reaction of Anhydrous Ferrous Chloride with Sulphur Chloride

As has been mentioned previously, ferrous chloride is considered to be a plausible intermediate in the reaction of iron sulphides with sulphur chloride. To test the stability of ferrous chloride under conditions in which sulphides react, samples of this material (broken under nitrogen to pass a 70 mesh screen) were treated with

S_2Cl_2 and 40 wt % $S.S_2Cl_2$. The experimental procedure was varied slightly for these tests: the solid reaction residues were washed with diethyl ether instead of water, and oven drying of the residue was omitted. The experimental results are summarized in Table 4.

In S_2Cl_2 , ferrous chloride reacted partially to form ferric chloride. However, the amount of iron (II) converted to ferric chloride was quite different from the amount reacting from pyrrhotite under the same conditions. In 40 wt % $S.S_2Cl_2$, ferrous chloride was converted rapidly and nearly completely to ferric chloride.

3.15 Reactions of Metallic Iron with Sulphur Chloride

The reactions of metallic iron with sulphur chloride and sulphur-sulphur chloride solutions were also investigated. This was done in order to explore the possibility that knowledge of these reactions might lead to a more complete understanding of the reactions of iron sulphides. Also, large flat specimens were readily available, and it was expected that such surfaces would simplify the detection of surface films if such films existed.

Strips of metallic iron were treated with S_2Cl_2 and 40 wt % $S.S_2Cl_2$. The behaviour of iron in this system is more complex than that of the iron sulphides. Results of the experiments are summarized in Figure 13.

It was observed that a film formed on the surface of

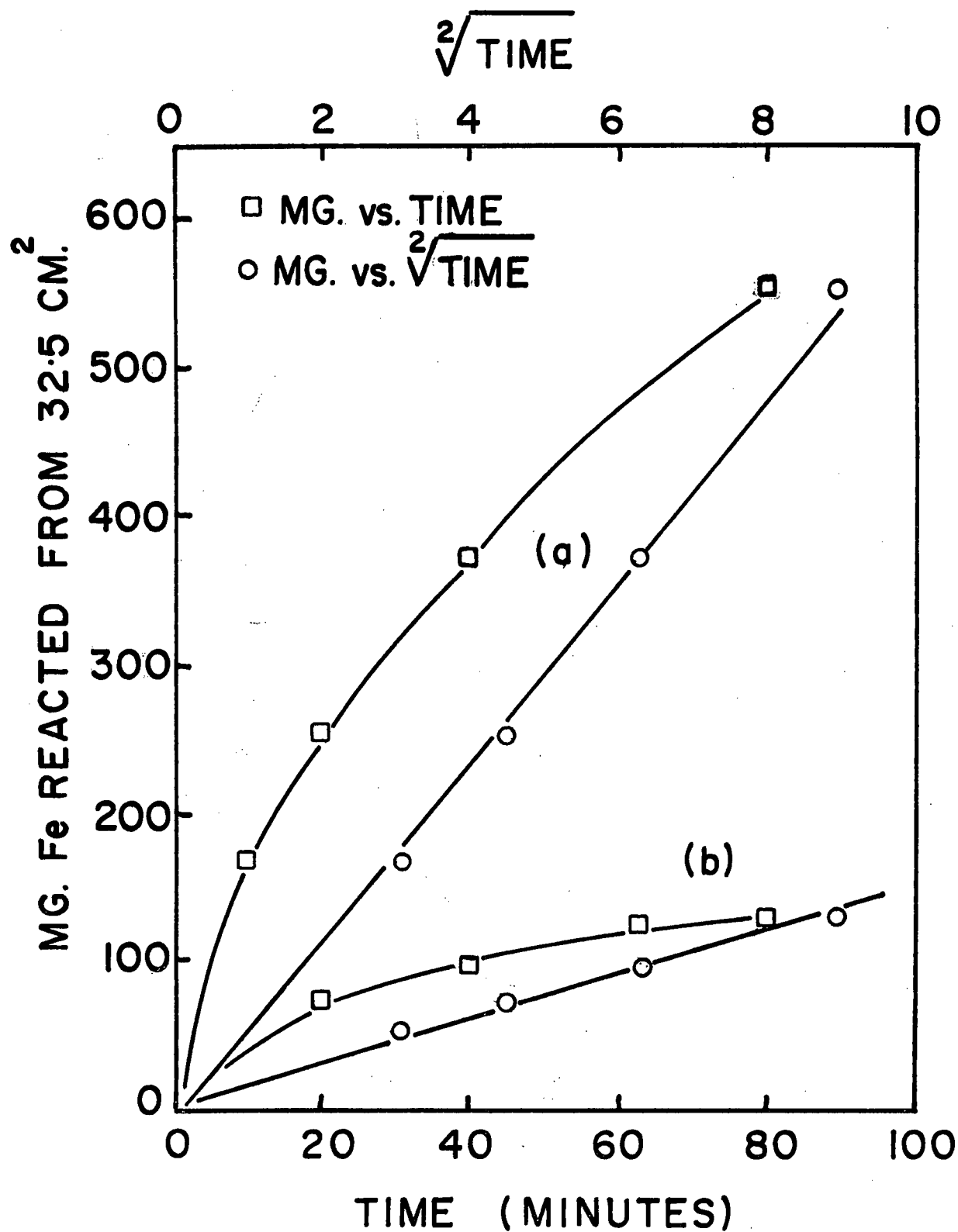


Figure 13: Reaction of Fe with 40 wt. % S.S₂Cl₂ (a) and S₂Cl₂ (b) at 133°C.

iron treated with S_2Cl_2 . The film was insoluble in acetone or water but readily soluble in dilute acid. When the film was dissolved in acid, a hydrogen sulphide smell was noted, so it was concluded that the surface film was iron sulphide. The film grew in a streaky form until it appeared to cover the entire surface of the specimen. The growth of this film is shown in Figure 14.

When iron was treated with 40 wt % S.S $_2$ Cl $_2$, a pale green film formed on the surface. This film was insoluble in acetone but soluble in water and was determined to be ferrous chloride. (See Appendix C-5) The form of the plot of weight of iron reacted vs. time (Figure 13) indicates that the ferrous chloride film gradually thickens and slows the reaction by forming a barrier to diffusion of reactants and/or products.

Figure 13 also shows plots of weight of iron reacted vs. $(t)^{1/2}$ for iron in S_2Cl_2 and 40 wt % S.S $_2$ Cl $_2$. These plots are approximately linear, thus providing additional evidence that film formation affects the rate of reaction.

3.16 Summary and Discussion of Experiments on Iron Compounds

3.161 Summary of Observations

It was observed that iron, the iron sulphides, and ferrous chloride all behave somewhat differently in their reactions with sulphur chloride. The possible chemical reactions in these systems are listed in Table 5 with some

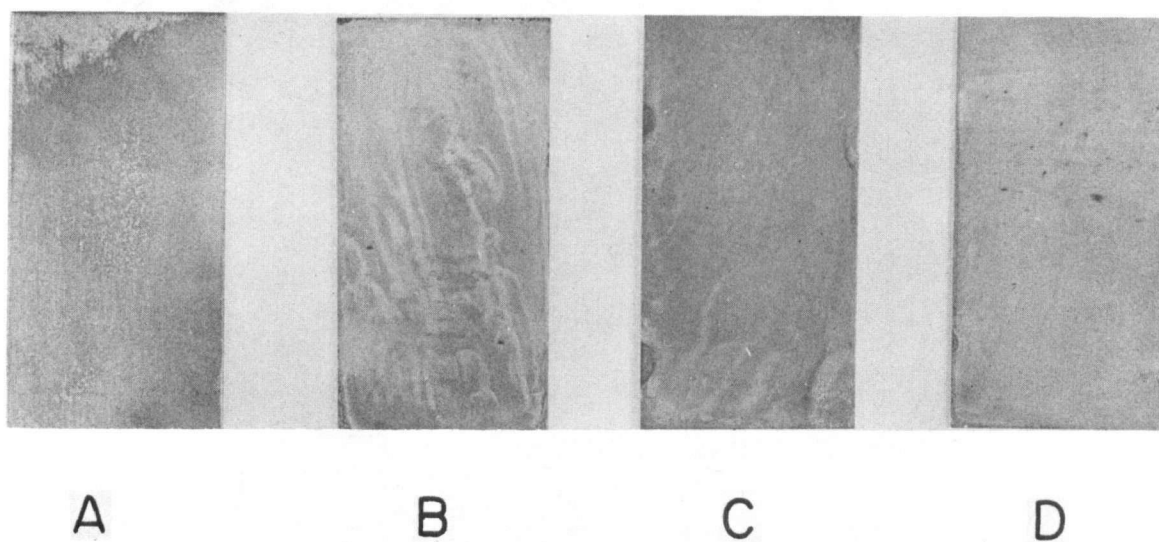


Figure 14: Growth of FeS Film on Iron Reacting with S_2Cl_2 .

- a before reaction
- b $t = 5$ minutes
- c $t = 10$ minutes
- d $t = 20$ minutes

appropriate observations. Table 6 shows the initial and extended time reaction rates for these systems.

Table 5: Reactions of FeS_2 , FeS , FeCl_2 and Fe with S_2Cl_2

Reaction	Observations
1) $\text{FeS}_2 + \text{S}_2\text{Cl}_2 \rightarrow \text{FeCl}_2 + 4\text{S}$	FeCl_2 was not observed
2) $\text{FeCl}_2 + \frac{1}{2} \text{S}_2\text{Cl}_2 \rightarrow \text{FeCl}_3 + \text{S}$	but is a possible reaction intermediate
3) = 1) + 2) $\text{FeS}_2 + \frac{3}{2} \text{S}_2\text{Cl}_2 \rightarrow \text{FeCl}_3 + 5\text{S}$	Observed stoichiometry. The reaction is incomplete unless the solvent contains >10 wt. % S.
4) $\text{FeS} + \text{S}_2\text{Cl}_2 \rightarrow \text{FeCl}_2 + 3\text{S}$	FeCl_2 was not observed.
5) $\text{FeS} + \frac{3}{2} \text{S}_2\text{Cl}_2 \rightarrow \text{FeCl}_3 + 4\text{S}$	Observed stoichiometry. The extent of reaction is dependent on sample size.
6) $\text{Fe} + n\text{S} \cdot \text{S}_2\text{Cl}_2 \rightarrow \text{FeCl}_2 \quad (n+2)\text{S}$	An FeCl_2 layer was formed in 40 wt % $\text{S} \cdot \text{S}_2\text{Cl}_2$.
7) $\text{Fe} + \frac{3}{2} \text{S}_2\text{Cl}_2 \rightarrow \text{FeCl}_3 + 3\text{S}$	FeCl_3 is the final product of S_2Cl_2 attack on Fe.
8) $4\text{Fe} + \frac{3}{2} \text{S}_2\text{Cl}_2 \rightarrow 3\text{FeS} + \text{FeCl}_3$	An FeS film was observed in reaction with (initially) 100% S_2Cl_2 .
9) $\text{FeCl}_2 + \frac{1}{2} \text{S}_2\text{Cl}_2 \rightarrow \text{FeCl}_3 + \text{S}$	Fast but incomplete in S_2Cl_2 . Fast and virtually complete in 40 wt % $\text{S} \cdot \text{S}_2\text{Cl}_2$.

Table 6: Initial and Extended Time Reaction Rates for FeS_2 , FeS , FeCl_2 and Fe in S_2Cl_2 and 40 wt % $\text{S.S}_2\text{Cl}_2$.

Substrate	T°C	Solvent	Initial rate ($\text{g cm}^{-2}\text{min}^{-1}$)	Rate after extended time ($\text{g cm}^{-2}\text{min}^{-1}$)
FeS_2	113	S_2Cl_2	$> 8 \times 10^{-4}$	$< 1 \times 10^{-5}$
"	133	40 wt % $\text{S.S}_2\text{Cl}_2$	4.2×10^{-4}	4.2×10^{-4}
FeS	113.5	S_2Cl_2	$\sim 2.1 \times 10^{-4}$	$< 1 \times 10^{-5}$
"	113.5	40 wt % $\text{S.S}_2\text{Cl}_2$	6×10^{-4}	1×10^{-5}
Fe	133	S_2Cl_2	1.7×10^{-4}	8.5×10^{-6}
"	133	40 wt % $\text{S.S}_2\text{Cl}_2$	5.1×10^{-4}	1×10^{-4}
FeCl_2	113.5	S_2Cl_2	X (area not known)	0.1 X
"	113.5	40 wt % $\text{S.S}_2\text{Cl}_2$	very fast	

It was observed that the initial reactions of pyrite, pyrrhotite and ferrous chloride with sulphur chloride are fast but that these rates decrease considerably before the reaction is complete (Table 6). The extent of the fast reaction was found to be dependent on sample size. Since thermodynamic calculations predict that ferric chloride should be the final reaction product, it may be supposed that in these systems the fast reaction continues only until the substrate surface is effectively covered by an inhibiting film of ferric chloride. The amount of ferric chloride

required to stifle the fast reaction appears to be a function of the form and composition of the substrate. In the case of metallic iron in sulphur chloride, a film of iron sulphide was formed on the surface and the reaction became equivalent to that of pyrrhotite.

3.162 The Reaction of Pyrite

It has been observed that the reaction of pyrite with initially pure sulphur chloride is inhibited by the presence of ferric chloride but that pyrite reacts uniformly to completion when exposed to excess sulphur chloride containing 25-40 wt % dissolved sulphur.

For the case of pyrite reacting in 25-40 wt % $S.S_2Cl_2$, reaction 2 (Table 5) would be suppressed at the reacting surface if the local concentration of sulphur from reaction 1 plus the high initial level of dissolved sulphur were high enough to depress the chlorine activity at the sulphide surface below the level of decomposition of ferric chloride. Ferrous chloride produced at the sulphide surface may then be transported away from the surface (as a suspended solid) by the motion of the liquid before conversion to ferric chloride. Any ferric chloride formed away from the reacting surface would not form a protective layer on the surface. An effect interpretable in this way is observed in an aqueous system when nickel-iron alloy is leached in ammonia-ammonium carbonate solution (57). At a

high solution oxidizing potential, iron is oxidized to iron(III) at or near the surface and forms a layer of hydrous ferric oxide which slows or stops the reaction. In the case of pyrite reacting with 40 wt % S_2Cl_2 , there is no indication that an initial ferrous chloride product is soluble, but it is possible that ferrous chloride is formed as a finely divided suspended solid which does not adhere to the reacting pyrite surface, and is chlorinated to ferric chloride at a point remote from the sulphide surface. Ferrous chloride produced in this system would be finely divided because it is believed to be insoluble in the solvent and thus incapable of recrystallizing by the solution-precipitation mechanism which is possible for ferric chloride. However, this hypothesis is not consistent with the observation that the reaction rate is independent of the stirring speed.

The observed kinetics of the reaction of pyrite with 40 wt % S_2Cl_2 are also consistent with rate control by diffusion through a surface film of constant thickness, but no analytical evidence of such a film was found.

3.163 The Reaction of Pyrrhotite

The failure of pyrrhotite to react completely at measurable rates in S_2Cl_2 and 40 wt % S_2Cl_2 solution is presumed to be due to suppression of the reaction by ferric chloride product which is formed or deposited on the sulphide

surface. There is no way of distinguishing between a film of ferric chloride formed on the surface and one that has deposited from solution. The observation is that the reaction is inhibited by ferric chloride..

3.164 The Reactions of Metallic Iron

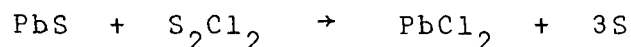
When metallic iron was treated with 40 wt % S_2Cl_2 , a film of ferrous chloride was formed on the surface. This observation would seem to be inconsistent with the observation that powdered ferrous chloride reacts rapidly with 40 wt % S_2Cl_2 at a lower temperature. However, it is possible that a thin film of ferrous chloride growing from a substrate might be stable under conditions in which a finely divided suspended powder is very reactive. It is also somewhat surprising that no visible layer of iron sulphide was formed on iron in 40 wt % S_2Cl_2 , but an extremely thin layer of sulphide may be present between the iron and ferrous chloride layers. Such a film would be continuously decomposed by sulphur chloride diffusing through the ferrous chloride layer, but a high local sulphur concentration at this interface may prevent the formation of inhibiting ferric chloride at the reacting surface. In S_2Cl_2 , when iron sulphide is formed (on iron) it is presumably protected by an inhibiting layer of ferric chloride and thus detectable as a layer on the surface.

3.2 Decomposition of Other Sulphides by Sulphur Chloride

3.21 Decomposition of Galena

3.211 Reactivity of Natural and Synthetic Galena

The reaction of galena (PbS) with sulphur chloride was studied initially using a Pine Point galena concentrate (Appendix A). The stoichiometry of the reaction was determined (Appendix C-6) to be:



but the experimental rate data were very erratic.

To eliminate the possible effect of chemical impurities on the reaction rate, a synthetic lead sulphide was prepared. This material did not react at a useful rate with pure sulphur chloride or sulphur-sulphur chloride solutions. It did, however, react slowly when small amounts of natural (Pine Point) galena were added to the reaction mixture. From this observation, it was inferred that some impurity in the natural galena might have catalyzed the reaction of galena with sulphur chloride.

3.212 Determination of Catalysts

The catalytic effect of various chemicals on the reaction of synthetic lead sulphide with sulphur chloride was investigated initially by adding small quantities (~0.1 g) of chemicals - corresponding to all the impurities present

in the natural mineral - to a refluxing mixture of sulphur chloride and synthetic lead sulphide. Complete reaction of the lead sulphide was observed in this experiment, so in succeeding tests various chemicals were omitted until incomplete reaction of the lead sulphide was observed. By this trial and error method the active catalyst combinations were found to be silver-bismuth and silver-antimony. Data on the effect of materials found to be catalytically active in this system are presented in Table 7.

Table 7: Effect of Various Additives on the Rate of Reaction of Synthetic PbS with S_2Cl_2

Material added (0.1 g of each chemical)	Solvent	Time (minutes)	T°C	% Reaction (of 1 g sample)
nil	S_2Cl_2	20	135-40	0.5
Ag_2S	"	"	"	8
$As_2S_3, Sb_2S_3, Bi_2S_3$	"	"	"	4
Ag_2S, As_2S_3	"	"	"	12
Ag_2S, Sb_2S_3	"	"	"	75
Ag_2S, Bi_2S_3	"	"	"	94

The reason for the catalytic effect is not known, but two possibilities are suggested. Antimony and bismuth chlorides form complexes with the general formula $M^{++}BiCl_5^-$ or $M^{++}SbCl_5^-$ (58). Complexes of this type may be

involved in the transport of product lead chloride from the reacting surface. If this is their role then the requirement for silver is unexplained. Alternatively, formation of such compounds may stabilize or solubilize silver (II) chloride. Silver (II) is a strong oxidant (59) and might be an intermediate in the reaction of lead sulphide with sulphur chloride.

3.213 Results of Experiments on Pine Point Galena

Representative sets of data for the reaction of Pine Point galena with sulphur chloride (with and without added catalyst) are shown in Figure 15. For measurements on the catalyzed reaction, catalytic material was added to the system by completely chlorinating a one gram sample of the mineral at high temperature ($\sim 100^{\circ}\text{C}$) and cooling this mixture to the desired reaction temperature before adding a weighed sample of fresh mineral. This method was found to give much more reproducible results than addition of catalyst in the form of reagent chemicals. The data for uncatalyzed reaction was obtained by reacting the natural mineral in initially pure solvent. The initial rates of reaction obtained in this way indicate the rate of reaction when only a small amount of active catalyst is present in the mixture. Obviously as the extent of reaction increases there will be an increasing catalytic effect on the reaction.

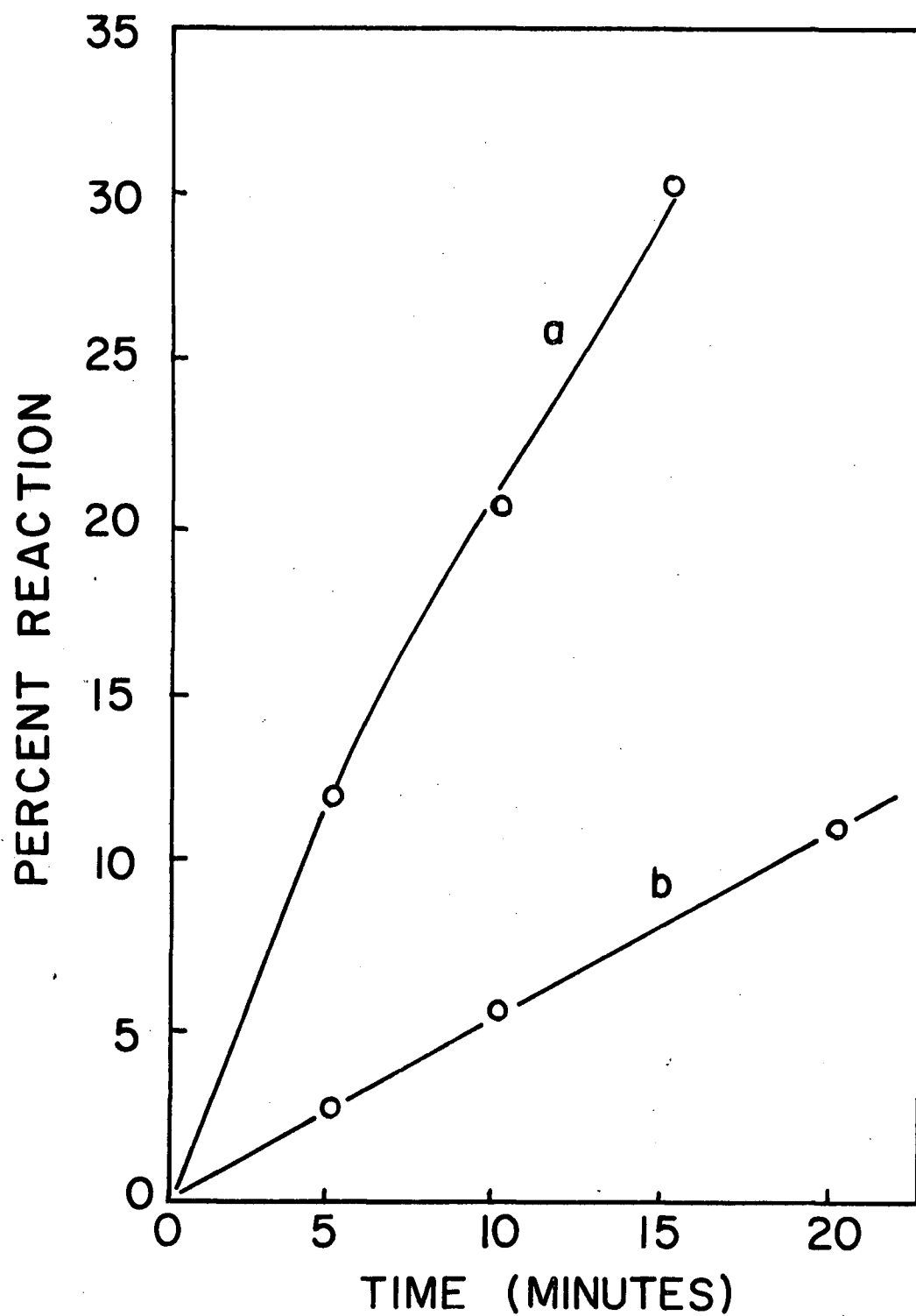


Figure 15: Reaction of -150 + 200 m Pine Point Galena with 10 wt. % $S.S_2Cl_2$.

a Catalyzed reaction at 40°C.

b Uncatalyzed reaction at 70°C.

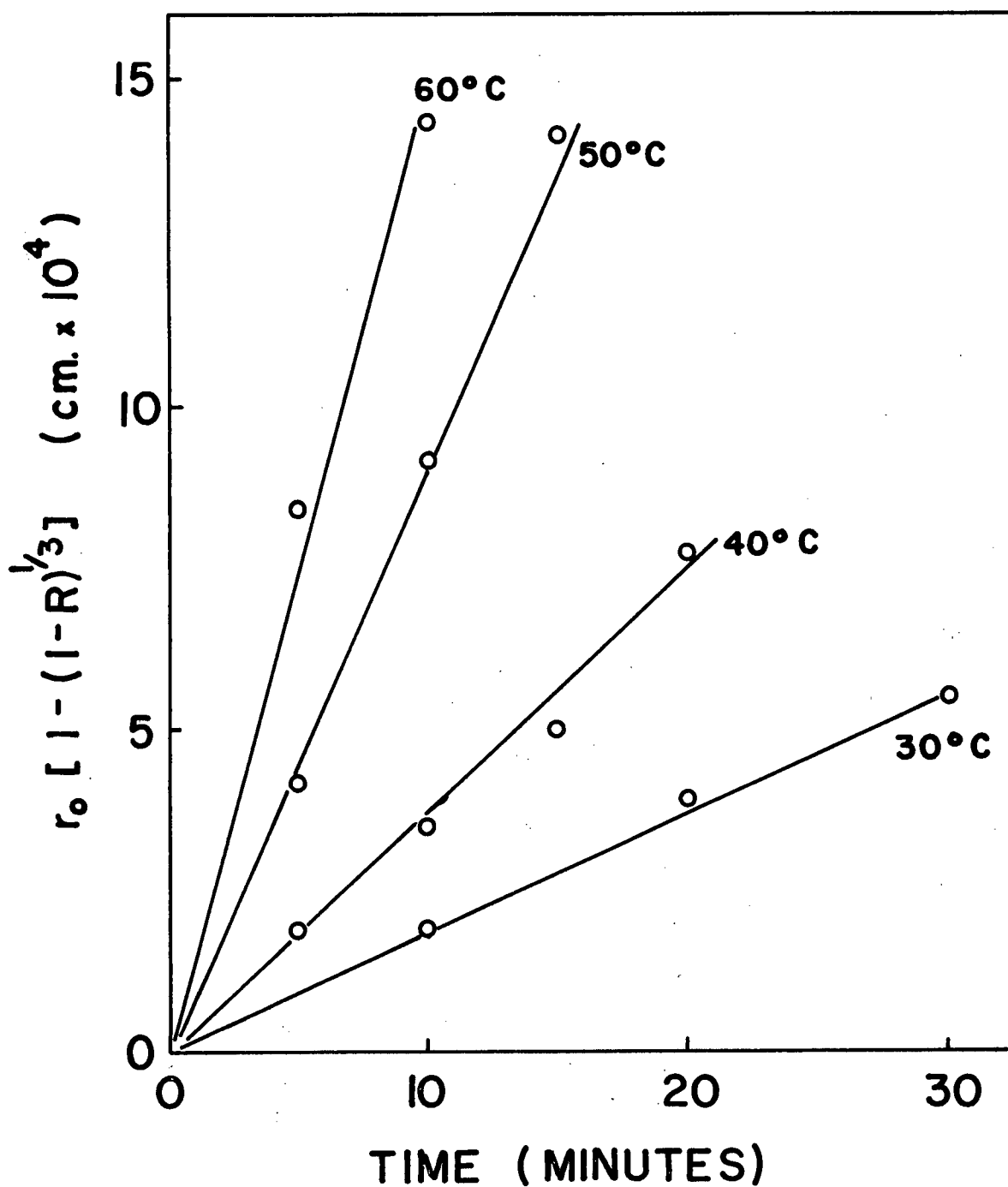


Figure 16 - Plot of $r_o [1 - (1-R)^{1/3}]$ vs Time for the Catalyzed Reaction of -150 + 200 m Pine Point Galena with 10 wt % S_2Cl_2

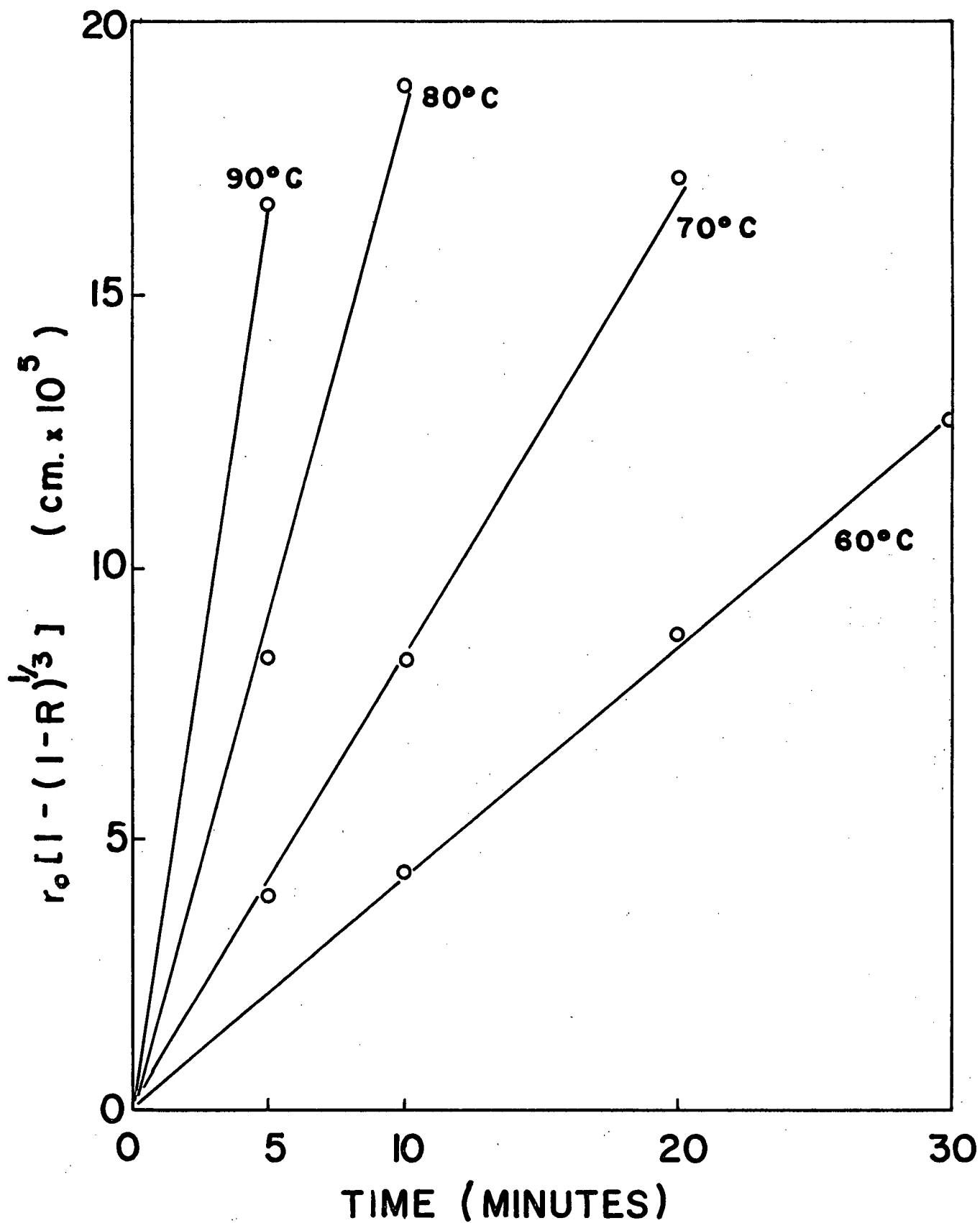


Figure 17: Plot of $r_0[1-(1-R)^{1/3}]$ vs Time for Uncatalyzed Reaction of -150 + 200 m Pine Point Galena with 10 wt % S_2Cl_2

The rate of reaction of Pine Point galena with sulphur chloride was found to be independent of the stirring rate once all solids were suspended.

In figures 16 and 17, data for the catalyzed and uncatalyzed reactions are plotted in the form $r_0[1-(1-R)^{1/3}]$ vs. time. Reaction rates calculated from the slopes of plots of this form are summarized in Table 8.

Table 8: Rate of Reaction of 150 + 200 m Pine Point Galena with 10 wt % S_2Cl_2

Uncatalyzed Reaction		Catalyzed Reaction	
T°C	Rate	T°C	Rate
	(cm min ⁻¹ x 10 ⁵)		(cm min ⁻¹ x 10 ⁴)
90	3.32	60	1.55
80	1.77	50	0.89
70	0.83	40	0.36
60	0.43	30	0.19

3.214 Calculated Activation Energies

The reaction rates presented in Table 8 were used to construct Arrhenius plots (Figure 18) for the catalyzed and uncatalyzed reactions. The activation energy for the uncatalyzed reaction was calculated to be 17.6 ± 2 Kcal mole⁻¹. A similar value of 15.4 ± 2 Kcal mole⁻¹ was calculated for the catalyzed reaction.

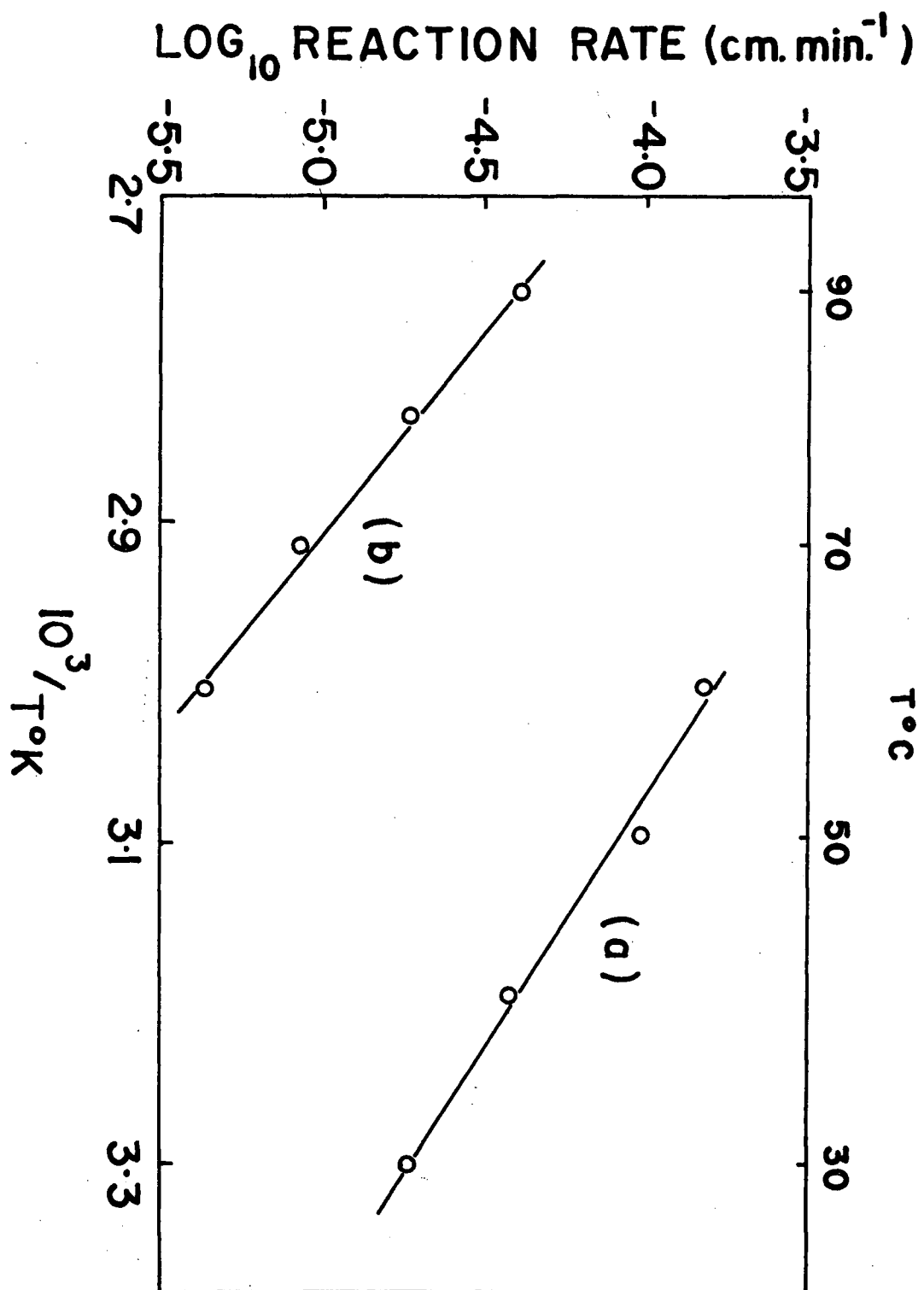


Figure 18: Arrhenius Plots for Catalyzed (a) and Uncatalyzed (b) Reactions of -150 + 200 m Pine Point Galena and 10 wt % $\text{S.S}_2\text{Cl}_2$.

These activation energy values, the lack of effect of stirring on the reaction rate, and the linearity of the plots of $r_0[1-(1-R)^{1/3}]$ vs. time indicate that the rate determining step is a chemical phase boundary reaction in both cases.

3.215 Miscellaneous Observations

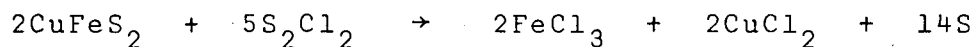
Qualitative observations made on the rate of reaction of the various chemicals added during the catalysis experiments were: arsenic, antimony and bismuth sulphides reacted on contact with sulphur chloride leaving no solid residue.

A lead sulphide matte based on Pine Point galena with gold and silver values added was also reacted with sulphur chloride. More than 90% of the gold and silver content of the matte were found in the solid reaction residue.

3.22 Decomposition of Chalcopyrite by Sulphur Chloride

3.221 Results of Experiments on Phoenix Chalcopyrite

Chalcopyrite (CuFeS_2) was found to react rapidly and completely with 40 wt % S_2Cl_2 . The overall stoichiometry of the reaction was determined (Appendix C-7) to be:



The best available chalcopyrite in a form suitable for this study contained a significant amount of pyrite (see Appendix A) but at the low temperatures used for chalcopyrite

decomposition the pyrite was not significantly attacked. Analysis of the residue from a chalcopyrite sample leached for 90 minutes at 70°C showed that the water insoluble residue contained 90% of the original pyrite but no significant amount of copper.

Representative plots of percent reaction vs. time for Phoenix chalcopyrite reacting with 40 wt % S_2Cl_2 solution are shown in Figure 19. These data are plotted in the form $r_0[1-(1-R)^{1/3}]$ vs. time in Figure 20. In the range of 30-70% reaction, these plots are linear. The reason for the initial period of fast reaction is not known.

The stirring rate - above that required to suspend the particles in the liquid - had no apparent effect on the rate of reaction. Using the straight sections (30-70% reaction) of the plots of Figure 20, rates of reaction (penetration) were calculated for various temperatures and summarized in Table 9.

Table 9: Rate of Reaction (Penetration) of $CuFeS_2^*$ in
40 wt % S_2Cl_2

T°C	Penetration Rate ($cm \cdot min^{-1} \times 10^5$)
80	10.6
70	5.4
60	2.7
50	1.3

* -100 + 140 mesh Phoenix $CuFeS_2$.

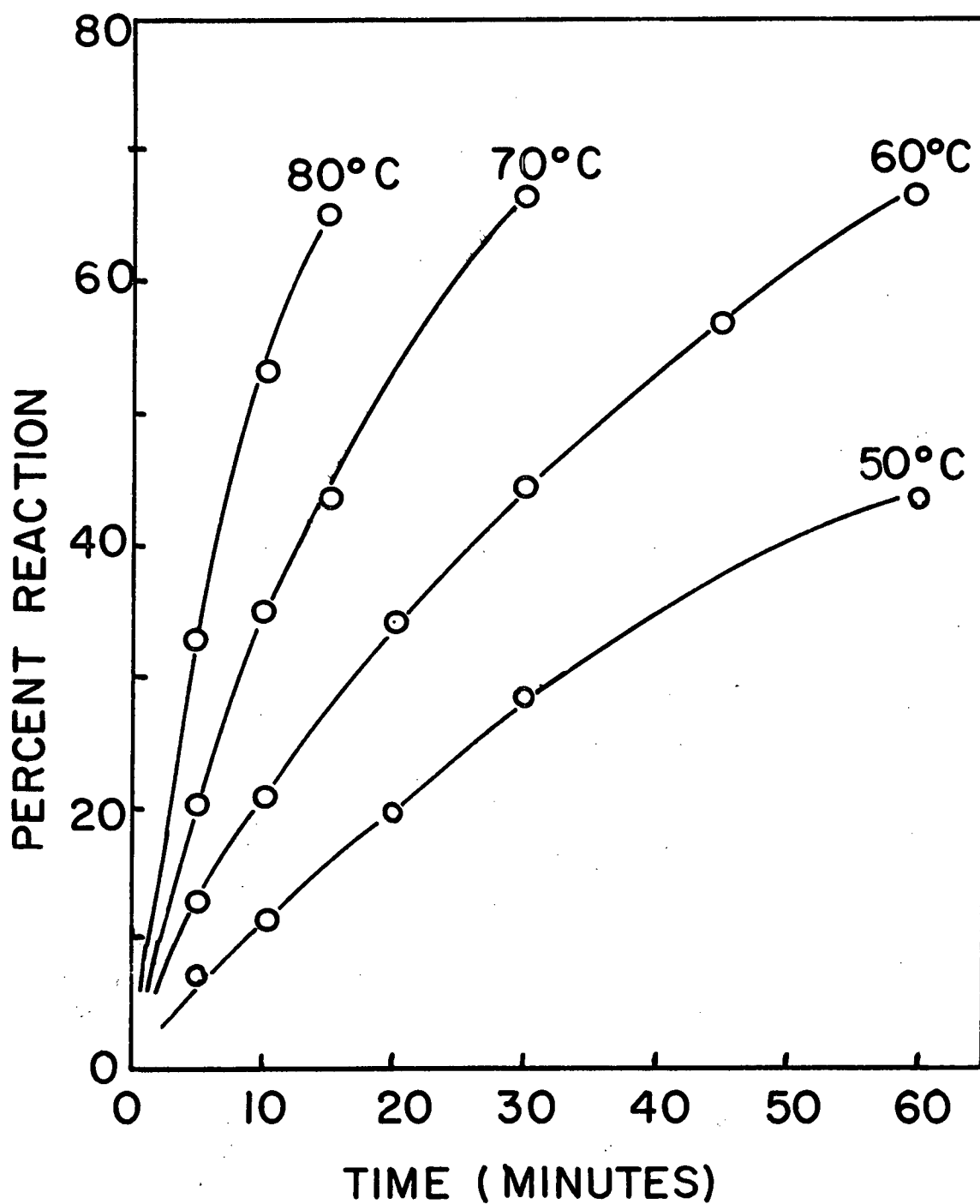


Figure 19: Percent Reaction vs. Time for -100 + 140 m Phoenix CuFeS_2 in 40 wt. % S_2Cl_2 .

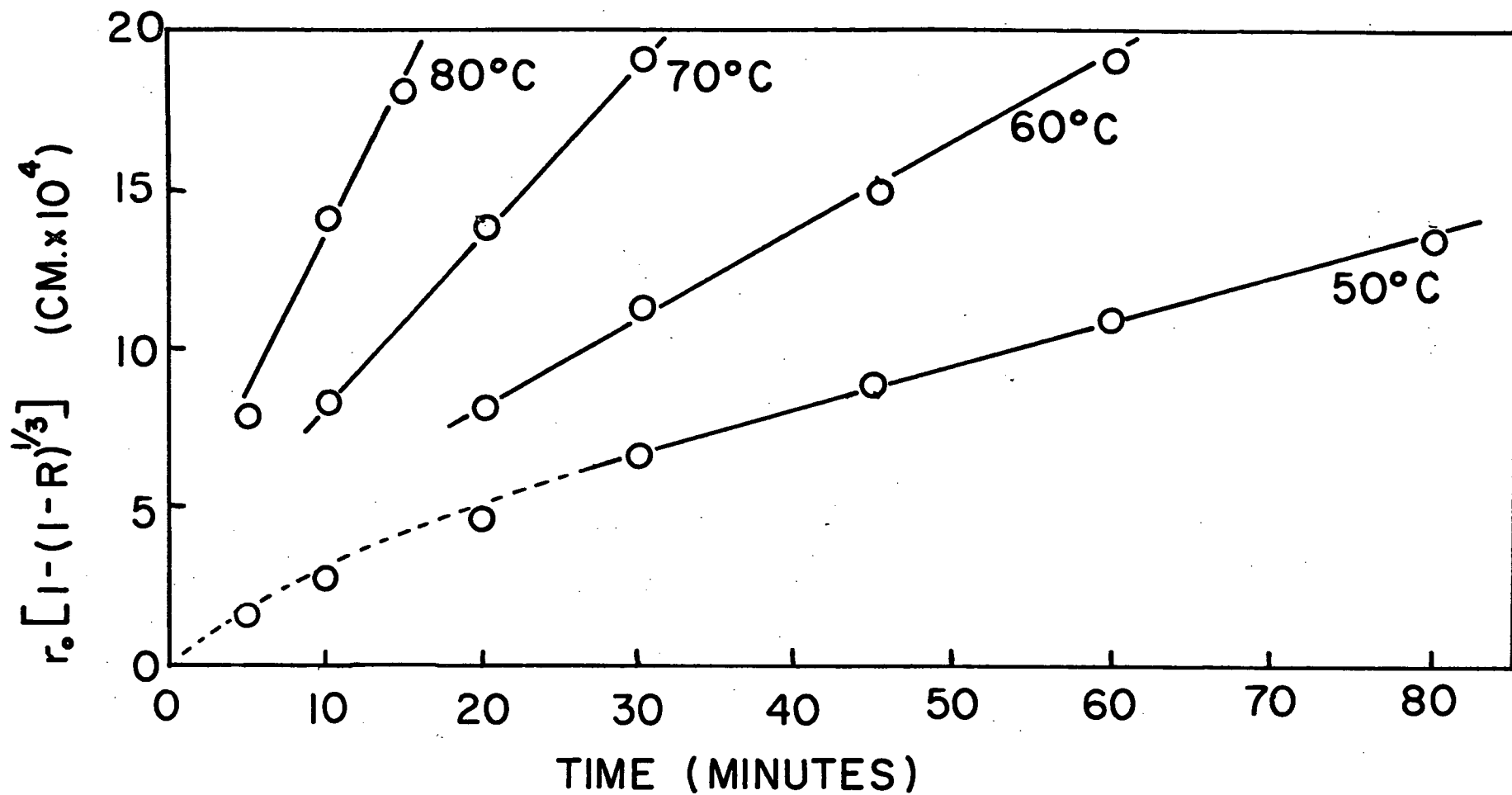


Figure 20: Plot of $r_o[1-(1-R)^{1/3}]$ vs. Time for -100 + 140 m Phoenix CuFeS_2 in 40 wt. % S_2Cl_2 .

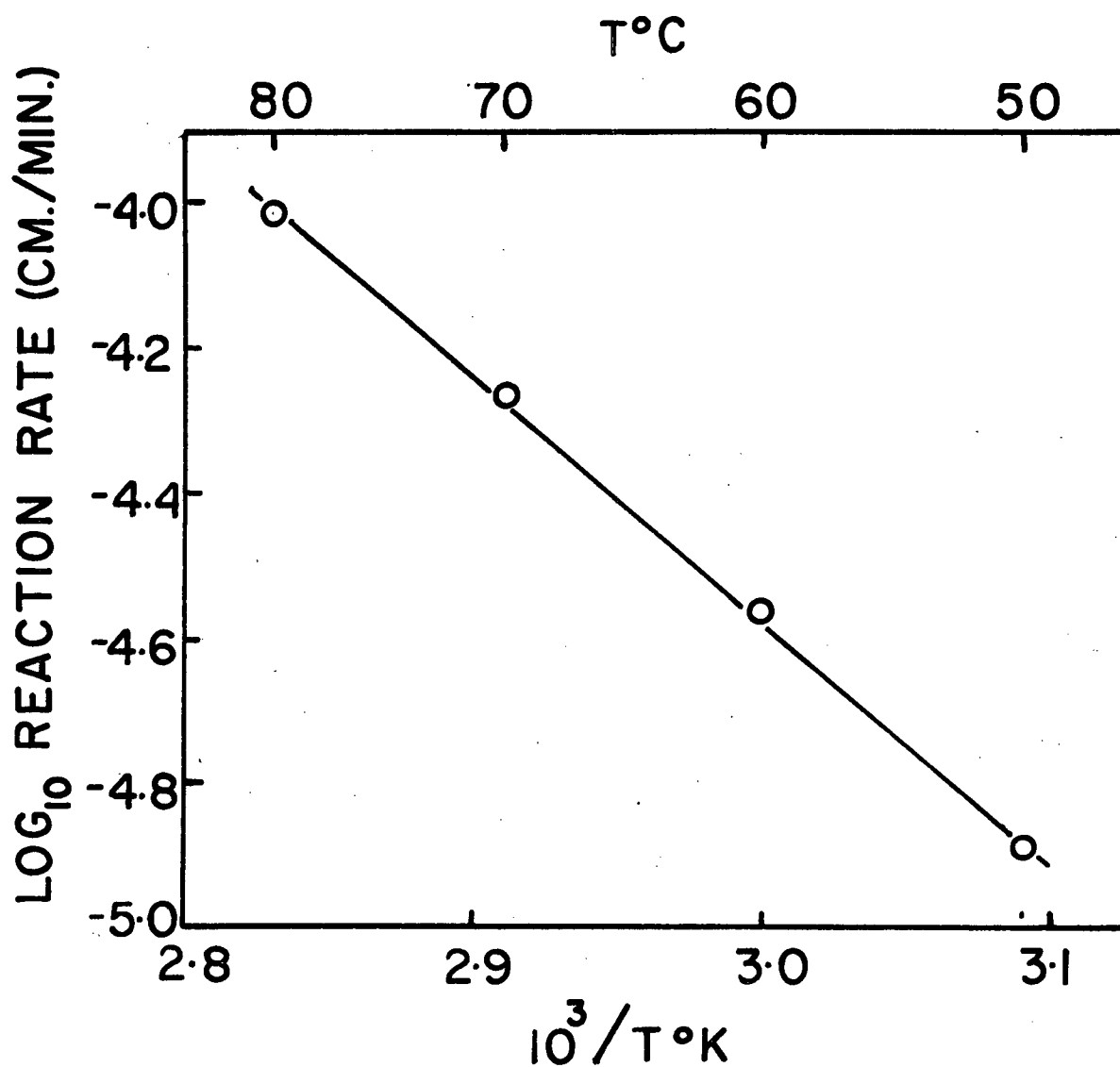


Figure 21: Arrhenius Plot for Reaction of -100 + 140 m Phoenix CuFeS_2 with 40 wt. % $\text{S.S}_2\text{Cl}_2$.

3.222 The Calculated Activation Energy

The rates summarized in Table 9 were used to construct an Arrhenius plot (Figure 21) for the reaction. The slope of this plot corresponds to an activation energy of 16.4 ± 2 Kcal mole⁻¹. This value, and the lack of effect of stirring on the reaction rate again indicate that the rate is controlled by a chemical phase boundary reaction.

3.223 Qualitative Observations on Other Copper Minerals

Qualitative experiments on uncharacterized samples of bornite (Cu_5FeS_4), covellite (CuS), and chalcocite (Cu_2S) indicated that these minerals react at least as fast as chalcopyrite in 40 wt % $\text{S.S}_2\text{Cl}_2$.

Copper metal is also attacked by 40 wt % $\text{S.S}_2\text{Cl}_2$.

3.23 Decomposition of Zinc Sulphide by Sulphur Chloride

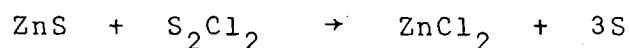
To investigate the reactivity of zinc sulphide in sulphur chloride, samples of two zinc concentrates - a relatively pure sphalerite from Pine Point Mines Ltd., and a marmatitic or high iron zinc concentrate from the Sullivan Mine (for analyses, see Appendix A) - were treated with sulphur-sulphur chloride solutions. The extent of reaction of the concentrates under various conditions of temperature and sulphur concentration is summarized in Table 10.

Table 10: Reaction of Sphalerite with S_2Cl_2

Substrate	Reaction Conditions	% Reaction (weight loss)
Pine Point ZnS (-150 + 200 m)	40 wt % S_2Cl_2 10 min at 146°C	0.8
"	40 wt % S_2Cl_2 30 min at 146°C	0.9
"	100% S_2Cl_2 10 min at 133°C	0.8
Sullivan ZnS (-70 + 140 m)	100% S_2Cl_2 10 min at 133°C	31.3*
"	40 wt % S_2Cl_2 40 min at 150°C	32.4*

* Residue assay (60.5% Zn, 0.4% Pb, 4.5% Fe) showed 18 (± 1)% of Zn in original sample was solubilized.

From the table it is apparent that the relatively pure (Pine Point) material is virtually unreactive to sulphur chloride despite the favourable calculated free energy (Table 1) for the reaction



It seems probable that a protective layer of zinc chloride is formed on the sulphide surface, and acts as a barrier to further reaction.

The Sullivan zinc concentrate contains an appreciable

amount (9.0%) of iron in solid solution and as pyrrhotite not removed in flotation. The water insoluble, solid residue after treatment of Sullivan zinc concentrate with sulphur chloride contained only 4.5% iron. The ratio of zinc to iron in the material decomposed was 1.3:1.

It is suggested that in the case of the Sullivan zinc concentrate (which contained 9.0% iron) the formation of a protective film of zinc chloride at the mineral surface is hindered by simultaneous reactions of iron sulphide in solid solution in the zinc mineral.

3.24 Decomposition of Molybdenite by Sulphur Chloride

The reactivity of molybdenite (MoS_2) in sulphur chloride solutions was studied by treating samples of a molybdenite concentrate (Appendix A) with S_2Cl_2 at 136°C , 40 wt % S_2Cl_2 at 150°C , and chlorine saturated S_2Cl_2 at 60°C . In no case was any significant amount of molybdenite reacted (as predicted by thermodynamic calculations - Table 1). The small (1%) but consistent weight loss observed in these experiments can be explained by reaction of the copper mineral content (0.4% Cu) of the concentrate - the samples gave negative qualitative tests for copper after treatment with sulphur chloride.

From these results, it is apparent that molybdenite is unattacked by sulphur chloride under a wide range of conditions. Thus, it is possible to selectively decompose

other sulphides such as pyrite, chalcopyrite or galena in the presence of molybdenite.

3.3 Interpretation of Experimental Results

3.31 Requirements for a Reaction Mechanism

The mechanism of the reaction of sulphur chloride with a metal sulphide will involve at least three steps:

- i. A surface reaction in which sulphur chloride or a dissociation product of sulphur chloride forms bonds directly to the mineral surface.
- ii. The generation of intermediate products (possibly transitory in nature) such as S_n ($n = 1-4$), free radicals such as $\cdot Cl$ or $\cdot S-S-Cl$, or mixed sulphur-chlorine compounds of the metal component(s) of the mineral.
- iii. Establishment of a solid deposit of reaction products at the mineral surface and/or the dissolution and diffusion of reaction products through a boundary layer.

Besides incorporating the three steps mentioned above, any proposed mechanism for the reactions studied should be consistent with the following observations:

- i. The activation energies calculated from experimental rate data are in the range of 16-22 Kcal/mole. These values are consistent with rate control by chemical reaction(s) and are higher than values expected for rate control by diffusion in the liquid state (56). Also, the lack of a significant stirring effect in the reactions

of pyrite, galena and chalcopryrite indicates that diffusion in a liquid boundary layer is not rate controlling.

- ii. Evidence indicating the formation of stable films of solid reaction products was obtained in the reactions of sphalerite, pyrrhotite, and pyrite (in pure S_2Cl_2). In the reaction of metallic iron with sulphur-sulphur chloride solutions definite evidence of surface film formation was obtained in the form of parabolic reaction kinetics and visible deposits on the metal surface.
- iii. The linearity of the plots of $r_o[1-(1-R)^{1/3}]$ vs. time for the reactions of pyrite, galena, and chalcopryrite indicate that the reaction mechanism for these materials must be consistent with a constant interface velocity in the reactions.

3.32 The Role of Sulphur

In considering mechanisms applicable to the reactions investigated, the role of sulphur - either present initially in the solvent or formed as a product - should be considered.

It is reasonable to assume that small S_n ($n = 1-4$) molecules are intermediates in the reactions of sulphur chloride with sulphide minerals. These S_n molecules will polymerize and may form a significant fraction of long chain S_N ($N \gg 8$) polymers instead of S_8 rings. Long chain sulphur molecules are known to be insoluble in carbon disulphide and

may therefore have a poor solubility in pure sulphur chloride while their solubility may be increased by the presence of a large fraction of S_8 molecules in solution in the sulphur chloride. Thus, factors determining the reaction rate could be dissolution of long chain sulphur molecules at a phase boundary, diffusion of sulphur chloride through a viscous boundary layer of product sulphur or conversion of S_N molecules to the equilibrium S_8 configuration at a boundary. This would imply a mixed mechanism in which long chain sulphur molecules are formed by reaction at the mineral surface, then dissolve in the solvent. The steady state thickness of an S_N film formed by such a reaction would depend on the relative rates of: sulphur removal, diffusion of sulphur chloride through a viscous boundary layer, and the surface reaction.

This process would be associated with high activation energies and constant interface velocities of the reactions as observed experimentally.

Another possible role for dissolved sulphur in the reactions studied is in the removal of solid reaction products from the mineral surface - thus preventing the buildup of a passive (or inhibitory) film of solid metal chloride on the mineral surface.

In the case of pyrite, sulphur may accomplish this function by either increasing the solubility of product ferric chloride so that removal by a dissolution-precipitation reaction can occur rapidly enough to maintain a clean

reacting surface or by forming unstable or transitional complexes with metal chloride reaction products so that metal chloride precipitation occurs away from the reacting surface.

Alternatively, sulphur might prevent formation of a coherent layer of metal chloride product by preferentially wetting the mineral surface so that metal chloride product will not adhere to the surface.

3.33 Surface Reactions

The sulphur chloride molecule can react with a mineral or metal surface in one of two ways: by dissociation into active species such as chlorine atoms which then attack the surface or by forming M-Cl bonds via an associative mechanism with an S_2 or $\cdot S-S-Cl$ molecule being formed as a remnant of the sulphur chloride molecule.

3.331 Dissociative Reactions of Sulphur Chloride

Average bond energy values (at 25°C) have been calculated (60) for S-S and S-Cl bonds. These values are respectively 51 and 60 Kcal per mole of bonds. From these values it appears most unlikely that the observed reactions proceed by a pure dissociation (or S_N1) type of mechanism since the calculated activation energies (16-22 Kcal) are significantly lower than those required for bond rupture.

3.332 Associative Reaction of Sulphur Chloride

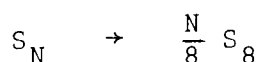
The alternative to a dissociative mechanism is an associative mechanism in which the sulphur chloride molecule interacts with the mineral surface to form at least a temporary $S..Cl..M$ bond before the sulphur-chlorine bond is completely broken. In this case a surface intermediate could be a sulphochloride (metal-sulphur-chlorine compound), with possible residual S-Cl bonds. However such compounds are not described in the technical literature and under the experimental conditions of this study are unstable with respect to decomposition to crystalline metal chlorides and sulphur.

The small (S_n , $n = 1-4$) sulphur molecules remaining after the chlorination reaction will polymerize (to S_8 or S_N , $N \gg 8$) leaving metal chlorides which may or may not adhere to the reacting surface.

3.34 Models for Metal Sulphide-Sulphur Chloride Reactions

Some possible modes of reaction of sulphur chloride with metal sulphides (as discussed in the previous sections) are presented in Figure 22.

Scheme A of Figure 22 represents the formation of a steady state layer of polymeric S_N molecules on the surface. In this case, rate control may be by diffusion of sulphur chloride through the viscous sulphur film, by the reaction



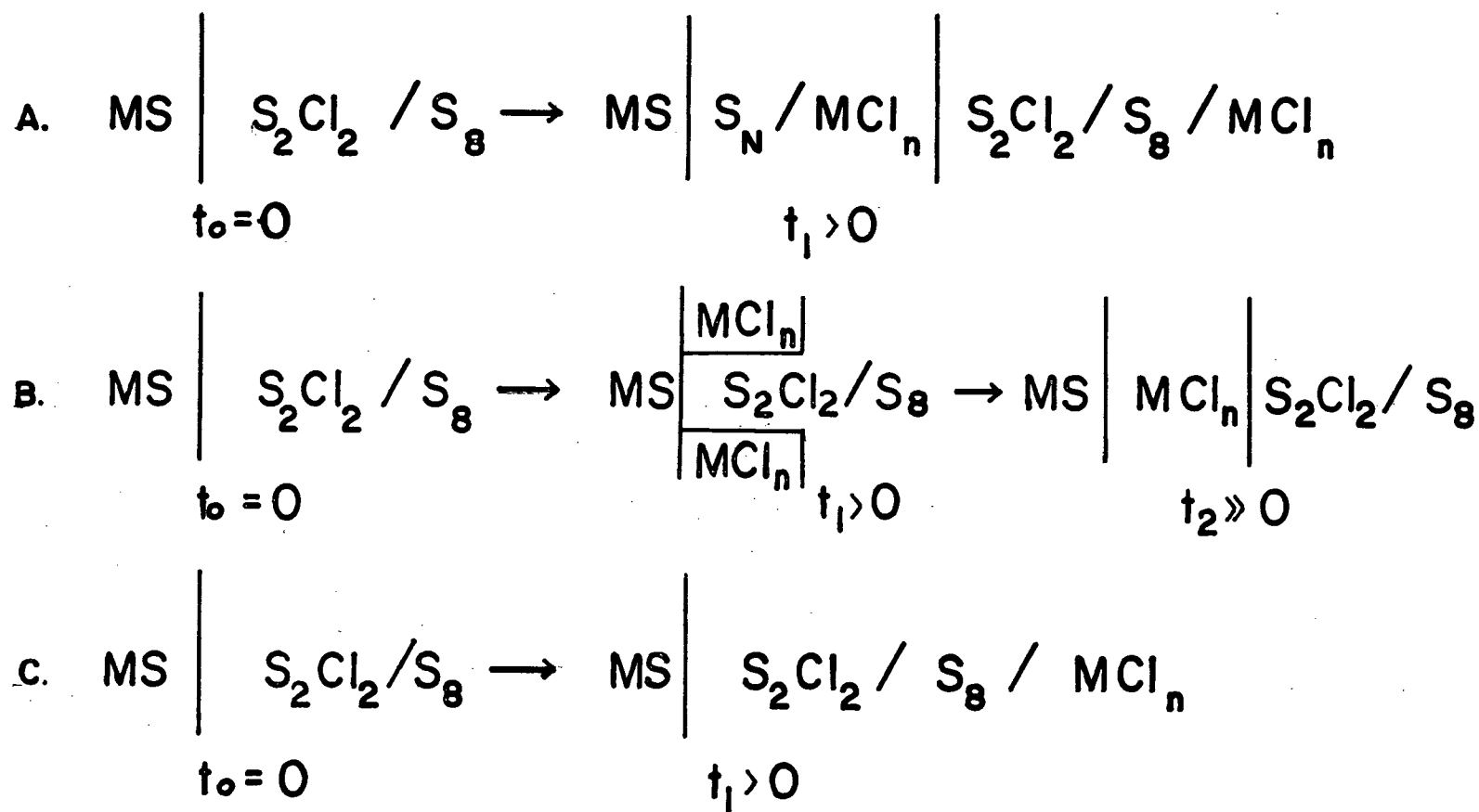


Figure 22: Models for the Reaction of Sulphur Chloride
with Metal Sulphides
(see text, Section 3.34)

at the $S_N/MCl_n - S_2Cl_2/S_8$ interface, by physical dissolution of S_N or a combination of these factors.

If such a sulphur film did form it would be expected to form in all cases but the complete reaction of galena with sulphur chloride does not require large amounts of sulphur dissolved in the sulphur chloride. Also, if the action of the catalysts (Ag, Sb etc.) in the galena reaction is to inhibit the formation of a viscous sulphur film then this effect should occur in the reaction of pyrite, but no such effect was observed. On this basis, rate control by the formation of a viscous layer of polymeric sulphur seems unlikely so it is reasonable to consider the properties of the metal chloride reaction product.

Scheme B of Figure 22 represents formation of an adherent layer of metal chloride product on the sulphide surface. Such a film may be porous or dense. Formation of a porous metal chloride layer on the reacting surface is consistent with the parabolic kinetics of the iron-sulphur chloride reaction: as the porous layer thickens the reaction rate decreases due to the increased diffusion path for reactant sulphur chloride and product sulphur. Formation of a dense metal chloride layer on the reacting interface is consistent with the reactions of sphalerite and pyrrhotite where the rates are initially rapid - corresponding to the period for build-up of a protective layer. Then the rate decreases to a very small value as the dense adherent

layer prevents access of the sulphur chloride to the surface.

Scheme C represents a metal sulphide-sulphur chloride reaction in which the metal chloride product either does not adhere to the sulphide surface or is removed by dissolution and precipitated away from the surface. In this scheme, rate control could be by liquid phase diffusion or surface reaction kinetics. In the reactions studied, the high activation energy values and independence of rate on stirring indicate rate control by surface reaction kinetics. Scheme C is consistent with the results of experiments on galena (with pure sulphur chloride) and pyrite and chalcocopyrite (with 40 wt % S_2Cl_2).

Thus, on the basis of the experimental evidence of this study, it seems probable that the differences in response of metal sulphides to reaction with sulphur chloride depend on the nature of the metal chloride product. If this metal chloride product forms a coherent surface layer then parabolic kinetics or virtual passivity are observed (depending on the porosity of the film) while if the metal chloride product is non adherent, rate control is by surface reaction and linear kinetics are observed.

3.4 Elemental Sulphur from Chlorination of Metal Sulphides

Elemental sulphur is a product of reactions between metal sulphides and S_2Cl_2 . The reactions were normally

done at temperatures such that the sulphur dissolved in excess sulphur chloride present. Elemental sulphur (in rhombic or monoclinic form) can be crystallized from S_2Cl_2 solution by cooling (29). The size of the precipitated sulphur crystals can be controlled by the cooling rate and/or by addition of seed crystals to act as nucleation sites. Two sizes of rhombic sulphur crystals precipitated from solution are shown in Figure 23. Such crystals are easy to filter and wash, and are free-flowing when dry.

Some chloride is always present in the crystal sulphur, both on the surface and in the bulk. The surface chlorine can be removed and recovered by washing the crystals with inorganic solvents such as carbon tetrachloride, and distillation of the wash liquor for separate recovery of solvent and sulphur chloride. Chloride remaining after this treatment can be removed down to very low levels - without disrupting the crystal structure - by water washing. Chloride removed by this procedure is hydrolyzed to aqueous hydrochloric acid (30) and lost from the process.

A summary of chlorine contents of sulphur crystals after various washing procedures is presented in Table 11.

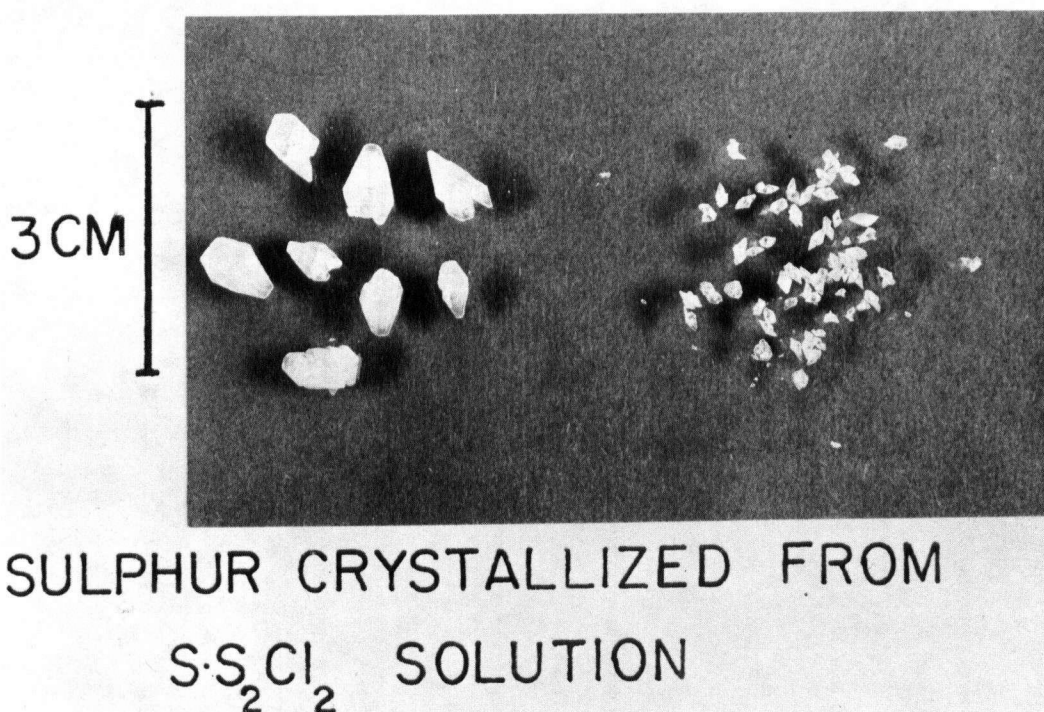


Figure 23: Rhombic Sulphur Crystals Precipitated from $S \cdot S_2Cl_2$ Solution.

Table 11: Chlorine Content of Precipitated Sulphur*

Wash Sequence	Wt. % Cl
1) excess solvent drained	1.54
2) washed in CCl_4 and filtered	0.12
3) water washed for 1 hr. and filtered	0.03

* -28 + 44 mesh rhombic crystals precipitated from S saturated S_2Cl_2 at 60-50°C.

3.5 Potential Metallurgical Uses for Sulphur Chloride

3.5.1 Useful Properties of Sulphur Chloride

The results of this study indicate that sulphur chloride has several properties which may be useful in the metallurgical treatment of sulphides. It was found that under appropriate conditions, sulphur chloride can rapidly and completely decompose certain sulphide minerals (pyrite, chalcopyrite, galena) to form metal chlorides and (dissolved) elemental sulphur. These reactions are exothermic (Table 1) and occur at temperatures below the boiling points of the solutions used, so the reactions can be thermally self-sustaining and pressure (above atmospheric) is not required. The sulphur product of such reactions can be completely recovered by cooling the solvent to crystallize dissolved sulphur. By crystallizing sulphur at temperatures below 95°C, stable rhombic sulphur crystals can be produced

(Appendix H, (47)) in a range of sizes. Sulphur in this form could be easily handled and free from dust.

Other metal sulphides (molybdenite, pure sphalerite) were found to be essentially unreactive to sulphur chloride so selective decomposition of various components of sulphide concentrates can be accomplished with sulphur chloride. Examples of such selective reactions are the decomposition of galena in the presence of sphalerite and the decomposition of chalcopryrite or galena in the presence of molybdenite.

On the basis of these results, some potential processes for metallurgical treatment of sulphides by sulphur chlorides are suggested.

3.52 Specific Potential Uses for Sulphur Chloride

3.521 Pyrite

It has been shown that pyrite can be completely and uniformly decomposed by sulphur chloride containing 25-40 wt % dissolved sulphur. On the basis of these results, a process (61) is proposed for the metallurgical treatment of pyrite to recover elemental sulphur, pure iron oxide, and a concentrate of the non-ferrous metals. In this proposed process, pyrite will be decomposed by reaction with 25-40 wt % S_2Cl_2 . The solid products (metal chlorides) of this reaction will be treated with oxygen to convert iron chlorides to oxides and generate chlorine for reuse in the sulphide decomposition reaction. Any non-ferrous metal chlorides

on the solid residue will not be converted to oxides and will be recovered by aqueous leaching of the iron oxide product. The liquid phase from the decomposition reaction will be cooled to crystallize an amount of sulphur equivalent to the sulphide content of the pyrite, product sulphur separated, and the remaining solution recycled to the decomposition step. A schematic flowsheet for this process is shown in Appendix E.

Of the unit operations in the proposed process, the decomposition of pyrite and crystallization of product sulphur have been demonstrated in this study, and the oxidation of ferric chloride has been accomplished (9) in a bench scale experiment.

Some advantages of the proposed process are the production of elemental sulphur in a convenient form, fast reactions, and the (expected) purity of the iron oxide and non-ferrous metals produced.

3.522 Galena

Results of experiments on galena concentrates have shown that galena can be completely decomposed by sulphur-sulphur chloride solutions under relatively mild conditions and that sphalerite is unreactive under these conditions. From these results, a process for treatment of lead concentrate is proposed. In this (proposed) process, lead concentrate will be decomposed by sulphur-sulphur chloride

solutions containing a certain amount of silver and antimony or bismuth as catalytic agents. The solid products of this reaction will be leached in hot brine to dissolve lead chloride leaving unreacted sphalerite as a residue. Lead chloride will be recrystallized by cooling the solution, filtered off, and electrolyzed in a chloride melt for production of lead metal and chlorine for recycle. Sulphur will be recovered by crystallization from the sulphur-sulphur chloride solution used in the decomposition reaction. A schematic flowsheet for this proposed process is shown in Appendix F.

The proposed process incorporates a metallurgical separation of lead from mixed lead-zinc concentrates and produces elemental sulphur. Consumption of chlorine by minerals other than galena will be small since in the presence of silver and antimony or silver and bismuth (as catalysts) galena has been shown to react with sulphur-sulphur chloride solutions under conditions in which other minerals (e.g. pyrite) react very slowly.

3.523 Molybdenite

Molybdenite was found to be unattacked by sulphur-sulphur chloride solutions under conditions in which pyrite, chalcopyrite and galena are completely decomposed. On the basis of these results, it is proposed that molybdenite concentrates containing deleterious amounts of these minerals can be purified by treatment with sulphur-sulphur chloride solutions to selectively decompose the impurities. The

solid residue from this reaction would be acid leached to remove soluble metal chlorides from the unattacked molybdenite.

Cleaning (removal of small amounts of impurities) of molybdenite concentrates by flotation frequently results in a lower final molybdenite recovery, so selective leaching of molybdenite concentrates by sulphur-sulphur chloride solutions would have the advantage of making a high grade product with high recovery since no molybdenite will be decomposed by sulphur chloride leaching.

3.53 Problems in the Use of Sulphur Chloride

It has been shown that sulphur chloride may be useful in the processing of sulphide minerals - particularly pyrite, galena, and molybdenite. However, the use of sulphur chloride as a metallurgical reagent poses a number of problems.

Sulphur chloride is highly corrosive to a number of metals (iron, titanium, copper, lead - see Appendix G) so a suitable material must be found for process equipment. Preliminary tests (Appendix G) indicated that monel alloy has significant resistance to attack by sulphur chloride.

Sulphur chloride hydrolyzes readily, so water must be excluded from any system using sulphur chloride to avoid production of the undesirable hydrolysis products (hydrogen chloride and sulphur dioxide).

Also, sulphur chloride is toxic (51) and has an offensive odour, so it must be completely enclosed in any large scale application.

4. CONCLUSIONS

From the foregoing, it has been established that the sulphide minerals pyrite, galena, and chalcopyrite can be treated with sulphur chloride (containing dissolved sulphur) to convert metals to their chlorides and extract sulphur. On this basis, processes have been formulated for potential commercial application in the treatment of flotation concentrates of pyrite, galena, and molybdenite.

Conditions have also been determined for the complete decomposition of pyrite, chalcopyrite, and galena by sulphur chloride. Under conditions in which complete reaction is observed, the reaction products are iron (III) chloride, copper (II) chloride, lead (II) chloride and elemental sulphur. Pyrite was found to react uniformly and completely in sulphur chloride containing 25-40% dissolved sulphur, but reacted only partially in sulphur chloride containing 0-10 wt % dissolved sulphur. Chalcopyrite was completely decomposed by sulphur chloride containing 40 wt % dissolved sulphur. Galena was decomposed by sulphur chloride containing 0-10 wt % dissolved sulphur when small quantities of silver and antimony or silver and bismuth were present as catalysts

in the reaction mixture. Calculated values of specific reaction rates and activation energies for these reactions are presented in Table 12. Under conditions where uniform reaction was observed, the rates of these reactions were found to be chemically controlled in the temperature range (40-150°C) of this study and to be proportional to the surface area of the solid substrate.

Table 12: Summary of Rates and Activation Energies

Substrate	Solvent	Rate of Penetration at T°C	ΔE_A
-70 + 100 m Sullivan FeS ₂	40 wt % S.S ₂ Cl ₂	1.96 x 10 ⁻⁴ cm/min at 147°C	21.3 ± 2 Kcal/mole
-150 + 200 m Pine Point PbS	10 wt % S.S ₂ Cl ₂	a. catalyzed 1.55 x 10 ⁻⁴ cm/min at 60°C b. uncatalyzed 0.43 x 10 ⁻⁵ cm/min at 60°C	a. 15.4 ± 2 Kcal/mole b. 17.6 ± 2 Kcal/mole
-140 + 200 m CuFeS ₂	40 wt % S.S ₂ Cl ₂	1.06 x 10 ⁻⁴ cm/min at 80°C	16.4 ± 2 Kcal/mole

Natural and synthetic pyrrhotite were found to react partially with sulphur chloride and sulphur-sulphur chloride solutions to form ferric chloride and elemental sulphur. This reaction is inhibited by the presence of ferric chloride in the reaction mixture.

Reaction of relatively pure (Pine Point) sphalerite with sulphur chloride and sulphur-sulphur chloride solutions

was found to be negligible at temperatures up to 150°C. Some iron and zinc sulphides were decomposed (to zinc chloride, iron (III) chloride and sulphur) when a marmatitic (Sullivan) zinc concentrate was treated with sulphur chloride.

Molybdenite was found to be inert to sulphur chloride as predicted by thermodynamic calculations.

The sulphur produced by decomposition of metal sulphides with sulphur chloride can be quantitatively recovered by crystallization of rhombic sulphur crystals. The crystallized sulphur contains chloride which can be partially removed by washing with carbon tetrachloride, and nearly completely removed - without disruption of the crystal structure - by water washing.

The results of this study indicate that sulphur chloride may be useful in the metallurgical treatment of pyrite, galena, and molybdenite concentrates.

5. SUGGESTIONS FOR FURTHER WORK

1. A study of the reactions of pyrrhotite and iron in $S.S_2Cl_2$ solutions containing >40 wt % S and in Cl_2/CCl_4 solutions may determine with more certainty the reasons for the incomplete reaction of pyrrhotite with $S.S_2Cl_2$ solutions under the conditions used in this study.
2. A study of the parameters affecting crystallization of sulphur from $S.S_2Cl_2$ solutions should lead to minimization of the chloride content of product sulphur.
3. A study of the corrosion behaviour of high nickel alloys (including monel) may indicate a material which can reliably resist corrosion in $S.S_2Cl_2$ solutions.
4. The production of lead by molten salt electrolysis of $PbCl_2$ should be studied further to determine the energy efficiency and maximum attainable current densities.

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Appendix A: Sources and Analyses of
Natural Minerals Used in this Study

Mineral	Source	Analysis
Pyrite	Sullivan Mine (Cominco Ltd.)	45.2% Fe, 52.4% S, 0.7% Pb, 0.15% Zn, 0.5% SiO ₂
Pyrite	Noranda Mines Ltd.	47.1% Fe, 52% S, 0.5% SiO ₂
Pyrrhotite	Sullivan Mine (Cominco Ltd.)	57.0% Fe, 38.8% S, 1.0% Pb, 1.8% Zn, 0.8% Cu
Galena	Pine Point Mine (Cominco Ltd.)	82.0% Pb, 15.1% S, 1.1% Zn, 0.03% As, 0.05% Sb, 0.03% Bi, 0.02% Ag, Ca, Cu, Mg, Mn, Si < 0.1%
Sphalerite	Pine Point Mine (Cominco Ltd.)	63.8% Zn, 31.5% S, 0.4% Pb, 1.6% Fe
Sphalerite	Sullivan Mine (Cominco Ltd.)	52.4% Zn, 29.4% S, 6.4% Pb, 9.2% Fe
Chalcopyrite	Phoenix Mine (Granby Mining Ltd.)	27.6% Cu, 29.6% Fe, 32.0% S acid insoluble 8%
Molybdenite	Alice Arm, B.C. (B.C. Molybdenum Corp.)	52.1% Mo, 36.5% S, 0.4% Cu, major impurity SiO ₂

Appendix B: Grades of Materials and Chemicals Used in this
Study

Reagent grade: Ce(SO₄)₂
1,10 -o-phenanthroline
Na acetate
FeCl₂·4H₂O
Pb, Sn

Technical: S(flowers), Cl₂
acetone, CCl₄, CS₂
As₂S₃, Sb₂S₃, Bi₂S₃, Ag₂S

Unspecified: monel alloy, Fe

Appendix C: Stoichiometry Determinations

C-1 Reaction of Pyrite with Sulphur Chloride

Reaction conditions: T = 133°C, time = 5 minutes

Reactants: S₂Cl₂, Sullivan FeS₂

Initial sample weight 1.000 g

Final sample weight
(after wash, p. 24) 0.759

Loss in weight 0.241

$$\% \text{ pyrite reacted} = \frac{\text{loss in weight}}{\text{initial weight} - \text{gangue correction}} = \frac{0.241}{1.00 - 0.03} = 24.9\%$$

Analysis of water soluble products: Fe (total) 114 mg
(after CCl₄/CS₂ wash, p. 24)

Fe (ferrous) trace

Cl (total) 227 mg

Observed $\frac{\text{Fe}^*}{\text{Cl}} = 0.502$ (vs. $\frac{\text{Fe}}{\text{Cl}}$ for stoichiometric FeCl₃ = 0.523)

C-2 Reaction of Pyrite with 40 wt % S.S₂Cl₂

Reaction conditions: T = 129°C, time = 5 minutes

Reactants: 40 wt % S.S₂Cl₂, Sullivan FeS₂

Initial sample weight 1.000 g

Final sample weight .808

Loss in weight .192

$$\% \text{ pyrite reacted} = \frac{.192}{1.00 - 0.03} \times 100 = 19.8\%$$

Analysis of water soluble products: Fe (total) 89 mg

Fe (ferrous) trace

Cl (total) 170 mg

Observed $\frac{\text{Fe}}{\text{Cl}} = .524$ (vs. $\frac{\text{Fe}}{\text{Cl}}$ for FeCl₃ = 0.523)

* Weight ratio

C-3 Analysis of Residue from Large Scale Pyrite Experiment

Initial sample weight 40.0 g

Insoluble residue* weight 1.317 g

Residue Digestion: HCl/HNO₃

Analysis Fe: 23.2% (306 mg)

Zn: 3.9% (51.4 mg)

S : 3.1% (40.8 mg)

* A large part of the insoluble residue adhered strongly to the magnetic stirring bar.

C-4 Reaction of Pyrrhotite with Sulphur Chloride

Reaction Conditions: T = 113°C, time = 40 minutes

Reactants: S₂Cl₂, Sullivan FeS

Initial sample weight 2.000 g

Final sample weight 1.296

Loss in weight .704

$$\text{Uncorrected \% reaction} = \frac{.704}{2.000} \times 100 = 35.2\%$$

Analysis of water soluble products: Fe (total) 438 mg

Fe (ferrous) 5 mg

Cl (total) 860 mg

$$\text{Observed } \frac{\text{Fe}}{\text{Cl}} = .509 \text{ (vs. } \frac{\text{Fe}}{\text{Cl}} \text{ for FeCl}_3 = 0.523)$$

C-5 Reaction of Metallic Iron with 40 wt % $S.S_2Cl_2$

Reaction Conditions: $T = 133^\circ C$, time = 20 minutes

Reactants: 40 wt % $S.S_2Cl_2$, iron strip

Loss in sample weight = 371 mg

Analysis of water soluble surface film*
(see section 3.15)

Fe (total) 33 mg

Fe (ferrous) 32 mg

Cl (total) 43

Observed $\frac{Fe}{Cl} = .767$ (vs. $\frac{Fe}{Cl}$ for $FeCl_2 = .787$)

* Only a fraction of the product remained on the metal surface

C-6 Reaction of Galena with Sulphur Chloride

Reaction Conditions: $T = 70^\circ C$, time = 20 minutes

Reactants: 10 wt % $S.S_2Cl_2$, Pine Point PbS

Initial sample weight 1.000 g

Residue weight before salt
or water wash (see section 2.22) 1.018 g

Residue weight after
final wash .891 g

Analysis of hot salt wash solution: Pb 94 mg
(sulphate
precipitation)

Cl 33 mg
(by difference)

Observed $\frac{Pb}{Cl} = 2.85$ (vs. $\frac{Pb}{Cl}$ for $PbCl_2 = 2.92$)

C-7 Reaction of Chalcopyrite with 40 wt % $S.S_2Cl_2$

Reaction Conditions: T = 70°C, time = 90 minutes

Reactants: 40 wt % $S.S_2Cl_2$, -100 + 140 m Phoenix
Chalcopyrite
concentrate

Initial sample weight 1.000 g

Final sample weight 0.208

Analysis of water soluble products Cu: 272 mg
Fe: 245 mg
Cl: 775 mg

Calculated Chlorine required for $CuCl_2$ & $FeCl_3$: 771 mg

Residue Analysis Cu: 5 mg
Fe*: 47 mg
S : 42 mg

*Partly present as magnetite

Appendix D: Selected Experimental Results

D-1 Reaction of Pyrite with 40 wt % S.S₂Cl₂

Substrate	Time (minutes)	T(°C)	Percent of Pyrite Reacted	$[1-(1-R)^{1/3}]$	$r_o[1-(1-R)^{1/3}]$ (cm x 10 ⁴)	Rate cm min ⁻¹ x 10 ⁴	Mean rate cm min ⁻¹ x 10 ⁴
-200 + 270m.							
Sullivan							
Pyrite	5	139.7	43.5	0.173	5.41	1.08	1.02
"	10	"	67.0	0.309	9.56	0.967	
"	5	129.0	19.8	0.071	2.22	0.444	0.449
"	10	"	37.5	0.145	4.54	0.454	
"	30	"	81.7	0.432	13.5	0.450	
"	45	"	96.4	0.670	21.0		
"	60	"	98.5	0.753	23.6		
"	10	119.7	16.6	0.059	1.85	0.185	0.186
"	20	"	30.9	0.116	3.63	0.182	
"	30	"	44.3	0.177	5.54	0.185	
"	60	"	75.0	0.378	11.6	0.193	
"	5	113.0	7.4	0.025	0.78	0.156	0.129
"	20	"	22.6	0.082	2.57	0.129	
"	40	"	40.3	0.158	4.95	0.124	
"	60	"	58.5	0.254	7.95	0.133	
-70 + 100m							
Sullivan							
Pyrite	20	113.0	13.2	0.046	4.07	.204	.201
"	40	"	24.9	0.091	8.04	.201	
"	60	"	35.3	0.135	11.9	.198	

D-1 (continued)

Substrate	Time (minutes)	T(°C)	Percent of Pyrite Reacted	$[1-(1-R)^{1/3}]$	$r_o[1-(1-R)^{1/3}]$ (cm x 10 ⁴)	Rate cm min ⁻¹ x 10 ⁴	Mean rate cm min ⁻¹ x 10 ⁴
-70 + 100m Sullivan							
Pyrite	20	120.0	20.0	0.072	6.36	.318	.314
"	40	"	36.9	0.142	12.6	.315	
"	60	"	50.7	0.210	18.6	.310	
"	10	126.2	17.4	0.062	5.48	0.548	0.538
"	20	"	32.8	0.124	11.0	0.550	
"	40	"	54.9	0.233	20.6	0.515	
"	10	133.0	28.0	0.104	9.19	0.919	.870
"	20	"	46.1	0.186	16.4	0.820	
"	15	139.7	51.5	Avg. = .215	19.0	1.26	1.26
"	15	"	51.7				
"	10	146.9	51.7	Avg. = .217	19.2	1.92	1.92
"	10	"	52.3				
-70 + 100m Noranda							
Pyrite	10	119.9	5.3	0.018	1.59	0.159	0.153
"	30	"	14.0	0.049	4.33	0.144	
"	45	"	21.9	0.079	6.98	0.155	
-70 + 100m Sullivan							
Pyrite	10	119.9	10.4	0.036	3.18	.318	.321
"	20	"	20.3	0.073	6.45	.323	
"	40	"	37.7	0.146	12.9	.323	

D-1 (continued)

Substrate	Time (minuted)	T(°C)	Percent of Pyrite Reacted	$[1-(1-R)^{1/3}]$	$r_o [1-(1-R)^{1/3}]$ (cm x 10 ⁴)	Rate cm min ⁻¹ x 10 ⁴	Mean rate cm min ⁻¹ x 10 ⁴
-270 + 325m Sullivan Pyrite	5	119.	11.9	0.041	0.988	0.198	.215
"	10		24.9	0.091	2.19	0.219	
"	20		44.5	0.178	4.29	0.215	
"	30		63.0	0.282	6.80	0.227	

D-2 Reaction of Galena with 10 wt % S_2Cl_2

D-2.1 Experiments Without Added Catalyst

Substrate	Time (minutes)	T(°C)	Percent of Galena Reacted	$[1-(1-R)^{1/3}]$	$r_o [1-(1-R)^{1/3}]$ (cm x 10^5)	Rate cm min^{-1} x 10^5	Mean rate
-150 + 200m Pine Point Galena	10	60	3.0	0.010	4.38	0.438	0.433
"	20	"	5.7	0.020	8.76	0.438	
"	30	"	8.5	0.029	12.7	0.423	
"	5	70	2.8	0.009	3.94	0.788	.825
"	10	"	5.6	0.019	8.32	0.832	
"	20	"	11.2	0.039	17.1	0.855	
"	5	80	5.4	Avg. 0.019	8.32	1.66	1.77
"	5	"	6.5				
"	10	"	10.5	Avg. 0.043	18.8	1.88	
"	10	"	14.0				
"	5	90	11.0	0.038	16.6	3.32	3.32

D-2.2 Experiments With Added Catalyst

Substrate	Time (minutes)	T(°C)	Percent of Galena Reacted	$[1-(1-R)^{1/3}]$	$r_o [1-(1-R)^{1/3}]$ (cm x 10 ⁴)	Rate cm min ⁻¹ x 10 ⁴	Mean rate cm min ⁻¹ x 10 ⁴
-150 + 200m Pine Point Galena	10	30	12.3	0.043	1.88	0.188	0.189
"	20	"	24.4	0.089	3.90	0.195	
"	30	"	33.0	0.125	5.48	0.183	
"	5	40	12.2	0.042	1.84	0.368	0.356
"	10	"	21.6	0.078	3.42	0.342	
"	15	"	30.2	0.113	4.95	0.330	
"	20	"	44.0	0.176	7.71	0.385	
"	5	50	25.6	0.094	4.12	0.824	0.893
"	10	"	50.5	0.209	9.15	0.915	
"	15	"	69.0	0.323	14.1	0.940	
"	5	60	47.0	0.191	8.37	1.67	1.55
"	10	"	69.4	0.326	14.3	1.43	

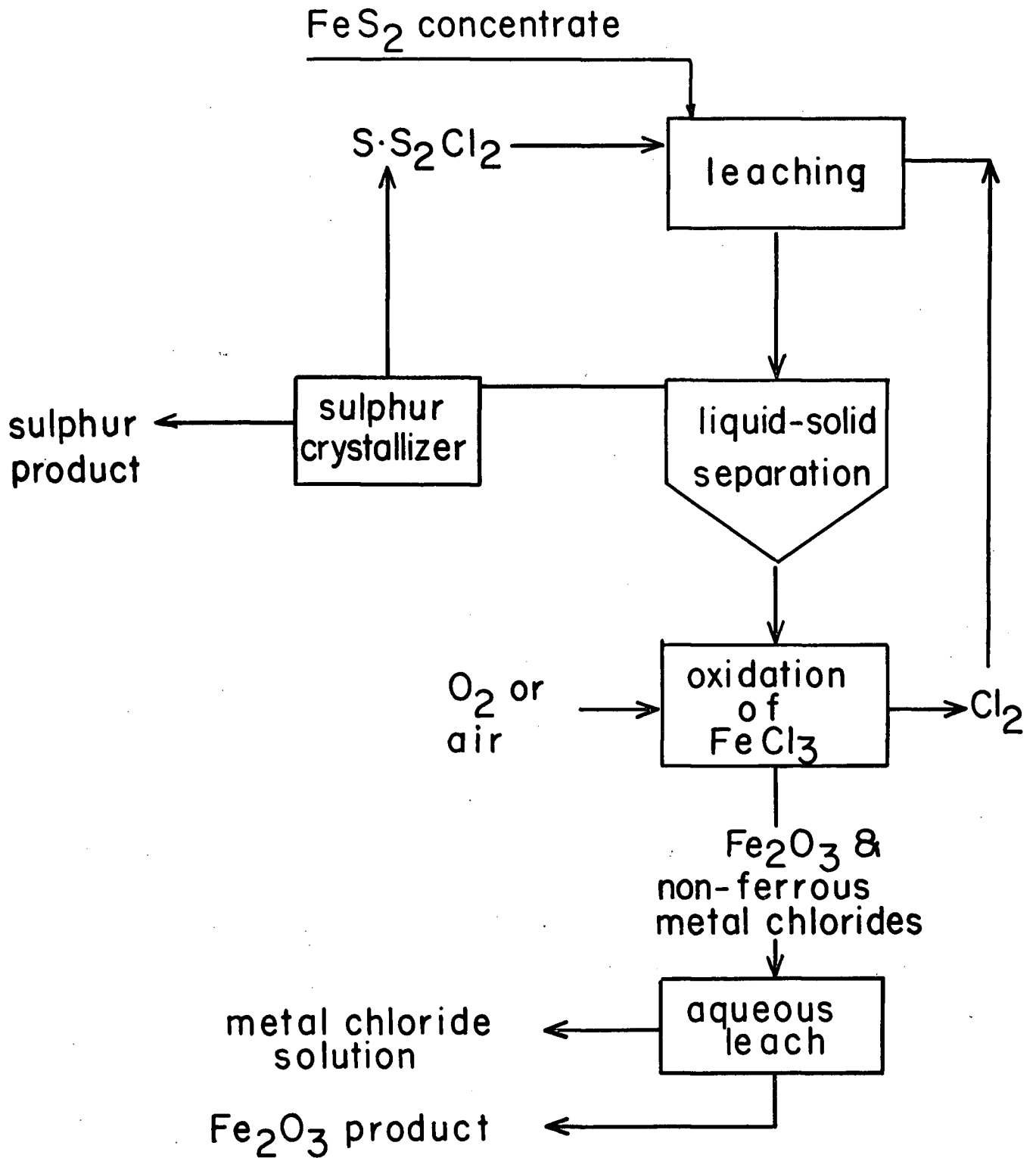
D-3 Reaction of Chalcopryrite with 40 wt % S.S₂Cl₂

Substrate	Time (minutes)	T(°C)	Percent of Chalcopryrite Reacted	$[1-(1-R)^{1/3}] r_o [1-(1-R)^{1/3}]$ (cm x 10 ⁴)
-100 + 140m Phoenix Chalcopryrite	5	50	7.2	0.025 1.56
"	10	"	11.4	0.040 2.50
"	20	"	19.7	0.071 4.44
"	30	"	28.4	0.105 6.56
"	45	"	34.7	0.132 8.25
"	60	"	43.9	0.175 10.9
"	80	"	52.7	0.221 13.8
"	5	60	12.4	0.043 2.69
"	10	"	20.7	0.074 4.63
"	20	"	34.4	0.131 8.19
"	30	"	44.3	0.177 11.1
"	45	"	57.4	0.248 15.5
"	60	"	66.9	0.308 19.3
"	5	70	19.9	0.071 4.44
"	10	"	34.9	0.133 8.31
"	15	"	43.2	0.172 10.8
"	20	"	53.8	0.227 14.2
"	30	"	66.5	0.305 19.1
"	5	80	33.2	0.126 7.88
"	10	"	53.5	0.225 14.1
"	15	"	64.5	0.292 18.3

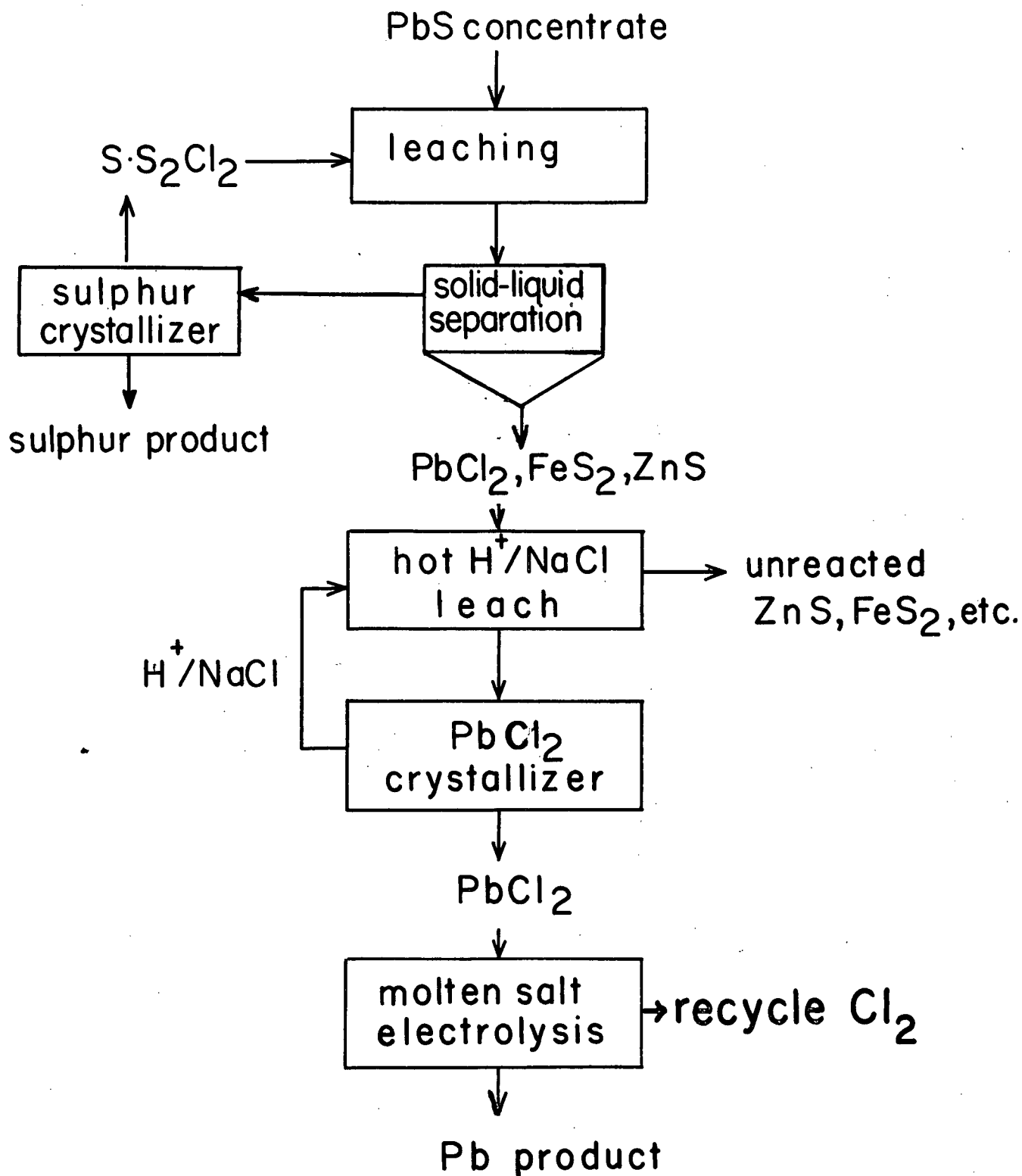
D-4 Calculated Values of r_o

Screen Size Fraction	Geometric Mean Diameter (cm)	r_o (cm)
- 70 + 100 mesh	1.77×10^{-2}	8.85×10^{-3}
-100 + 140 "	1.25×10^{-2}	6.25×10^{-3}
-150 + 200 "	8.77×10^{-3}	4.38×10^{-3}
-200 + 270 "	6.26×10^{-3}	3.13×10^{-3}
-270 + 325 "	4.83×10^{-3}	2.41×10^{-3}

Appendix E: Schematic Flowsheet for Treatment of Pyrite with Sulphur Chloride.



Appendix F: Schematic Flowsheet for Production of Lead and Sulphur from Galena Concentrate.



Appendix G; Corrosion of Metals in Sulphur Chloride

In the course of this study, various metals were tested for reactivity towards S_2Cl_2 .

Monel alloy (67% Ni, 30% Cu, 1.5% Fe) is known to be resistant to chlorinating environments so a sample disc (1.2 cm diameter x 0.4 cm thick) was cut and polished. This specimen was held in the standard experimental apparatus in contact with 40 wt. % $S.S_2Cl_2$ for 18 hours at 120°C. The weight of the disc after this treatment (and the standard wash sequence) was within ± 0.1 mg of the original weight. While this was not a definitive corrosion test, it indicates that monel is relatively immune to corrosion in a $S.S_2Cl_2$ environment.

Titanium metal turnings were contacted with S_2Cl_2 in a beaker at room temperature. No immediate reaction occurred so the mixture was warmed slightly. After a short time (~ 30 seconds), a violent reaction occurred and the metal was completely consumed in a few seconds leaving only a small solid residue. Tin shot reacted in a similar (but less violent) way. The absence of solid products in these reactions indicates formation of $TiCl_4$ and $SnCl_4$ - liquids which would be expected to be miscible with S_2Cl_2 .

Appendix H: Calculated (a) and Experimentally Determined (b) Solubility of Sulphur (S_8) in Sulphur Chloride:

(a) Calculated (Ideal) solubility of S_8 in S_2Cl_2 using the method of Glasstone (49) and the data of Meyer (50).

(b) Experimental solubility of S_8 in S_2Cl_2 after Aten (47). See section 1.322.

