A DETAILED DESIGN STUDY
OF
LEACHING AND ANCILLARY PROCESSES
IN THE
HYDROMETALLURGICAL EXTRACTION OF IRON
FROM
IRON BEARING FEEDSTOCKS

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SUMMARY

A systematic survey of the possible methods of chemical extraction of iron by chloride formation has been presented and supported by a comparable study of feedstocks, products and markets.

The generation and evaluation of alternative processes was carried out by the technique of morphological analysis which was exploited by way of a computer program. The final choice was related to technical feasibility, and economic viability, particularly capital cost requirements and developments were made in an estimating procedure for hydrometallurgical processes which have general applications.

The systematic exploration included the compilation of relevant data, and this indicated a need to investigate precipitative hydrolysis of aqueous ferric chloride.

Arising from this study, two novel hydrometallurgical processes for manufacturing iron powder are proposed and experimental work was undertaken in the following areas to demonstrate feasibility and obtain basic data for design purposes:

(1) Precipitative hydrolysis of aqueous ferric chloride.

(2) Gaseous chloridation of metallic iron, and oxidation of resultant ferrous chloride.

(3) Reduction of gaseous ferric chloride with hydrogen.

(4) Aqueous acid leaching of low grade iron ore.

(5) Aqueous acid leaching of metallic iron.

The experimentation was supported by theoretical analyses dealing with:

(1) Thermodynamics of hydrolysis.

(2) Kinetics of ore leaching.

(3) Kinetics of metallic iron leaching.

(4) Crystallisation of ferrous chloride.

(5) Oxidation of anhydrous ferrous chloride.

(6) Reduction of ferric chloride.

Conceptual designs are suggested for both the processes mentioned. These draw attention to areas where further work is necessary, which are listed.

Economic analyses have been performed which isolate significant cost areas, and indicate total production costs. Comparisons are made with previous and analogous proposals for the production of iron powder.

To Gill

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1. INTRODUCTION

The notion of extracting iron by methods alternative to orthodox thermal treatment has attracted attention for nearly a hundred years. It is convenient to refer to these other methods as "chemical" and this term is used throughout the dissertation. Many of the early attempts were based on electrolysis, but as technology advanced more separation techniques were developed, and processes also tended to become more complex (1-1). However, none of the processes suggested has yet proved both technically and economically viable. The O.S.C.A.T. (Ore to Steel, Chemical and Associated Techniques) project was one of the most recent attempts to explore this field, very comprehensive in its scope, and has been reported in detail (1-2). A novel technique, known as morphological analysis (1-3, 1-4), was employed to generate and select the "best" process routes from all conceivable alternatives. The conclusions of this initial study were that a chemical route to iron was feasible both technically and economically, and might offer substantial advantages over conventional production methods within some areas of the iron and steel industry, particularly those likely to grow. These conclusions form the basis of this dissertation, which is concerned with the total system of producing a directly useful iron/steel product from an ironbearing feedstock. To this end, it is necessary to discuss not only the process itself, but also each aspect of the problem from alternative feedstocks to present and future markets of possible products. This examination extends through the following section, concluding with two proposals for possible processes. The rest of the dissertation is devoted to the design of the essential features of these two processes, with particular emphasis on the novel aspects and their interactions, supplemented where necessary with experimental work. The immediate objective is to present the basis of a viable industrial proposition; in the longer term, due to the complexity of the problem, the objectives must deepen and provide for a detailed examination of smaller areas.

From the inception of the O.S.C.A.T. project, a considerable lack of enthusiasm for the idea of chemical iron-making has been encountered, particularly from the industry itself. This may be understandable to a certain extent when it is remembered that all previous attempts have failed (1-1), including one of the few U. K. originated processes - the FLOX project at Appleby Frodingham about fifteen years ago. The reasons for these failures were complex and peculiar to individual processes, but were often superficially due to insufficiently advanced technology. Perhaps more important was the inability both to fit the new products from these chemical processes into the company's existing organisation, and to create the new technology to make best use of such products. In 1963 the Iron and Steel Board report on research and development in the industry recommended that alternative methods to conventional manufacture of iron and steel should be examined, and this resulted in the establishment of the O.S.C.A.T. project. From about the same period, the market for iron powder has increased substantially every year, and in 1969 exceeded

100,000 tons in North America. The change in possibilities for iron powder caused the British Steel Corporation to set up a working party in 1968, to examine iron powder prospects, and methods of manufacture likely to be of short term value to the Corporation. While no conclusions have yet been published, it has been publicly acknowledged (1-6) that steel strip may well be made from powder in the mid-1970's. An appreciable amount of research into iron powder metallurgy for making strip, foil, rod, tubes and other high tonnage products is proceeding both in this country and abroad, which has formed the subject of a report by other members of the project (1-7). There is, however, still a very substantial amount of work to be done in this area.

2. EXAMINATION OF PERTINENT LITERATURE AND PRACTICE

The whole of this section is devoted to a study of each of the various aspects that make up the total system of a chemical iron extraction process. Preliminary selection of a suitable process has been carried out for hydrometallurgical processes (1-2), and for gaseous processes (2-1). The conclusions were that the following six processes should be examined in greater detail:

Leaching Electrolysis
Leaching Crystallisation Electrolysis
Leaching Crystallisation Reduction
Leaching Crystallisation Thermal decomposition Reduction
Leaching Precipitation Thermal decomposition Reduction
Leaching Evaporation Thermal decomposition Reduction

These may be expressed more generally as:

Leaching Purification Reduction

where leaching is a separate operation and purification may be carried out separately or at the same time as reduction. The review that follows includes an examination of relevant unit operations with particular regard for iron purification and/or separation, and also economics. Where necessary analogous metal extraction processes have also been examined.

2.1 Chemical Processes Producing Iron

The literature on chemical processes for extracting iron has been exhaustively reviewed (1-1) and the paper is appended (Appendix IV) to this dissertation. A list of the processes and a very brief description is included here:

Siemens (1887) - $FeCl_3$ leaching pyrite, electrolysis

Brest (1917) - Chlorination with HCl, reduction of $FeCl_2$

Eustis (1920 et seq.) - Many processes based on Siemens

Traill et al. (1925) - $FeCl_3$ leaching, electrolysis

Westcott (1925) - Chlorination with Cl_2, oxidation, reduction of Fe_2O_3

Firth and Root (1942) - H_2SO_4 leaching, oxide reduction

Six (1944) - HNO_3 leaching, oxide reduction

I.G. Farbenindustrie (1946) - Carbonylation, thermal decomposition to Fe

Primavesi (dry) (1948) - Chlorination with HCl, chloride reduction

Primavesi (wet)(1948) - HCl leaching, oxide or chloride reduction

S.M.W. (1949) - HCl leaching of scrap, chloride reduction

FLOX (dry) (1952) - Chlorination with HCl, reduction of chloride

FLOX 1 (wet) (1952) - HCl leaching, oxide or chloride reduction

Konrad (1953) - $FeCl_3$ leaching, electrolysis

Marshall (1955) - Chlorination of metal with HCl, chloride reduction

Crowley (1955) - Chlorination with HCl, chloride reduction

Hill (1955) - Chlorination with Cl_2, oxide reduction

Rao (1957) - H_2SO_4 or HCl leaching, electrolysis

Lewis et al. (1958) - Carbonylation process

Eberhardt (1958) - Chlorination with HCl + Cl_2, oxide reduction

Schaufelberger (1959) - HNO_3 leaching, oxide reduction

Francis (1959) - HCl leaching, oxide reduction

Novak et al. (1959) - Chlorination with Cl_2, oxide reduction

FLOX 2 (wet) (1959) - HCl leaching, oxide reduction

Illis et al. (1960) - Carbonylation process

Queneau et al. (1960) - Carbonylation process

State of South Australia (1960) - Chlorination with Cl_2, oxide reduction

Schreiner et al. (1961) - Chlorination with HCl + Cl_2, oxide or chloride reduction

Sheer et al. (1962) - Carbonylation process

R.C.A. (1962) - HCl leaching, chloride reduction

FLOX 3 (wet) (1966) - HCl leaching, oxide reduction

None of these processes has been successfully exploited commercially for a variety of reasons. These include lack of technology, poor economics and perhaps most important, lack of market and product opportunities. For example in the U.K., the FLOX project (2-10, 2-16, 2-20) attempted to produce pure iron oxide from low grade ores to feed to the blast furnace as replacement material for high grade ore. The resultant processes were technically successful at bench and pilot scale, but could not produce pure iron oxide quite as cheaply as imported high grade ore. The project was ultimately abandoned for these reasons. Iron powder could have been made, and was in fact made on a limited scale, very cheaply from this pure iron oxide, but there was no market and no forseeable one at that time.

In 1969 the market for iron powder exceeded 100,000 tons p.a. in North America and 10,000 tons p.a. in the U.K., where it is expanding at the rate of 15-20% p.a. at the current price of around £100 per long ton. New plant for making iron powder is being installed in North America at an equivalent rate greater than 20% p.a. employing atomisation of molten steel, oxide and concentrate reduction, and a chemical process. At the present time a 15,000 t.p.a. iron powder plant is being constructed in the U.K. at Round Oak, by Tube Investments Ltd.

The only known chemical extraction route at present under commercial consideration is the R.C.A. (Research Council of Alberta) process (1-5), which has been developed by Peace River Mining and Smelting of Canada and Woodall Duckham of the U.K. This particular process has been under investigation since about 1960, and has now reached the stage when a substantial plant is being built near Windsor, Eastern Canada. It is understood that scrap metal is taken from the motor industry in Detroit, a few miles away, and iron powder returned.

2.2 Feedstock

There are a number of possible iron bearing feedstocks existing and arising in the U.K. that may be employed as feed material to a chemical process. These are approximately:

	Long tons Fe
High grade iron ore	10,000,000 available, plus imports
Low grade iron ore	2,000,000,000 available
Scrap metal	15,000,000 p.a.
Millscale	50,000 p.a.

B.O.F. fume	25,000 p.a. (increasing)
Pickle liquor wastes (sulphate or chloride)	50,000 p.a.
Aluminium industry wastes	5,000 p.a. (increasing)
Titanium industry wastes	1,000 p.a. (increasing)

There is a change taking place in the grade of iron ore used in conventional iron and steel making. High grade is preferred to fit current blast furnace practice and this is imported in preference to lower grade ores available in the U.K. While these latter ores are still employed, their use is falling off, although substantial reserves are available. There are also considerable imports of iron and steel products, of which iron powder is particularly important.

The potential market for iron powder in the U.K. is expected to reach 100,000 tons p.a. by the end of the 1970's (see Section 2.7), and may substantially exceed this if prices can be reduced. In view also of the potential market for both product and any new process abroad, it would not be sensible to employ a feedstock that is not both widely and freely available. Ore and scrap are the only feedstocks that may be considered therefore and are discussed further.

2.2.1 Ore

The major iron minerals are listed in Table 2.1, their mode of formation depicted in Figure 2.1, and world iron ore resources tabulated in Table 2.2.

TABLE 2.1

Iron Minerals

Mineral	Approximate Composition	Fe % wt.		
Hematite	Fe_2O_3	70.0	More widely distributed than magnetite	Both highly favoured as sources of iron
Magnetite	Fe_3O_4	72.4		
Goethite	$Fe_2O_3.H_2O$	62.9		Form a substantial part of low grade ores
Hydrogoethite	$3Fe_2O_3.4H_2O$	60.9		
Limonite	$2Fe_2O_3.3H_2O$	60.0		
Siderite	$FeCO_3$	48.3		
Chamosite (et al.)	Complex iron silicates	10-40	Difficult to treat by pyrometallurgical methods	
Pyrite	FeS	64.6	Of limited usefulness due to sulphur	
Pyrrhotite	$Fe_{11}S_{12}$	61.5		

N.B. Iron ore deposits are never found as pure minerals, but invariably as a mixture of two or more of the above minerals and often a number of a wide range of impurities as well. Sometimes the "impurity" is the valuable metal and iron the byproduct; for example Ilmenite ($FeTiO_3$) gives titanium and iron.

FORMATION OF IRON BEARING ORES

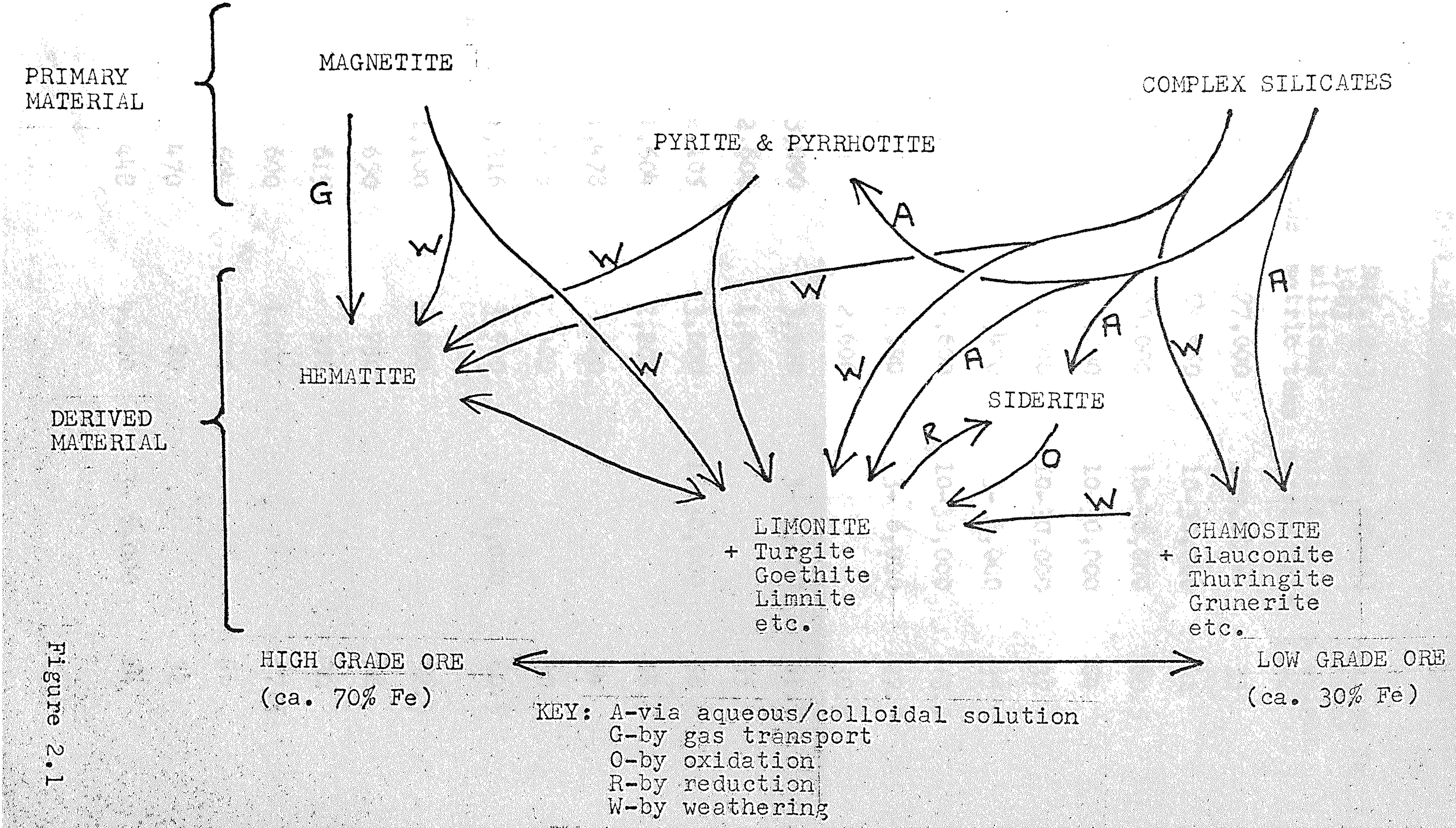


Figure 2.1

TABLE 2.2

Iron Ore Reserves and Resources

Country	Ref.(2-2) 1962 millions metric tons	Ref.(2-3) 1963 millions metric tons	Ref.(2-33) 1966 millions metric tons	Average Fe content % weight (2-2)
U.S.S.R.	42,007	77,000	100,000+	35
U.S.A.	27,778	54,450	10-30,000	31
Brazil	16,965	20,000	10-30,000	60.5
India	15,539	21,000	10-30,000	64
Canada	12,259	11,000	10-30,000	37
France	11,680	4,400	3- 6,000	35
China	10,758	4,600	10-30,000	43.5
W. Germany	5,352	5,500	3- 6,000	27.5
U.K.	3,306	2,600		30.5
Sweden	3,090	3,900	3- 6,000	61.5
Guinea	2,600	1,000		55
Australia	2,105	13,000	10-30,000	56
Venezuela	1,604	2,200		58.5
Norway	1,478	120		34
Korea	1,435	400		30
Union S. Africa	1,316	3,500	3- 6,000	60.5
Spain	1,100	1,000		52.5
Gabon	650	750		58
Poland	615	370		30
Liberia	600	1,000		57.5
Peru	594	740		56
Finland	470	80		32
Chile	448	4,600	3- 6,000	64

Country	Ref.(2-2) 1962 millions metric tons	Ref.(2-3) 1963 millions metric tons	Ref.(2-33) 1966 millions metric tons	Average Fe content % weight (2-2)
Austria	340	340		34
Angola	296	-		(66.5)
Bulgaria	270	220		35
Luxemburg	270	270		30
Sierra Leone	255	200		60
Mexico	251	500		59.5
Czechoslovakia	230	230		34
Yugoslavia	219	230		41
Rhodesia and Nyasaland	217	200		(58)
Ivory Coast	200	-		65
Argentine	186	180		45
Greece	167	70		48
Egypt	165	200		50
Mauritania	150	200		63.5
Algeria	140	500		(54)
French Morocco	130	200		42.5
Indochina	110	100		60.5
Swaziland	109	60		59
Colombia	100	100		48
French Cameroons	100	-		40
Italy	70	80		55
Switzerland	70	80		28
Iran	63	-		54
Spanish Morocco	60	See French M.		61.5

Country	Ref.(2-2) 1962 millions metric tons	Ref.(2-3) 1963 millions metric tons	Ref.(2-33) 1966 millions metric tons	Average Fe content % weight (2-2)
Turkey	58	140		62.5
Japan	53	40		45
Malaya	50	40		57.5
Tunisia	39	60		55
E. Germany	35	-		33
Phillipines	34	1,300		56
Thailand	28	-		45
Hungary	20	-		48
Israel	15	40		35
Bolivia		50,000		
Nigeria		11,000		
Cuba		3,000	3- 6,000	
Indonesia		850		
Puerto Rico		100		
Senegal		100		
Somalia		100		
Rumania		100		
Pakistan		100		
New Zealand		50		

The large reserves of low grade iron ore in the U.K. are of particular interest. These are used to a limited extent in conventional iron and steel manufacture, but higher grade imported ores are preferred in order to obtain a higher iron yield per unit of equipment. In a chemical process however there are advantages in using a low grade home ore. Although greater handling facilities may be required in the early stages of a process up to leaching and the residue may require more extensive washing, these disadvantages are considered relatively trivial compared to the advantages of home produced ore at a considerably reduced cost per unit of iron. There are also a number of byproducts that could arise such as high purity alumina, phosphorus, and vanadium, which are particularly valuable. It must be emphasised however that the chemical processes designed here are based technically and economically on iron manufacture, with no value attached to such byproducts. The possibility of siting the extraction plant on, or near, the ore field may make this advantage even greater by reducing transport costs. Other possibly higher costs, for example energy, may be offset in the case of the Northamptonshire ore field by utilising the natural gas pipelines which are planned for crossing the area.

Approximate costs of imported and homeproduced ore are given in Table 2.3, together with approximate transportation costs, which are also shown in Figures 2.2 a and b.

The mineralogy and petrology of ores is beyond the scope of this dissertation, but representative analyses of several low grade ores, and a high grade ore for comparison,

TABLE 2.3

Ore and Transport Costs

(long tons)

Ore - imported (1968)

Cost - mined, loaded, transported to U.K. port, unloaded	17d per unit Fe

A "unit" is one part in a 100

e.g. 70% ore costs	99/2 per ton, 141/8 per ton Fe
60% ore costs	85/- per ton, 141/8 per ton Fe

Ore - home produced (33% Fe) (1969)

Cost - mined and loaded on to rail wagons	10/- per ton, 30/- per ton Fe

Transport

Rail (1970): About 4d/ton mile for large contracts including loading and unloading. Precise figures for scrap (see Figure 2.2A also) in wagon loads of 8 tons minimum are:

10 miles	20/7 per ton
20 miles	23/2 per ton
50 miles	31/- per ton
100 miles	44/3 per ton
200 miles	67/5 per ton

Minimum charge £10-17-0d.

Whole train loads and/or long-term or large contracts would expect a reduction (2-74).

Table 2.3 continued

Sea (1969): For most U. K. imports, transportation costs lie between 20/- and 30/- per ton; loaded, transported, unloaded and insured. Full details are given in Figure 2.2B. Average journey distances from ore source to steel industry are:

Japan	6,000 n. miles	
France	3,500 n. miles	
Italy	3,000 n. miles	
W. Germany	3,000 n. miles	
U.K.	2-2,500 n. miles	
U.S.A.	2,000 n. miles	(2-75)

Road (1970): Precise figures are difficult to obtain but 6d./ton mile appears to be a reasonable overall figure for the U.K. (2-82).

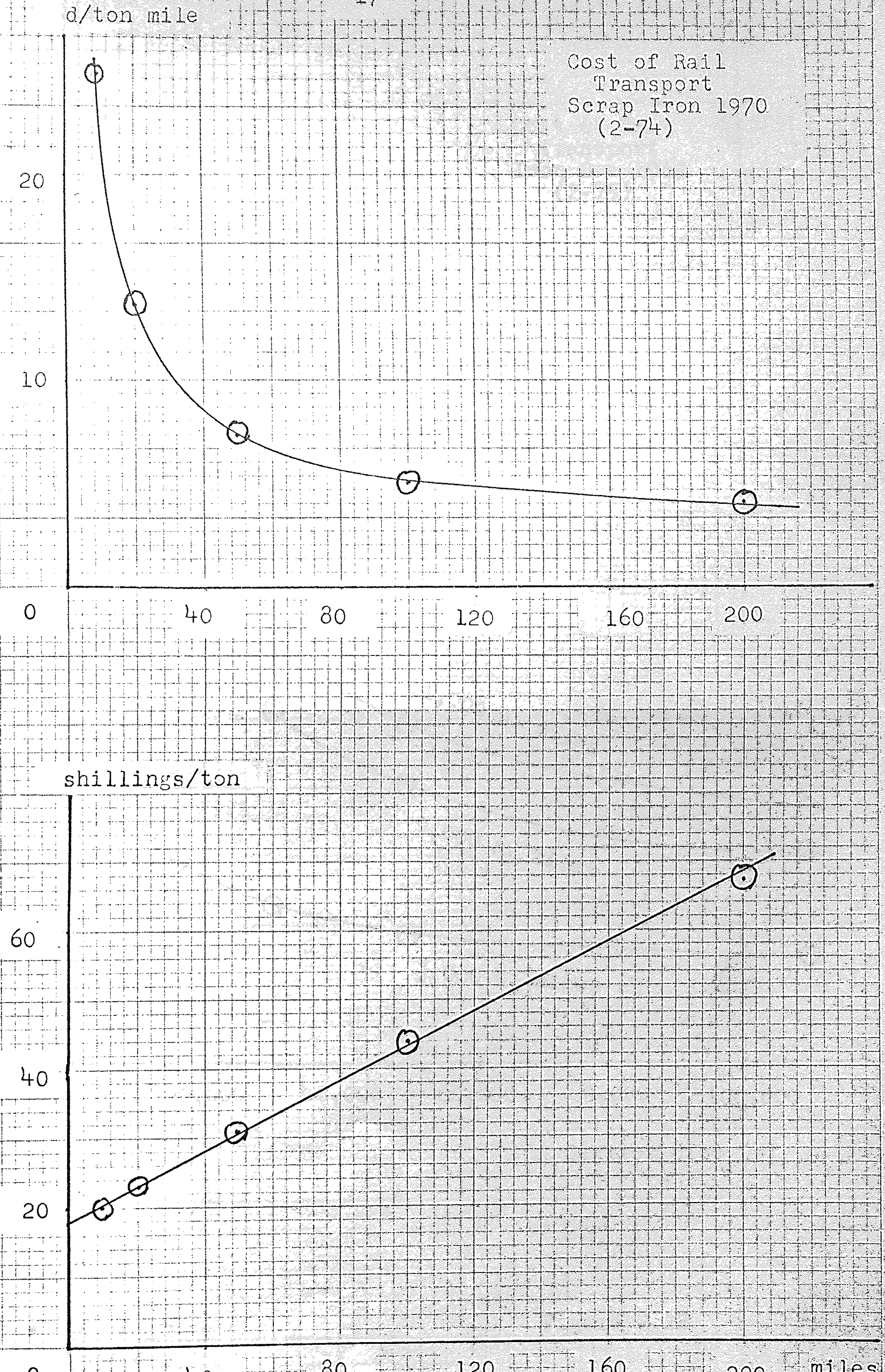

d/ton mile
Cost of Rail
Transport
Scrap Iron 1970
(2-74)
20
10
0
40
80
120
160
200
shillings/ton
60
40
20
0
40
80
120
160
200
miles

Figure 2.2A

Cost of Sea
Transport
Iron Ore 1969
(2-75)

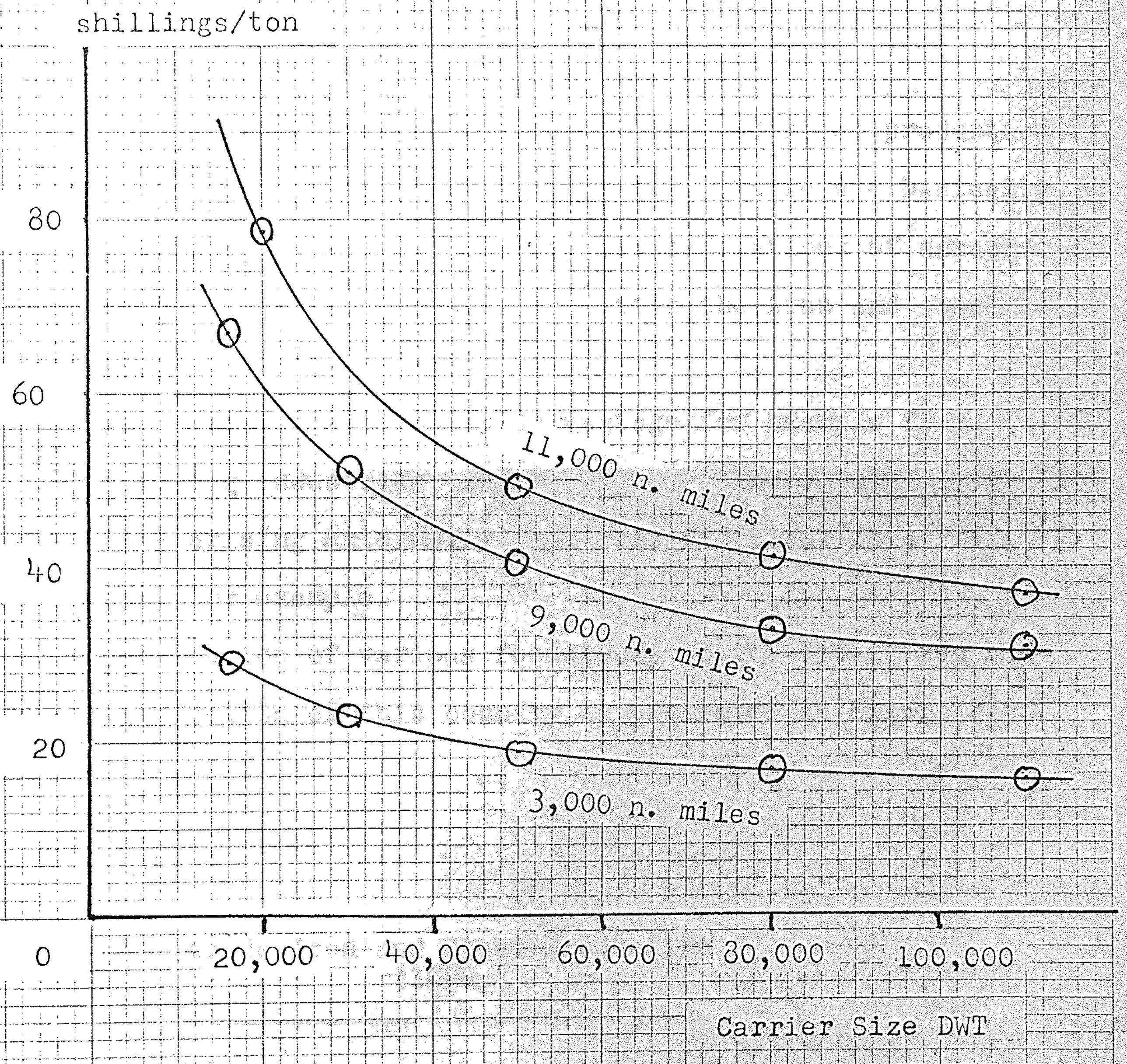


Figure 2.2B

is given in Table 2.4. The low grade ore in the U.K. exists either as unweathered or weathered, i.e. oxidised ore. The former contains iron in the ferrous state, and high amounts of lime and carbonates which tend to waste acid by neutralisation. The subsequent recovery is expensive. The oxidised ores contain iron in the ferric state and relatively little lime.

2.2.2 Scrap

Roughly half of the total iron and steel production in the U.K. is derived from scrap metal. There are basically three "official" (steel industry) classifications of scrap:

circulating - arising internally within the iron and steel industry;

process - arising externally as wastage for example from manufacturing industries; and

capital - arising externally from obsolete plant or wornout machinery for example.

The contribution of various feedstocks to the total iron and steel production of this country is presented in Figure 2.2**C.**

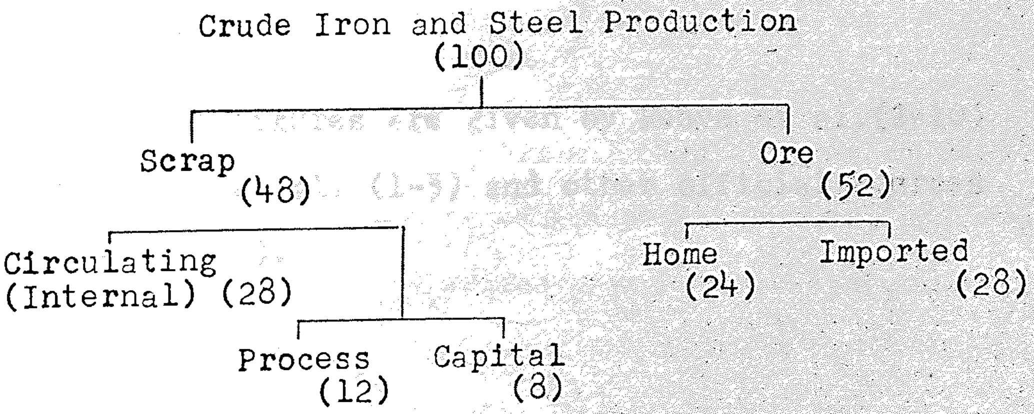


Figure 2.2 C

TABLE 2.4

Representative Ore Analyses

	Low Grade		High Grade
	Northamptonshire Ironstone (3-8)		
	(Deene Pit, Corby)	(Upper Brookfield Pit, Corby)	Hematitic
	Unweathered	Weathered	
	wt.%	wt.%	
Fe	32.6	46.8	64.6
FeO	39.5	0.2	0.3
Fe_2O_3	2.6	66.6	92.0
Al_2O_3	9.0	7.5	2.0
SiO_2	9.2	7.6	4.5
CaO	6.7	1.4	0.04
MgO	2.1	1.0	0.01
MnO	0.1	0.3	0.04
P_2O_5	2.7	1.8	0.10
S	0.04	0.03	0.01
CO_2	23.0	0.8	
L.O.I. + H_2O	31.6	26.2	1.0

Relevant figures are given by Reeve et al.(2-10) Gravenor et al. (1-5) and other official sources (2-5, 2-33).

Scrap available on the market is process or capital scrap which is further classified or graded as in Table 2.5. There are set prices for each grade of scrap depending on the area, of which there are thirteen. Prices (1968) for the Midlands, and the cheapest and most expensive areas are also included in Table 2.5 (2-6).

There is another grade of scrap known as destructor scrap which is not included in the official classifications of Table 2.5. It is unsuitable for charging to a steel furnace on account of the high level of impurities, but may be used for certain pig iron production. Due to the limited use for this grade, the price is generally about 40 shillings below the cheapest grade. For a chemical process, however, destructor scrap may be attractive due to its low price, and valuable impurities such as copper which may be readily recoverable. Approximate compositions of the various grades of scrap are given in Table 2.6.

2.2.3 Discussion

There appears to be a case for stressing the close analogy between the non-ferrous metal industry, for example copper and nickel, and the iron and steel industry with regard to feedstocks and method of treatment. Pyrometallurgy has traditionally been employed to extract copper from its ores, and this is more efficient and economic when a high grade ore is used as feedstock. This applies similarly to the blast furnace. There is, however, concern at the shortage of new high grade non-ferrous ore deposits, and more attention is being paid to alternative extraction methods to handle low-grade ores: for example the Sherritt Gordon process for nickel, cobalt and copper recovery by ammoniacal leaching

TABLE 2.5

Scrap Prices, 1968 (2-6)

(Scrap Industry Classification)

Grade	Description	Price (sh. per ton) Midlands	Corby	N.W. Coast
1	Heavy steel	220	219	238
2	Heavy wrought iron and steel	199	198	214
3	Medium wrought iron and steel	199	198	214
4	Hydraulically compressed new and heavy faggotted steel	220	-	238
5	Hydraulically compressed old wrought iron and steel	178	-	192
6	Old light wrought iron and steel	122	-	-
7	Short, heavy or crushed steel turnings	170	-	187
8	New loose light steel cuttings	170	-	188
9	Heavy cast iron scrap	208	193	205
10	Light cast iron scrap	206	188	200
11	Cast iron borings	157	-	-

TABLE 2.6

Scrap Compositions (2-6)

	Grades 1-8	Grades 9-11	Destructor
Fe	97-99%	95-97%	85-95%
O	0-1.5%	0-1.5%	0-5%
C	0-1.0%	2-5%	0-1%
Cu	Negligible	Negligible	0-2%
Cr	Trace	Trace	0-1.5%
Mn	0.5%	0.5%	
Ni	Trace	Trace	
P	Negligible	Negligible	
Pb	Negligible	Negligible	
S	Negligible	Negligible	
Si	Trace	0.2%	
Sn	Negligible	Negligible	
Zn	Negligible	Negligible	
Other	-	-	0-3%

(2-7), and copper waste dump leaching by bacterial oxidation (2-8). In general, hydrometallurgy is considered more economic and efficient for low grade ores, and pyrometallurgy for high grades, although how far this is dependent on capital already invested in the latter it is difficult to assess. There is also greater flexibility in a chemical process in that the yield can be varied considerably whereas it is more or less fixed in a pyrometallurgical process. The recovery and cost effects are depicted graphically in Figure 2.3 derived from the copper industry (2-9). A similar picture has been drawn by Tilley et al. (2-11) in relation to the aluminium industry.

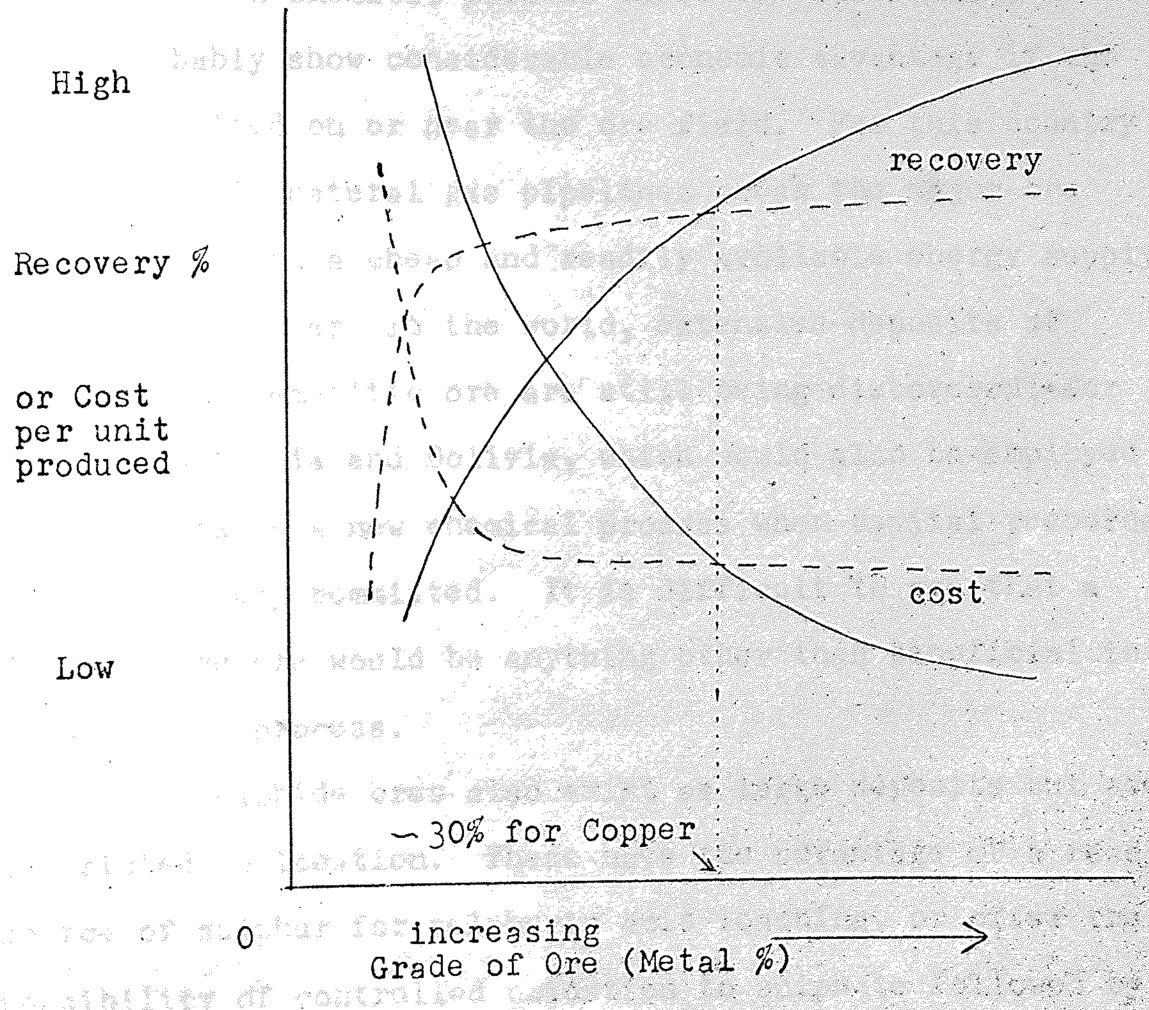


Figure 2.3

Vast capital is already invested in conventional pyrometallurgical iron extraction, which gives greatest throughput most economically with high grade ore. This has to be imported as there are no similar economic reserves in this country and existing low grade home ores cannot be economically upgraded by established techniques. The high grade ore reserves around the world are also those likely to be depleted first (see Table 2.2). The analogy is completed by the recent work on hydrometallurgical extraction of iron - the R.C.A./Peace River (1-5 and 1-1) and FLOX (2-10 and 1-1) projects, both of which consider only a low grade ore as feedstock (as well as scrap).

There are very large reserves of low grade ore both in central England, and widespread over Europe (see Table 2.2). A chemical process based on this feedstock would probably show considerable economic advantage if the plant was sited on or near the ore field. For this country also, the main natural gas pipelines cross the major ore fields providing a cheap and readily available energy supply.

Elsewhere in the world, extensive deposits of higher grade hematitic ore are still being discovered, for example Australia and Bolivia, which could also be employed as feedstock in a new chemical process when capital resources are not already committed. It is difficult to see that a higher grade ore would be anything other than beneficial in an ore based process.

Sulphide ores also exist as large deposits but are restricted in location. These have the advantage of a ready source of sulphur for sulphuric acid leaching, or offer the possibility of controlled oxidation to sulphate followed by water leaching (see 1-2). (Both of these alternatives have, however, already been discounted on current form (1-2)).

The other possible feedstock is scrap which offers a relatively cheap and readily available source of metallic iron. There are possible advantages in that the leaching system may be considerably simplified, hydrogen would be produced for later reduction, and impurities would be at a lower level. The leach liquor would contain iron in the ferrous state which is advantageous for crystallisation.

It is necessary to specify the feedstock for any proposed chemical process (see section 2.4.1.1), and for the design studies that follow, both low grade home ore, and scrap will be employed.

2.3 Pretreatment

There are two types of heat pretreatment which may be applied to an ore to increase its reactivity and ease of extraction. These are:

Heating under reducing conditions - "prereduction"
Heating under oxidising conditions - "roasting"

Other forms of pretreatment are common in mineral processing, for example concentration by froth flotation, or by sedimentation, but these are unsuitable for either proposed feedstock. Pretreatment is discussed here with reference to the effect on leaching.

Prereduction ensures that ferrous salts are formed in the leach liquor, as for example in the R.C.A. process (see 1-1), as well as affecting the solubility of constituent minerals. Roasting is usually used to alter the solubility of the different minerals. This is exemplified in Tilley's work on alumina extraction from clay (see Section 2.4.1.2).

Roasting of sulphide ores is also carried out either partially to oxidise metal sulphides to sulphate, or completely oxidise them to metal oxides and sulphur oxides. Neither of these possibilities falls within the scope of this dissertation (see also 1-2).

The necessity of prereduction or roasting is strongly dependent on the mode and conditions of extraction in the subsequent ore leaching step. Very little work has been carried out in this field with regard to iron ores. Both Reeve et al. (2-10 and 1-1) on the FLOX project and Gravenor et al. (1-5 and 1-1) on the R.C.A. process, prereduced part of the ore to ensure that iron was in the ferrous state. Rao et al. (2-19) however found that lateritic ore dissolved readily in hydrochloric acid with no pretreatment (see also Appendix 1)

No methodical investigation of the effect of heat pretreatment on iron ores for hydrometallurgical extraction appears to have been attempted. Tilley et al. (2-11) however, carried out a very comprehensive study of roasting clays for acid alumina extraction, concluding that roasting is only particularly beneficial for reducing the solubility (colloidal) of silica. In later processes such as R.C.A. (1-5) the colloidal silica is successfully precipitated by addition of finely ground ore after the leaching/filtering stage. It is unlikely therefore that heat pretreatment of ore will be necessary, although it may be necessary to investigate this prior to commercial development.

The Northamptonshire sandstone ores that were chosen as a possible feedstock in Section 2-2, are often very "sticky" and may require drying to improve their handling characteristics.

2.4 Leaching

Leaching is probably one of the more important steps in a chemical extraction process, as it is the first operation in all of the processes recommended for investigation (see Section 2). The review in this section covers the practical aspects of leaching metal bearing ores. The theory is discussed when appropriate in later sections.

Acid leaching of oxide ores is the principal topic, with reference to both ferrous and non-ferrous metal extraction. Neutral leaching and sulphide ore leaching are also included for completeness.

No data on acid leaching of iron in the metallic state has been found in the literature, apart from references on pickling when it is the removal of oxide layers that is investigated.

The action of hydrochloric acid on both metallic iron and low grade ore has been investigated in connection with this dissertation and the results are presented later (see Section 3).

2.4.1 Acid leaching - ferrous metal extraction

A comprehensive review of iron extraction processes has been carried out (1-1), providing a critical appreciation and flow diagrams, which is appended. Relevant data and information have also been extracted from the pertinent processes and is presented in tabular form in Appendix 1.

The processes covered are:

Firth and Root	(2-12)
Sinter metallwerkes Berghaus (S.M.W.)	(2-13)
Six	(2-14)
Primavesi	(2-15)
FLOX 1	(2-16)
Schaufelberger	(2-17)
Francis	(2-18)
Rao et al.	(2-19)
FLOX 2	(2-20)
R.C.A.	(1-5)
FLOX (Reeve and Blakey)	(2-10)

All the above employed on ore based feedstock, and one of the mineral acids for dissolution. The data of Appendix 1 is summarised and presented in Table 2.7.

TABLE 2.7

Rough comparison of requirements for satisfactory acid extraction of iron from ore

Acid employed	HCl	HNO_3	H_2SO_4
Comminution	Yes	Yes	Yes
Thermal pretreatment	Possible	?	Probable
Acid concentration	10-35%	40-65%	10-100%
Temperature requirements	70-100°C (autothermic)	> 60°C	40-130°C
Pressure requirements	None	Helps	None
Time requirement	5-60 mins.	> 3 hrs.	> 3 hours
Number of stages	1	1	Multiple (5)
Expected extraction efficiency	90%+	85%+	70%+

It is clear that a wide range of conditions have been found by different workers to be necessary for successful extraction. Scott (2-21) gave a list of factors affecting extraction efficiency:

Nature of ore
Particle size
Pulp density
Acid concentration
Temperature
Time
Excess acidity

He adds that "generalisations are impossible. Each ore has its own characteristics and any process, whether acid or alkaline, must be tailored to cater for the idiosyncrasies of the source material."

Scrap is to be considered as an alternative feedstock. Data on the dissolution of metallic iron in acid is practically non-existent - pickling being the only area where this has been studied, and even here data is very sparse. Bablik (2-22) provides the only quantitative information found so far, which is discussed in a later section.

2.4.2 Acid leaching - non-ferrous metal extraction

Since there is a dearth of literature on acid leaching iron bearing ores to recover the iron as the prime value, literature on hydrometallurgical extraction of non-ferrous metals has been examined in an attempt to elicit further information.

The extractive metallurgy of aluminium, copper, nickel and, to a lesser extent, zinc, cobalt, chromium, and titanium, has been investigated. Due to the higher worth of these metals, considerably more industrial attention has been paid to their extraction and recovery than iron, particularly as the latter is considered to be manufactured reasonably economically in a well proven process. As in Section 2.4.1, data relevant to iron extraction has been extracted from references and is presented in Appendix 1. There is a much wider variety of processes available for non-ferrous metal extraction due to the considerably wider range of ores, both in a chemical and mineralogical sense. In many cases specific processes have to be designed to fit a particular ore in a particular location.

Aluminium:

There is very considerable literature on the extraction of aluminium or alumina, covering acid extraction, alkali extraction (including the orthodox Bayer process) and a wide range of processes based on roasting with solubilising compounds to form salts such as alums which are readily soluble in water (see 2-23).

While practically all aluminum is produced via the Bayer process, which includes an alkali leach of ore to extract the aluminium, leaving impurities such as iron behind, a considerable amount of investigation has been carried out upon acid leaching lower grade aluminous ores such as clays. A study of such proposed processes is interesting as alumina is the most predominant soluble impurity likely to be present in a low grade iron ore feedstock. Similarly iron is probably the most deleterious impurity in an aluminium feedstock, and most of the effort into alternative alumina extraction processes has been expended on aluminium/iron separation.

Probably one of the most comprehensive quantitative studies of acid extraction of alumina was carried out by Tilley et al. (2-11) in 1927, including a thorough literature review. Each step in a possible process of recovering pure alumina from clays was carefully studied from both experimental and literature standpoints, including such parameters as comminution, roasting and leaching conditions. Only sulphuric acid leaching was investigated although other workers results using hydrochloric acid were included. They asserted that pure alumina could be produced economically compared to the Bayer process, but no figures are given. Their more important conclusions relating to both aluminium and iron extraction are summarised in Table 2.8 and also in Appendix 1 based on sulphuric acid leaching. The authors state, however, when discussing hydrochloric acid leaching, that "the efficiency of the two acids in dissolving alumina from clays is about the same." It would not be unreasonable to suppose a similar statement may be made about iron, as their behaviour is quite similar. An important point to note is that the aluminium:iron ratio in the clays under investigation was between 60:1 and 10:1, whereas in the proposed low grades of iron ore for this dissertation, the ratio is approximately 1:5. The behaviour of iron in such small amounts in aluminous clays may be far from realistic. Tilley et al. concluded that "the cost of aluminium oxide made from clay by means of the sulphuric acid treatment should rival the cost of the Bayer process oxide."

TABLE 2.8

Requirements for maximum extraction of Al and Fe, and for minimum extraction of Si with dilute hydrochloric and with dilute sulphuric acid (after Tilley et al. (2-11)).

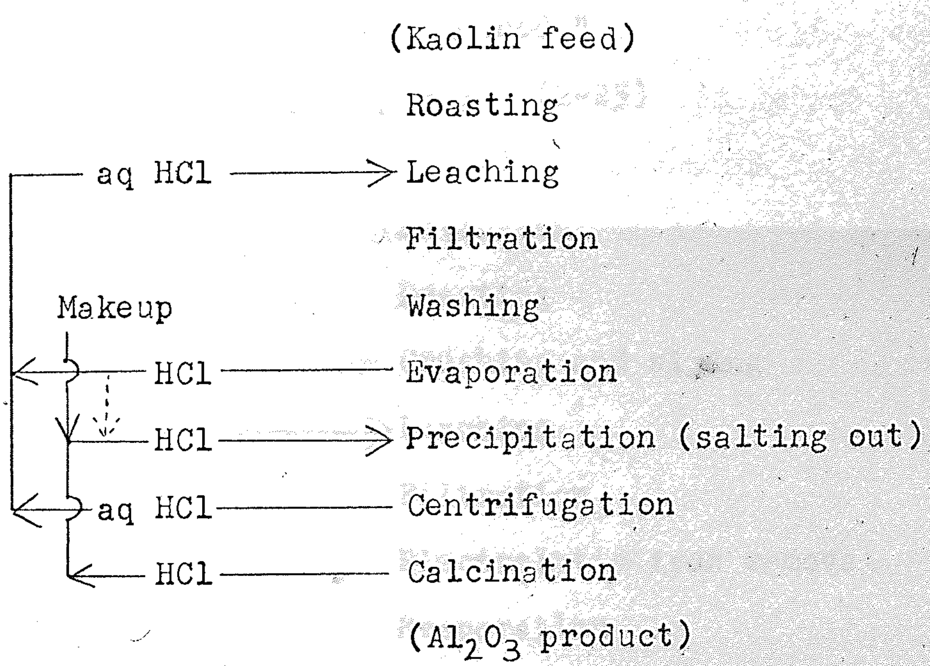
	Fe (maximum)	Al (maximum)	Si (minimum)
Feedstock	Clays and related minerals		
Grinding	Essential to 80-100 mesh		
Roasting requirements: Temperature	500-700°C (H_2SO_4)	600-800°C (HCl and H_2SO_4)	500-600°C (H_2SO_4)
	X --	700-800°C (HCl)	--
Time	--	No significance 1 hr.	--
Sulphuric acid: Concentration	Usually less soluble at high concentrations	Marginally less at higher concentration	High concentrations may tend to give colloidal silica
Excess	Greater gives higher extraction efficiency Less extracts Al at expense of Fe		--
High T and P (220°C)	Improvement by $\sim$50%		Little effect

X Control experiments with no roasting were not carried out for iron. Walthall (2-25) found maximum extraction of iron from ore dried at 100°C.

Several years later, Edward's et al. (2-23) reviewed acid leaching of aluminous ores, using sulphuric, hydrochloric, hydrofluoric, and nitric acids. They found that aluminium and iron are, to a great extent, soluble in all four acids, and while the halogen acids are easiest to recycle, they are also the most corrosive.

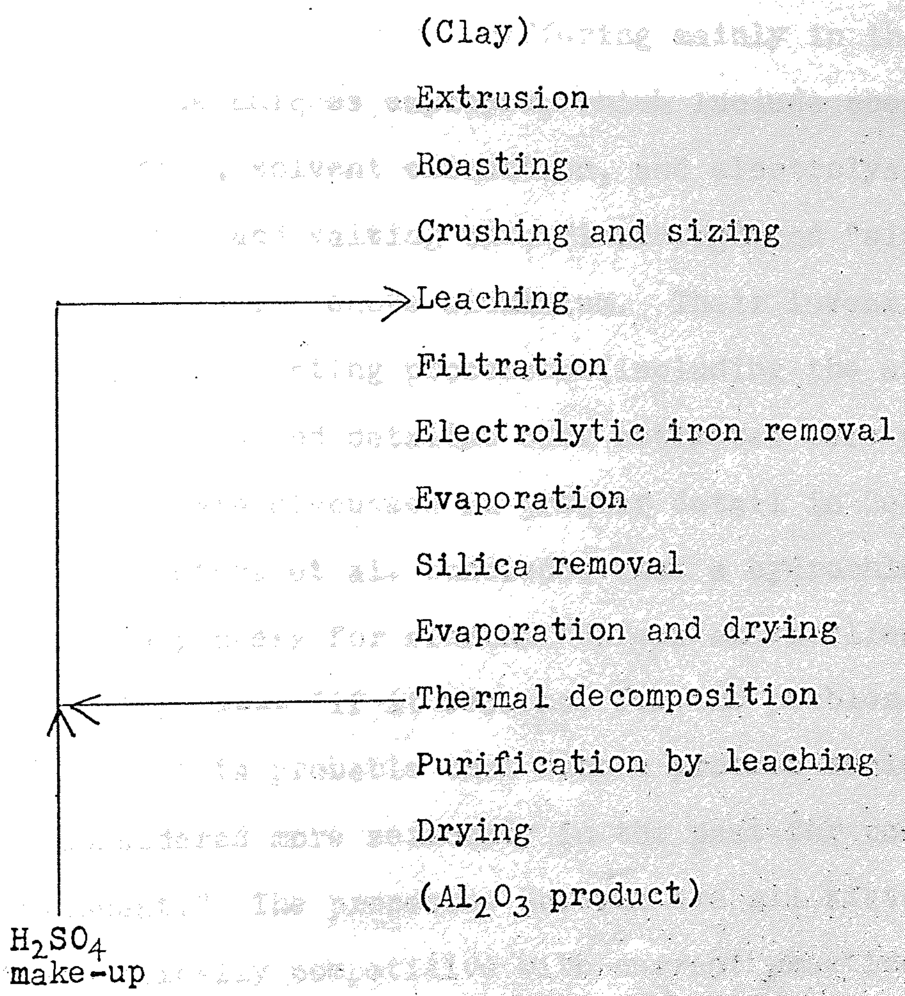
Specific proposals for acid extracting alumina have since been put forward by Hoffman et al. (2-24), Walthall et al. (2-25) and Peters et al. (2-26, and 2-27) which are summarised below and in Appendix 1B.

<u>Hoffman's process</u>: (2-24)



The process is interesting on account of its close resemblance to one of the six routes chosen for further study, viz. Leaching, Crystallisation, Thermal decomposition, (Reduction). (see Section 2). Constant boiling aqueous hydrochloric acid (20%) was employed for simplicity of recycling, the versatility of which is clear from the complicated recycling procedures adopted. Of interest also is the lack of colloidal silica formation when using this concentration of acid. A considerable amount of information and data were included in the paper to enable detailed mass balances and specific heats of solutions or slurries to be calculated, but this was practically all in respect of aluminium. Many operating details are likely, however, to be of importance in later stages of the present problem. Some important data is given in Appendix 1. Cost information is given comparatively in Table 2.10. A pilot plant was built, but no suggestion of costs for a commercial plant provided. Hoffman stated that "the alumina costs more than that produced from bauxite by the present well known method."

Walthall's process: (2-25)



This was a second very thorough investigation of an acid alumina extraction process employing sulphuric acid which was taken to pilot plant scale with considerable technical success. Every possible aspect and stage of the process was fully examined, and the technical feasibility of the resulting process appearedto be beyond doubt. However no mention was made of costs or economics at all which is very disappointing. Walthall et al.'s findings agree very much with those of Tilley et al.

In 1962 and 1963 a number of reports by Peters et al. (2-26, 2-27) were issued by the U. S. Bureau of Mines, summarising alternative processes for acid extraction of alumina. All follow a similar pattern to the previous processes described above, differing mainly in the iron separation techniques employed, which include chemical precipitation, solvent extraction, and electrolysis to remove iron; and salting out, "leaching" and "sintering" to preferentially remove aluminium. Their investigations were based on existing processes (including the above mentioned ones) and detailed cost estimates were worked out. These are discussed in greater detail in Section 2.8.

Peters et al. concluded that a hydrochloric acid extraction process for alumina "Offers an excellent opportunity" ---- "if it were not for the problem of corrosion it is probable that such a process would have been considered more seriously in the past for commercial development." The processes however are all stated to be not economically competitive with current practice.

There have been numerous other proposals for similar processes which have been reviewed by the above mentioned authors, but with no further useful information. In addition the extractive metallurgy of copper, nickel, cobalt, zinc and other metals has been studied, but no other useful data has been found. Sulphuric acid is used in most of the processes examined, and the iron is usually prevented from dissolving or removed, by high temperature hydrolysis to form insoluble basic sulphate. A similar technique is employed in nitric acid leaching to separate the iron as oxide. A number of examples are included in Appendix 1 for illustration.

2.4.3 Neutral Leaching

This category covers those methods when a conventional acid is not used to extract the metals. The action may take place in several ways:

a) Oxidation in either neutral aqueous medium; or by roasting, followed by water leaching.

b) Chemical reaction in either neutral aqueous medium; or by roasting with a reagent, followed by water leaching.

The former has been adequately discussed in (1-2) since when the position does not appear to have materially altered. The latter in aqueous medium, is exemplified by the Eustis process and related methods (see 1-1) which employ oxidation/reduction of $FeCl_3/FeCl_2$ in a closed cycle. Such processes are very attractive in their apparent simplicity. The costs, however, appear to have proved sufficiently high to deter any major interest.

Either sulphide ore, or metallised (pre-reduced) ore may be employed as feedstock. The other alternative - chemical roasting followed by water leaching - has been discussed (1-2), with the conclusion that there is little likelihood of further interest in the near future. This may be due to the necessity of two distinct operations employing reagents and conditions more expensive than aqueous chemical leaching, but with similar end-products. It is not envisaged at this stage that such a system be employed in any design.

2.4.4 Sulphide Ores

Much attention has been devoted to the acid pressure leaching of sulphide ores in the last 10 years (1-2). Noteworthy in this field are Forward and Mackiw who have been responsible, with co-workers, for several excellent reviews of work carried out in this field (2-30 to 2-32). Iron present as pyrite initially passes into solution as sulphate and is then mostly precipitated as basic sulphate and/or oxide, while pyrrhotitic iron is converted more directly to oxide (2-31). Forward (2-30) summarises the reactions taking place with sulphuric acid:

$$\begin{aligned}
FeS + H_2SO_4 + \tfrac{1}{2}O_2 &\rightarrow Fe\,SO_4 + H_2O + S^\circ \\
FeS + 2O_2 &\rightarrow FeSO_4 \\
4Fe_nS_{n+1} + 3O_2 &\rightarrow 2Fe_2O_3 + 4S^\circ \\
FeS_2 + 2O_2 &\rightarrow FeSO_4 + S^\circ \\
2FeS_2 + 2H_2O + 7O_2 &\rightarrow 2FeSO_4 + 2H_2SO_4 \\
2FeS_2 + 4H_2O + 7\tfrac{1}{2}O_2 &\rightarrow Fe_2O_3 + 4H_2SO_4 \\
2\,FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 &\rightarrow Fe_2(SO_4)_3 + H_2O \\
Fe_2(SO_4)_3 + 6H_2O &\rightarrow 2Fe\,(OH)_3 + 3H_2SO_4 \\
Fe_2(SO_4)_3 + FeS &\rightarrow 3FeSO_4 + S^\circ
\end{aligned}$$

The products formed depend on the initial reagents, pH, temperature and oxygen partial pressure. In addition, where there are other metals present as sulphide (as usually occurs naturally) the ferric sulphate effectively dissolves these (2-30):

$$Fe_2(SO_4)_3 + Cu_2S \rightarrow CuS + CuSO_4 + 2FeSO_4$$

$$Fe_2(SO_4)_3 + CuS \rightarrow CuSO + 2FeSO_4 + S^\circ$$

$$Fe_2(SO_4)_3 + ZnS \rightarrow Zn\ SO_4 + 2FeSO_4 + S^\circ$$

$$Fe_2(SO_4)_3 + PbS \rightarrow PbSO_4 + 2FeSO_4 + S^\circ$$

The overall reaction is thus very complex and it is extremely difficult to forecast the products, except by experimentation. Hydrochloric and nitric acid leaching of sulphide ores are also reviewed by Forward (2-30), but both are rejected as possible reagents. This is due to the high corrosivity and high solubility of nearly all metal compounds in the case of hydrochloric acid; and high cost, unpredictability of reaction, and easy formation of gaseous by-products in the case of nitric acid.

Ferric chloride leaching operations however have been favoured by a large number of workers since 1887 to extract the iron from pyrrhotite (natural or artificial) as ferrous chloride, followed by electrolytic precipitation. Examples of these processes are Siemens, Eustis and Konrad which are covered in (1-1; appended). Such an operation has proved technically successful but the economics and/or corrosion problems have always appeared unfavourable.

Work on the aqueous oxidation and dissolution of iron sulphide minerals has already been reviewed by the author (1-2).

2.4.5 Choice of acid

Previous work by the author (1-2) suggested that only the common mineral acids - hydrochloric acid, nitric acid and sulphuric acid - could be considered as the leaching agent.

Hydrochloric acid appears to have more advantages and wider potential use than the other two acids, namely:

Production of either iron chloride or oxide for reduction.

Greater ease of recycling acid.

Wider versatility in choice of phases for contacting (see later).

Greater ease of separating iron and/or impurities.

Higher rates of extraction.

The most severe disadvantage to date in all proposed processes employing hydrochloric acid has been corrosion (see 1-1), but with modern materials of construction, this should not prove to be more than a mild inconvenience.

A morphological analysis of the three alternative acids was attempted but the criteria eventually exceeded 40 and even with a weighting/factor technique, gave inconclusive results.

2.5 Purification

2.5.1 Pressure precipitation

Previous discussion (1-2) has shown that either hydrolytic/oxidative pressure precipitation, or "salting out" can be considered as a precipitative separation method.

The former is a proven technique for sulphuric acid based non-ferrous metal extraction processes when iron is an unwanted impurity. Iron is precipitated or prevented from going into solution by autoclaving at elevated temperature and pressure, when ferric sulphate, basic ferric sulphate and/or ferric oxide are formed according to conditions. The reactions might be represented by:

$$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$

$$Fe_3O_4 + 4H_2SO_4 \longrightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O$$

$$Fe_2O_3 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 3H_2O$$

$$2FeSO_4 + \tfrac{1}{2}O_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O \quad (2\text{-}29)$$

$$Fe_2(SO_4)_3 + 3H_2O \longrightarrow Fe_2O_3 + 3H_2SO_4 \quad (2\text{-}29)$$

$$Fe_2(SO_4)_3 + 2H_2O \longrightarrow 2\,Fe(OH)SO_4 + H_2SO_4 \quad (2\text{-}29)$$

Mancke, for example, exploited this technique in a number of patent specifications for extracting nickel (2-34, 2-35) and copper and cobalt (2-36) from lateritic ores. Iron has also been recovered from sulphuric acid pickling liquors by this technique (1-2).

Similar reactions occur more readily and more selectively with nitric acid, giving a fairly pure iron oxide. Six (2-14) employed this process for manufacturing pure ferric oxide and Schaufelberger (2-37) has carried out a considerable amount of work on separating iron and other metals by nitrate formation and selective decomposition. It has also been used in a similar manner to sulphuric acid to recover nickel from lateritic ores (2-35), nonferrous metal values from mixed ores, and iron from spent nitric acid pickle liquors (1-2, 2-39). The reaction may be represented by:

$$2\,Fe(NO_3)_3 + 3H_2O \longrightarrow Fe_2O_3 + 6HNO_3$$

No mention has been found in the literature of similar reactions occurring with aqueous iron chloride solutions, although such behaviour is thermodynamically feasible and has been reported (2-40). Practical workers are aware of the tendency of ferric chloride to decompose. The reactions are not known but may be conjecturally:

$$2FeCl_2 + O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4HCl$$

$$2FeCl_3 + 3H_2O \longrightarrow Fe_2O_3 + 6HCl$$

probably involving ferric oxychloride as an intermediate, but the chemistry of this compound is not well known. The gaseous phase hydrolysis of iron chlorides has been studied in depth by Topliss (2-1). Section 4 deals with these topics in greater detail.

2.5.2 Precipitative Crystallisation

Precipitative Crystallisation by the common ion effect has been used to separate metal chlorides and occasionally sulphates, particularly for recovering iron from spent pickle liquor (see 1-2). Chloride precipitation is usually achieved by passing gaseous hydrogen chloride through the solution, and sulphate precipitation by adding concentrated or fuming sulphuric acid. The latter alternative has not proved popular due to inherent problems of recycling sulphuric acid.

The action of excess chloride ions on solutions of iron and other metal chlorides depends on the valency state of the iron. If ferrous iron is present, then $FeCl_2.2H_2O$ is precipitated (1-1, 2-10, 2-13), and if ferric iron is present then aluminium (if present) is precipitated preferentially as $Al\ Cl_3.6\ H_2O$ (2-24, 2-26). As ferric chloride is very soluble in water, this will only precipitate under extreme conditions of high concentration.

If scrap is employed as feedstock, ferrous chloride solution is produced, from which pure ferrous chloride dihydrate may be readily precipitated. Alternatively if a low grade iron ore such as Northants is the feedstock, ferric chloride solution would be produced from which the main impurity, aluminium chloride, may be separated in a pure form. These suggestions are discussed further in Section 4. Data is available on the system $FeCl_2 - HCl - H_2O$ and is included in Appendix II.

2.6 Reduction

A chloride based process can produce either a pure chloride or a pure oxide for reduction, or possibly an oxychloride although this is unlikely. The chloride may be in the gas, liquid or solid phase as ferrous or ferric chloride, while the oxychloride or oxide in a chemical process is only likely to be formed as solid ferric oxide.

Pertinent data has been presented in tabular form in Appendix II.

2.6.1 Oxide Reduction

Iron is conventionally produced by reduction of an impure oxide (ore or concentrate) with an impure reductant (coke) with added limestone for impurity separation by way of slag. The product is "pig-iron" containing about 94% Fe, which is then further purified to make steel (97-99% Fe). A vast amount of work has been put into devising new processes to produce refined iron or steel directly from ore, employing a high grade or superbeneficiated ore and low impurity reductant. The literature on this subject is far too extensive to be adequately covered in this dissertation.

Out of the several hundreds of different processes that have been suggested (2-41 to 2-45, 2-79) only a few have reached large scale pilot plant or commercial size. These are summarised in Table 2.9. It is important to note that the economic viability of each process is usually dependant on peculiar local conditions, such as abundant cheap electricity or natural gas. Also the purity of the iron produced depends on the purity of both oxide and reductant.

It is considered that the pure iron oxide product from a chemical process may conveniently be reduced by a suitable existing direct reduction process, without the necessity of yet another one being specified. (Although it is conceded that such a development may eventually prove necessary: i.e. a reduction process designed specially for a pure iron oxide feedstock to give a specific product.)

If it is assumed that the processes listed in Table 2.9 are the most successful from a technical and economic viewpoint as only they have been developed to a commercial level, then the choice of a suitable oxide reduction process should be made from that list. Since a pure iron oxide would be produced from a chemical process, it is necessary to specify a reduction stage using a pure reductant in order to produce an uncontaminated iron powder. The only process listed in Table 2.9 that satisfies these conditions is the H-Iron process.

2.6.2 Chloride reduction

Hydrogen reduction of iron chlorides has only been studied in depth by a few workers, although reported on and specified widely in the literature, most of which has been reviewed by Topliss (2-1). Solid ferrous chloride reduction

TABLE 2.9

Commercial Direct Reduction Plants (2-41 to 2-45)

Plant	Reductant	Product	Notes
H-Iron	H_2	Fe powder	Better the higher grade the ore
Hoganas	Coal	Impure sponge	Magnetic separation and further H_2 reduction required
HyL	Reformed Natural gas ($CO + H_2$)	Sponge	Electric furnace feed
Krupp Renn	Coke	Nodular Fe lumps	Blast furnace or steel furnace feed
R-N	Coal	Briquettes 90% Fe.	
Esso Fior	Reformed naphtha	Briquettes 95% Fe.	
Stelco Lurgi	Coal	Sponge iron	Magnetic separation Electric furnace feed
Wiberg	H_2+ CO	Sponge	
Electric Arc	Carbon	Molten steel	

was the most common reaction discussed, but vapour ferrous chloride reduction to iron whisker crystals has also been investigated at length. This is not considered further.

Most of the relevant data on the iron chloride-hydrogen systems has been obtained by:

1) Rigg (2-46): Kinetics of reduction of solid ferrous chloride with hydrogen, equilibrium constant, reaction mechanism. Correlation of equilibria data.
2) Yannopoulos and Themelis (2-47): Rate equation for the reduction of ferrous chloride by hydrogen. Effect of temperature, gas velocity, particle diameter, and hydrogen chloride concentration.
3) Kangro and Petersen (2-48): Solid ferrous chloride-hydrogen equilibria both experimental and calculated (480-1020°C). Association of ferric chloride and partial pressures (250-350°C). Data on ferric chloride reduction to ferrous chloride. Specific heats.
4) Bagdasarion (2-49): Fused ferrous chloride-hydrogen equilibria (700-1000°C). Qualitative statements on reduction of ferric chloride.
5) Stone and Rigg (2-55): Discussion of necessary parameters for design of a commercial reactor for hydrogen reduction of ferrous chloride based on earlier work.

Ferric chloride reduction

This proceeds via ferrous chloride thus (2-48, 2-49):

$$2\ FeCl_3 + H_2 \longrightarrow 2\ FeCl_2 + 2HCl$$

$$2\ FeCl_2 + 2H_2 \longrightarrow 2\ Fe + 4HCl$$

The first stage, reduction to ferrous chloride, is stated by Bagdasarion (2-49) to be detectable at 100°C and rapid at 200°C. Kangro and Petersen (2-48) however, assert that reduction of solid ferric chloride is slow, but reduction of volatilised ferric chloride is very rapid and goes completely to ferrous chloride. Measurement of the equilibria of these reactions could not be made for unstated reasons. This is likely to be due to the complications of ferric chloride vapour association to the dimer and also thermal dissociation to ferrous chloride and chlorine which are discussed later. McIntosh and Broadley (2-50) investigated the behaviour and reduction of ferrous and ferric chlorides in connection with the purification of niobium. Their results showed that ferric chloride (vapour) can be reduced completely to ferrous chloride in 3½ minutes at 350°C, falling to 2 minutes at 375°C. Five times stoichiometric hydrogen was used. The reaction was found to be approximately first order. Under the conditions given above, and assuming homogeneity, they state that the time necessary for complete reduction of ferric chloride is independant of the scale of operation.

It may be concluded from the above information that reduction of ferric chloride to ferrous chloride is much slower for solid than vapourised ferric chloride, and the rate of reduction increases as temperature increases. Work on reduction of ferrous chloride (see following section) indicated that rate of reaction is inversely proportional to a particle size parameter, and at molecular level therefore may be expected to be very fast. This theory is supported by the complete reduction of ferric chloride vapour to metallic iron which proceeds extremely quickly and may reach explosive proportions under certain circumstances (2-52).

Complete reduction of ferric chloride has not been found to have been discussed in the literature, although vaguely specified in a number of patents (2-53, 2-54), and is clearly an area which merits investigation.

Ferrous chloride reduction:

Hydrogen reduction of bulk ferrous chloride has aroused considerably more interest recently, primarily on account of the R.C.A. process (1-1, 1-5) for producing iron powder by hydrochloric acid extraction, and reduction of crystallised ferrous chloride in briquette form. Rigg (2-46) has reported on the reduction end of this process in considerable detail, including for the first time data on the kinetics. Yannopoulos and Themelis (2-47) have also studied the rate of reduction of a single particle of ferrous chloride with hydrogen, arriving at a similar rate equation as Rigg (2-46 b).

At a practical level, Stone and Rigg (2-55) have designed large scale reactors for incorporation into the R.C.A. process. They found that the only successful way of reducing ferrous chloride was in briquette form in a series of fixed bed semibatch reactors. These apparently have a maximum size and need to be duplicated for increased throughputs which removes any economic advantages of scale. No other references have been found relating to large scale/ commercial reduction of ferrous chloride. A more complete list of references on ferrous chloride reduction in general may be found in Topliss's thesis (2-1).

2.6.3 Electrolytic reduction

An extensive review on the electrolysis of iron is appended (2-59) as part of this thesis. While this method of reducing aqueous solutions to metallic iron has many attractions and advantages, over-riding economic factors eliminate this method of producing metallic iron on a large scale. Economies of scale are unlikely, operating costs are relatively very high, and the versatility of the process in producing directly a useful product is severely limited. Although electrolysis may be useful in manufacturing specialised products, it is not suitable for processes covered in this dissertation.

2.7 Markets

There are a number of possible products from a chemical iron making process. These include:

Powder - direct (chemical),
via sponge,
electrolytic.

Electroforms - foil,
direct shapes (e.g. gauze).

Molten iron

Whiskers

2.7.1 Iron powder

The market for iron powder, past, present and future, has been studied in considerable depth by Sturges and Billington (2-56). Without repeating any of their work, their conclusions may be summarised as:

Production capacity (short tons p.a.) :-

	1968	Early 1970's Estimated	Late 1970's Estimated
North America	210,000	ca.400,000	ca.¾-1 million
U.K.	6,000	ca. 30,000	ca. 100,000
Europe (excluding U.K.)	ca.60,000	ca.150,000	ca. 300,000

Present iron powder market :-

North America	100,000 sh. tons p.a.
U.K.	14,000 sh. tons p.a.
Europe (excluding U.K.)	30,000 sh. tons p.a.

Market expansion rate :-

North America	20 - 25% p.a.
U.K.	ca. 20% p.a.
Europe (excluding U.K.)	15 - 20% p.a.

The potential market for iron powder would appear therefore to be in little doubt, and it is in this product that most interest lies at the moment as far as chemical process exploitation is concerned. Possible products from an iron powder technology include, in use sequence:

Present:

Welding rods - Uses impure iron powder
Engineering compacts - 1st and 2nd generation
Investment casting - dependant on economics

Future:

Foil)
Bar)
Strip)
Rod)
Tube)

In each case alloy steel would be expected to come in before iron, and batch operation before continuous (where relevant).

While the only applications at present are welding rods, engineering compacts and to a lesser extent forging preforms, both foil and strip have already been successfully manufactured continuously on pilot plant scale (2-57), and the other products may be expected to follow.

Iron powder is at present made in bulk by a variety of methods that include grinding and refining of sponge, direct reduction processes, atomisation of molten iron or steel, and millscale reduction (2-80). There is also a new chemical process (R.C.A.) being built in Canada which is due to be commissioned in the near future (see Section 1). Preliminary tests on iron powder samples from this chemical route have been very successful (2-66). Very small quantities of iron powder are also made for special applications by carbonyl and electrolytic processes, but these are very expensive costing about £700 and £500 per ton respectively. In 1947 Gardam (2-58) estimated the cost of producing electrolytic iron powder at 12-16 d per lb., compared with about 50-55 d per lb. in 1969/70.

2.7.2 Electroforms

The electrolysis of iron with particular reference to electrowinning from leach liquors has already been extensively reviewed (2-59).

The continuous production of strip has been patented (2-59) and it is understood that work is proceeding at a number of places in the U.K. on the continuous high speed production of iron foil electrolytically (2-57, 2-60). There is a more extensive patent literature on electroforming tubes which goes back to Siemen's process (see Section 2.1) and electroforming in general is well covered in the literature. Relevant references and discussion can be found in the above-mentioned review.

The economics of electroforming, however, remain in doubt except for specialist applications. From the early

1920's when Eustis made electrolytic iron tubes, there have been many patents and claims but, as far as is known, no substantial proof of economically producing iron electroforms. The only possible "tonnage" product at the present time appears to be thin iron foil. If produced by conventional methods this would be very costly, the cost bearing an inverse relationship to thickness. When produced electrolytically however, the main cost lies in energy which is roughly proportional to weight produced, and not thickness of material. The product can be very pure and therefore does not suffer from corrosion normally associated with iron and steel. There is however no established market for large scale production of electroforms and this product is not further investigated.

2.7.3 Molten iron

Practically all iron and steel products now manufactured are via molten metal from conventional processes. A chemical route to bulk molten iron would suffer from many of the disadvantages, particularly thermal, inherent in conventional methods, and is not considered further. However one of the new techniques of casting - investment casting - employs a preweighed quantity of metal powder that is melted into the mould. This considerably reduces heat and metal losses. The technique has been developed and automatic bottom poured investment casting with induction heating is available.

2.7.4 Whiskers

A considerable amount of work has been carried out on the formation, properties and uses of iron whisker crystals. (see (2-1)). There is no established market or industrial application at the moment, so despite interest in this field iron whiskers are not to be considered a likely product. It is worthwhile adding that one of the most successful methods of preparation is by deposition from the vapour phase, and one of the processes considered employs such an operation in the reduction stage (see later sections).

2.8 Economic considerations

Economic criteria are among the most important in evaluating alternative processes. This can be difficult in situations of minimal information as exist in novel process design.

Overall costs of producing a chemical are conventionally divided between fixed capital or investment costs and variable or running costs. The latter are not too difficult to estimate from actual data and analogy with existing similar processes (see Section 2.8.3). This has been done for a number of ironmaking processes and is contained in a paper (co-author S. A. Gregory)which forms part of this dissertation and is appended (Appendix III). Capital cost estimates were also included but are discussed further in the following section. Overall cost estimates for the proposed processes are presented in Section 7.

2.8.1 Capital cost estimation

A considerable amount of effort has been put into finding a reliable method of estimating capital costs over the last few decades. The most reliable method is of course to cost the complete process after the plant has been built, commissioned and set into operation and accounts received. This requires a fully detailed knowledge of the process to the "last nut and bolt" practically, and is therefore very costly in time and money and can only be achieved after the event. Many attempts have been made to simplify capital cost estimation and most methods developed fall into two categories of:

1) Factor methods
2) Functional unit methods

Factor methods of capital cost estimation which are the most common, are typified by the Lang Factor method (2-61) in which the overall installed cost of a process is the cost of the basic equipment (D.E.C. - delivered equipment cost) multiplied by one of three factors: 4.74 for processes involving primarily fluids, 3.10 for solids and 3.63 for mixed fluids-solids. This bulk factor method has a number of disadvantages: for example the D.E.C. of a stainless steel plant is likely to be considerably higher than for a mild steel plant, yet the foundations, buildings, labour requirements etc. may not be substantially changed. There is a range of factor methods available which permits choice for accuracy needed in estimating from ± 25% to ± 5%.

The functional unit approach appears to have first been employed by Wessel (2-62) in estimating labour requirements. Zevnik and Buchanan (2-63) derived a numerical/graphical technique for estimating the overall capital cost of a "liquid" process based on the product of: number of process steps (i.e. functional units); cost per functional unit which is based on plant capacity; a complexity factor incorporating maximum temperature deviation from ambient, maximum pressure deviation, and materials of construction allowance; and finally a cost index. The authors claimed an accuracy of ± 25% on selected processes. Again a number of disadvantages may be pointed out such as exclusion of recycle streams which can considerably increase the size of a plant in relation to capacity. This technique is however attractive, particularly if the necessity of graphical interpolation is removed, but a number of inexplicable anomalies exist in the sample derivations of capital cost within the published paper.

One of the major drawbacks of Zevnik and Buchanan's approach is the use of plant capacity which often bears no relation to throughput, and the size of a given piece of equipment is based on its throughput. Gore (2-64) attempted to overcome this difficulty when he derived the following equation for the capital costs of processes based on gaseous feedstocks:

$$£C = 1670\ N.\ Q^{0.62}.T^{Y}.\ P^{0.395}.\ Fm.\ \frac{CEI}{114}$$

where C = capital cost

N = number of functional units

Q = function of throughput/capacity (not clearly defined)

T = represents maximum temperature t°K of the process. $T = \frac{(t^{\circ}K - 300)}{(300)}$

Y = 1.07 (or more accurately $Y = \frac{Q^{0.206}}{2.52}$)

P = represents maximum pressure p of the process $P = \frac{p\ atm}{1\ atm} = \frac{p\ psi}{14.7\ psi}$ etc.

Fm = 1.0 (in the absence of further information on materials of construction)

CEI = Cost engineering index (any similar index would be satisfactory in fact)

This equation was derived from a wide survey of published capital cost data, covering ten process industries and about one hundred individual cases. The equation above was obtained as a "best fit" correlation from the data. An agreement of ± 20% is claimed.

Although some difficulty in using the equation in practical examples has been encountered, it is clear from Gore's work that the technique is potentially fairly reliable; and in a situation of minimal information, such as comparison of new processes within a particular industry, should prove valuable.

The application of this method of capital cost estimating to the present problem can be developed in a number of ways. A similar simplified equation may be employed on a comparative basis, alternatively actual data may be used to develop a similar equation to give the actual capital cost of a hydrometallurgical process. In the latter case simplifications such as deletion of Fm (materials of construction factor), P (pressure factor) and perhaps T and C.E.I. may be possible. This is investigated further in Section 7.

Stallworthy (2-65) has developed the functional unit concept a little further to arrive at the following equation for liquid based processes:

$$C_2 = \frac{0.075}{A} \sum_{1}^{S} (N \times Fm \times Fp \times Ft \times R)$$

where C_2 = Capital cost

A = Size factor for capacity of plant required (graphical)

S = Number of main and process side streams

R = Ratio of the stream to the main stream

N = Number of significant process steps in the main stream or side stream (i.e. functional units)

Fm = Factor for materials of construction (1→2)

Fp = Factor for design pressure (1→ 1.3)

Ft = Factor for design temperature (1→1.5) .

This approach was developed by Stallworthy at about the same time as Gore, in an attempt to overcome the problem of relating plant capacity to an often variable and unrelated throughput. He does this by considering both main and subsidiary process streams, hence requiring considerably more information than Gore's approach which considers total material input in moles (the equation was developed only for basically gas phase processes). Another approach (see Section 7) attempts to combine the simplicity of the total number of functional units with the accuracy of a throughput quantity rather than plant capacity.

As well as the problem of relating throughput to plant capacity, there are also difficulties with definitions of functional units. Stallworthy admits to this providing the greatest problem. Gregory (2-69) provides a lengthy "definition":

> "Significant pieces of plant which carry out operations on the main process stream. Any unit operation which carries out a stage of purification and involves mass transfer (e.g. distillation column). Items that carry out unit processes.
>
> Pieces of equipment that carry out mechanical separation only count if they constitute substantial systems in their own right, and cannot be built in as part of a

unit operation or process (e.g. centrifuge, rotary vacuum filter, etc.) not included are cyclones, simple gravity settlers, etc. Heat transfer equipment may be divided similarly (e.g. waste heat boilers, molten salt heat exchanges are included but not reboilers or condensers, etc.).

Mechanical items used for feeding or discharging complete process systems count as functional units, as does a solids feeder plus major hopper. A vacuum pump associated with a vacuum filter would not count nor do tanks, hoppers, surge tanks, etc."

An example may help to make the above explanation more clear. Finlayson (2-67) has published the following flow diagram, Figure 2.4, which is the most recent version of the R.C.A. process. According to the flow diagram there are 12 qualifying functional units. However in addition to these, the following units are likely to be required:

Hydrogen (or HCl) recycle blower
Iron scrap feed system
Hydrogen cooler/dryer

of which the last is not a functional unit. There are thus 14 functional units in this process.

It is possible that two levels of functional unit number estimation may be established - one based on a block diagram such as Figure 2.4 which is useful in situations of minimal information; and one based on more detailed knowledge when numbers of functional units making up a unit stage are known, e.g. a bank of six centrifuges or four reactors. This is explored later. It must be remembered that there are

R.C.A. Process

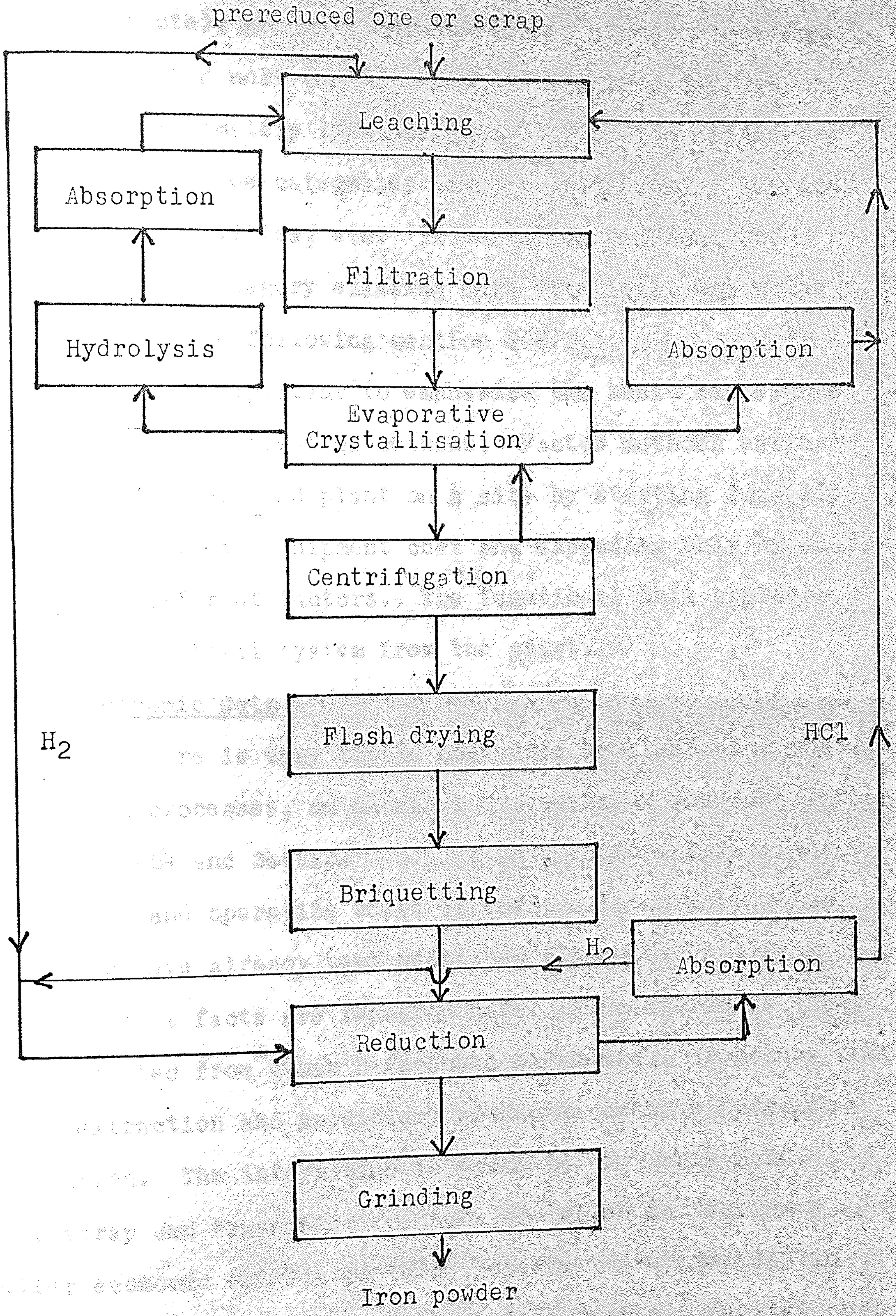


Figure 2.4

basically three categories of capital projects: greenfield (or grass roots), new unit on established site, or enlargement of existing unit (2-76), which fall into a capital cost ratio of approximately 130-140: 100: 70-80. The difference between these three categories lies in provision of services and offsite facilities, etc. It was often difficult to discover which category existing data fits into, which was necessary for the following section 2.8.2.

It is important to emphasize the basic difference between the two estimating methods. Factor methods estimate the cost of an erected plant on a site by starting (usually) with the delivered equipment cost and expanding this by multiplying by different factors. The functional unit approach considers the total system from the start.

2.8.2 Economic data

There is very little cost data available for metal extraction processes, or chemical processes of any description as Gore (2-64 and Section 2.8.1) found. Some information on capital and operating costs of chemical iron extraction processes have already been published (Appendix IV) from which salient facts are repeated here. In addition data has been collated from other references on chemical processes for metal extraction and subsidiary processes such as hydrogen generation. The information is presented in Table 2.10. Ore, scrap and transportation costs are given in Section 2.2. Fuller economic details of these processes are provided in Section 7 (q.v.) where they are used to derive a capital cost estimation equation.

Table 2.10

Capital Cost Data

Process	Feed	Product	Capacity long tons p.a.	Cost £000	Reference
R.C.A./ Woodall	Scrap	Iron powder	44,600	5,350	App.III
Duckham	"	"	17,900	3,075	"
"	"	"	83,300	8,170	"
FLOX (wet)	Low grade ore	Iron powder	350,000	17,300	2 - 68
"		"	50,000	4,550	2 - 68
Alumina (HCl)	Clay	Al_2O_3	312,480	28,629	2 - 26
"	"	"	"	35,895	"
"	"	"	"	44,574	"
"	"	"	"	33,310	"
"	"	"	"	34,892	"
Alumina (H_2SO_4)	"	"	"	37,615	2 - 27
"	"	"	"	33,072	"
"	"	"	"	31,018	"
Sherritt Gordon	Pure pyrite	Sponge Iron	109,375	6,288	2 - 70
"	"	"	218,750	11,212	"
"	"	"	437,500	19,470	"
"	Impure pyrite	"	109,375	7,841	"
"	"	"	218,750	13,599	"
"	"	"	437,500	24,016	"

Process	Feed	Product	Capacity long tons p.a.	Cost £000	Reference
Sherritt Gordon	Laterites	Nickel	22,320	31,250	2 - 73
Firth & Root	Carbonate slate	Fe powder	29,460	1,727	2 - 12
(Freeport (Nickel (	Laterites	NiS.concentrate	62,430	26,786	2 - 77)))
(Freeport (Nickel	NiS.concentrate	Nickel	22,320	15,714	2 - 77))
Kwinana	NiS. ore	Nickel	13,390	15,000	2 - 78
Everest et al.	BeO ore	BeO	375	1,382	2 - 71
"	"	"	375	3,129	"
"	"	"	188	1,052	"
"	"	"	188	2,060	"
"	"	"	375	1,913	"
"	"	"	375	3,908	"
"	"	"	188	1,507	"
"	"	"	188	2,555	"
"	"	"	375	1,684	"
"	"	"	188	1,382	"
"	"	"	375	1,663	"
"	"	"	188	1,318	"
Outokumpn	Pyrite	Cobalt	1,071	4,000	2 - 72
Hydrogen (S.R., Oxidn)	Natural gas) Naphtha)	98% H_2	(10-100 SCFD ((	500-6,000	2 - 66

2.8.3 Running costs

The total running costs of a chemical process are usually made up of the following:

Feedstock
Chemicals
Labour
Energy
Maintenance
Overheads

Allowances for capital cost and interest are also included to give an overall operating cost.

There are many ways of estimating the overall operating cost of a process - each company probably has its own particular method, and there is a considerable literature on the subject. For the purpose of estimating the operating costs of the processes considered in this dissertation, a simple method will be used of considering each of the above items:

Depreciation: (recovery of capital cost) This is usually spread over a number of years ranging from 3 for a high risk plant and/or short life product, to 20 for the other extreme and high cost plants. The apportionment per year may be calculated in a number of ways, the most simple being an equal part of the total capital cost per year of plant life (straight line depreciation).

Return on capital: A rate of return is selected according to some criteria of which there are a range.

Feedstock: Feedstock costs are given in Section 2-2.

Chemicals: Where chemicals are required on a once-through basis it is not difficult to estimate requirements and obtain costs from trade journals or supplier. For recycle streams however, it is necessary to assume losses and hence make-up requirements which is where the information in Appendix I is helpful. The cost of the make-up chemical is relatively easy to find once the quantity involved has been estimated or assumed.

Labour: Manning requirements are often more difficult to estimate, and an approximate figure is usually reached by analogy with similar industries. The cost of labour may then be calculated by assuming operating hours, and allowing a fixed sum per man year, which is often taken as £2,500 (1970). This figure allows for wages and direct management expenses associated with his employment.

Energy: An energy balance is necessary for estimation of energy requirements, which are usually divided into electricity, gas, steam and water. The flow diagram should allow for waste heat useage which is taken into account together with losses, when specifying energy requirements. Individual costs may be used:

electricity	1d/Kwh
gas (town)	12d/therm
gas (natural)	6d/therm

steam	12d/therm
water (cooling)	30d/1000 gals.

or a global figure employed.

Maintenance: A percentage of the total capital cost is often used for maintenance allowance, which ranges from 1% to 10% depending on the type of plant. For a corrosive acid plant as is likely to be employed in iron extraction a generous figure of around 8% may be realistic.

Overheads: These cover everything else, including distribution, marketing, administration, welfare, reseach and development, etc.

Other items: Salvage value, taxes and such indefinite and peripheral costs are not included in this scheme.

2.9 Conclusions and process selection

The previous eight sections 2.1 to 2.8 have reviewed most of the relevant aspects of chemical extraction of iron and other metals. Although it is apparent that previous workers have met with little actual success in their attempts to find a viable process to replace existing methods of manufacture of the more common metals such as iron, aluminium, copper, etc., the possibilities still seem attractive particularly in the light of technological progress and also of a change in emphasis in industrial economics, which might overcome many of the failings of earlier ideas.

Previous work (1-2) employed the then novel technique of morphological analysis which found the six "best" hydrometallurgical processes from all possible alternatives. Although these were more precisely defined, all were based on:

Leaching (ore or scrap)
Purification (crystallisation, precipitation etc.)
Reduction to metal

Hydrochloric acid has since been suggested as the best leaching agent (Section 2.4.4). Parallel work by Topliss (2-1) on gas-phase processes concluded with a recommendation that the following four processes based on chlorides be studied further:

Gaseous "leaching" (ore or scrap or metallised ore)
Oxidation (optional) - purification
Reduction to metal

While it is not intended to pursue these latter gas phase processes in any detail, it may be helpful to include them for comparison and analogy.

A scrap based process has a number of attractions for initial consideration.

1) Scrap is freely available in certain areas.
2) Hydrogen is generated on dissolution which may be recycled for reduction later.
3) Ferrous chloride is produced which is more suitable for purification by crystallisation without requiring prior reduction.
4) Valuable byproducts in low grade scrap, such as copper, may be easily recovered which could help offset the initial costs of setting up such a process. Low grade scrap containing copper cannot usefully be used conventionally, and is therefore cheap.

However there is a limited supply of scrap in any given area, and while the above attractions hold for a relatively small scale initial process of around 50,000 to 100,000 tons per year, in the long term an ore based process would be necessary for large economically viable plants. Since iron ore usually exists in the oxidised (ferric) form, leaching would give ferric chloride which is not easy to crystallise and is more amenable to precipitation by hydrolysis. It would be possible to reduce the ferric chloride so formed to ferrous with scrap but again this would require large quantities of scrap.

Before specifying proposed processes it is necessary to look at one of the gaseous processes: "leaching," oxidation, reduction. Gregory (2-69) has taken out a provisional patent on a variation of this basic process. Briefly, scrapiron is treated with a mixture of hydrogen and hydrogen chloride gas under suitable conditions to form anhydrous ferrous chloride. This is oxidised with air or oxygen to give ferric oxide and ferric chloride, which is volatilised by the heat of reaction (A further purification step of condensation and re-sublimation may be necessary). The final step is reduction of vapourised ferric chloride to iron powder, using the recycled hydrogen/ hydrogen chloride gas mixture under suitable conditions. The already commercial R.C.A./Woodall Duckham process (1-5 and appended) crystallises ferrous chloride from aqueous solution, partially dries it, then reduces solid ferrous chloride briquettes. The poor technical and economic viability of their technique has been discussed (1-1), and it is not likely that this may easily be improved.

An attractive proposition may be, therefore, to take a crystallised/precipitated ferrous chloride from a scrap leaching stage, dry it then treat it as for the last two stages of the gaseous process discussed above; that is oxidise then reduce the vapourised ferric chloride. One main disadvantage of this method is that one third of the iron throughput is converted to oxide. (The chemistry of all these processes is given later).

From the above discussion and conclusions reached in Section 2, the following two processes, Figures 2.5 and 2.6, are considered in the rest of this thesis, and have the following outline specifications:

Process I dissolves scrap iron in aqueous hydrochloric acid, crystallises ferrous chloride dihydrate with hydrogen chloride, oxidises it to ferric oxide and ferric chloride which is reduced with hydrogen to iron powder. The plant capacity is 50,000 tons p.y.

Process II dissolves iron ore in aqueous hydrochloric acid, precipitates ferric oxide by hydrolysis and reduces this to iron powder. The plant capacity is 350,000 tons p.y.

Process I

Feedstock = scrap iron

Capacity = 50,000 tons per year

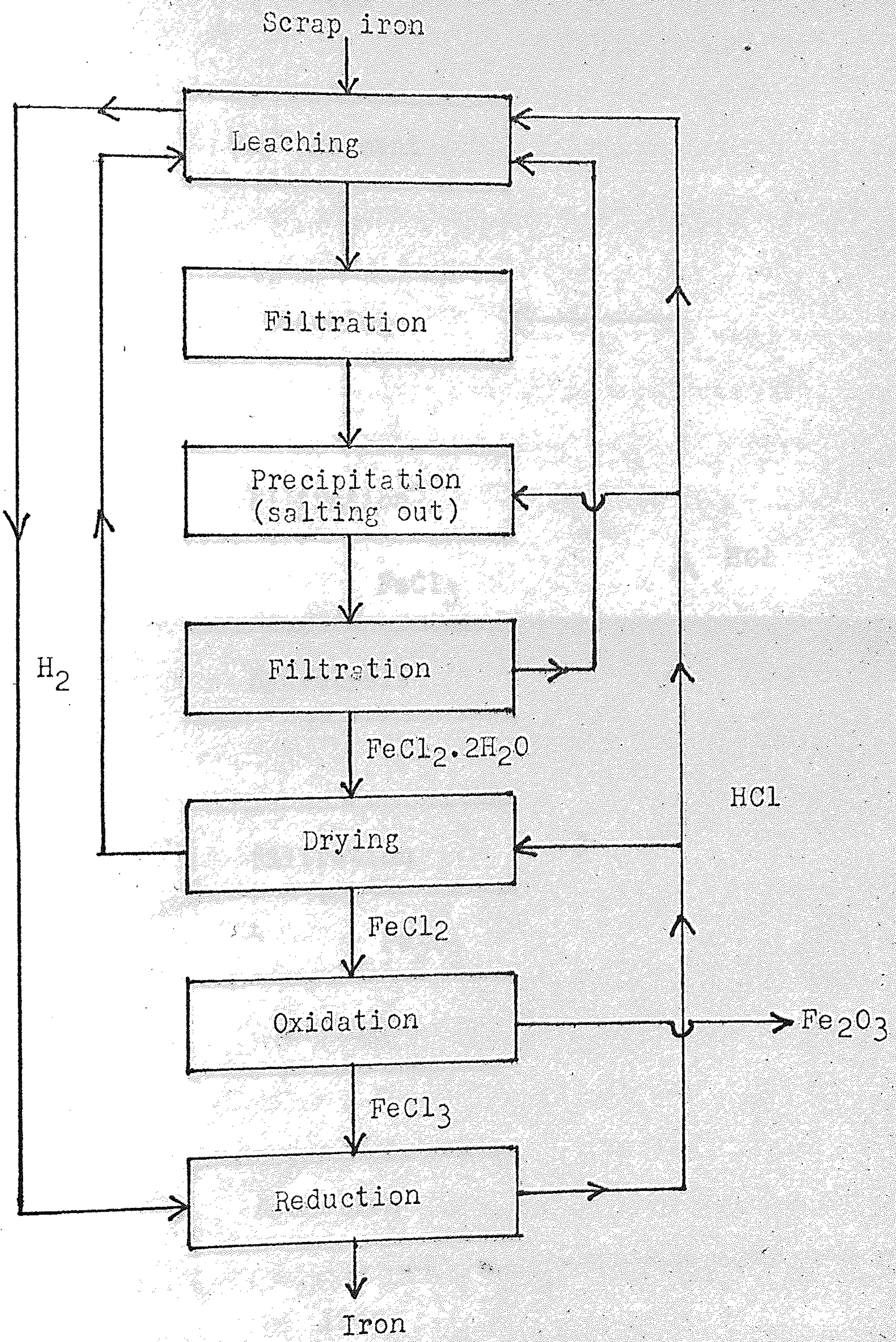


Figure 2.5

PROCESS II

Feedstock = low grade iron ore

Capacity = 350,000 tons per year

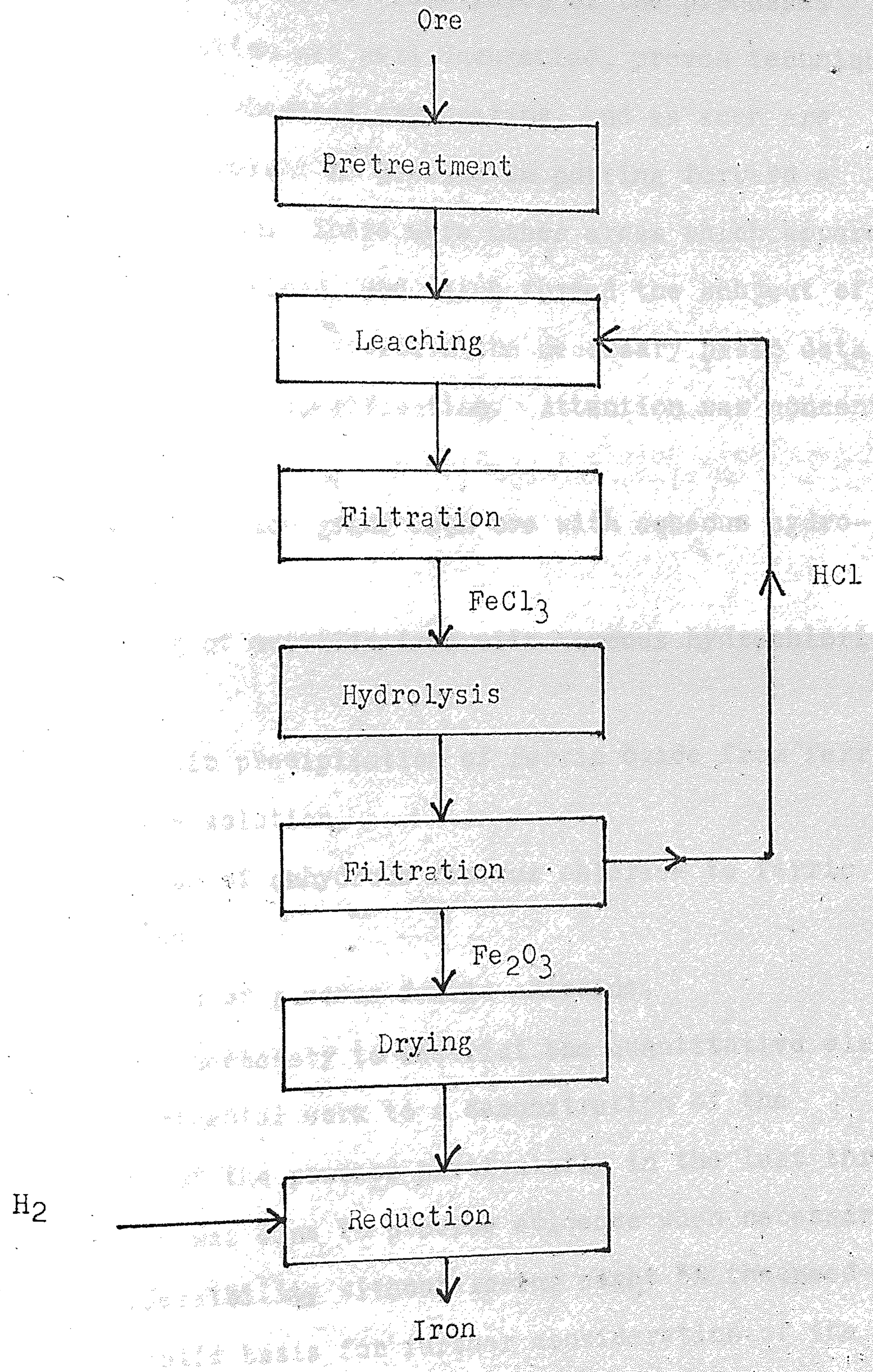


Figure 2.6

3. PROCESS DESIGN - LEACHING

It is not intended that Sections 3, 4 and 5 on process design, should in any way be similar to an undergraduate design problem. Some parts of the processes under consideration are well documented, proven techniques or conventional chemical engineering, and as such are considered to present no problem in putting forward a viable proposition. There were other areas which apparently have not been examined, and which formed the subject of experimental work to ascertain the necessary basic data for initial design specification. Attention was concentrated on these:

leaching of low grade iron ore with aqueous hydrochloric acid,

leaching of metallic iron with aqueous hydrochloric acid,

hydrolytic precipitation of ferric oxide from ferric chloride solution,

oxidation of anhydrous ferrous chloride to ferric chloride,

reduction of gaseous ferric chloride,

It was found necessary to restrict the quantitative elements of the experimental work to a demonstration of the feasibility of the process particularly in the last three areas. This was done to provide evidence when necessary of technical feasibility without losing sight of the need to provide a solid basis for further consideration of the process systems discussed in this dissertation. In many instances severe curtailment on both practical and theoretical grounds prevented development of what appeared to be very interesting and worthwhile research problems.

3.1 Leaching theory and parameters

In many chemical engineering textbooks (such as 3-1, 3-2) leaching is conventionally studied either quantitatively in terms of pure physical processes involving phase equilibria and number of stages etc., or qualitatively in terms of equipment designed on an empirical basis that has been found by experience to give acceptable results. An example of the latter is the Pachuca tank for copper ore leaching.

The complete mechanism of a general leaching operation may be considered as:

1) Diffusion of active solute (e.g. HCl) through solvent (e.g. H_2O) bulk
2) Diffusion of solute through solvent boundary layer round particle
3) Diffusion of solute through solvent and pores of particle
4) Chemical reaction
5) Diffusion of product (e.g. $FeCl_3$) through solvent and pores of particle
6) Diffusion of product through solvent boundary layer
7) Diffusion of product into solvent bulk

The parameters that usually influence the efficiency of a leaching operation are:

Temperature
Time
Particle size
Acid concentration

Acid excess
Pressure
Pretreatment, e.g. roasting conditions

These have been collected from various sources and formed the basis of the experimental work.

3.1.1 Ore

Very little published work has been found on leaching iron ores. A little information was contained in papers describing both the R.C.A. and FLOX processes (1-1 and 1-2) but was inconclusive and not sufficient to form a basis for design studies. A considerable amount of work has been carried out into general leaching theory at the University of British Columbia (3-3, 3-4) with particular reference to metal extraction. Peters et al.(3-4) derived a mathematical model to predict the degree of extraction of uranium which agreed closely with practical results. Essentially the degree of extraction was found to be a function of particle size and time of reaction, and this is discussed more fully later. Carley-Macauley et al. (3-5) have carried out work on continuous dissolution of uranium dioxide pellets in a fixed bed and developed a simple theory for prediction of bed volume. Such a reactor system may prove interesting in subsequent design of a scrap iron leaching reactor (see Sections 3.1.2 and 3.3).

On a theoretical basis, the development of a satisfactory model to predict the behaviour of acid leaching an ore is extremely difficult. Although models may be developed on the basis of certain assumptions to derive rate equations for prediction of leaching rates (for example Levenspiel (3-6)), there are difficulties in relating the assumptions employed to the behaviour encountered in acid leaching of ores. Peters successfully overcame these difficulties for the system studied. In view of the likely problems to be encountered in a theoretical study, and the need to obtain data as a basis for design, it was decided to carry out some exploratory experimentation which is reported in Section 3.2 et seq. While an attempt was made to obtain a realistic model based on the experimental results, it was felt that an accurate model would quickly develop into complexities beyond the scope of this dissertation; although of considerable interest and use.

3.1.2 Metal

As with iron ore, very little published work has been found on dissolution of metallic iron. There is qualitative information on corrosion of iron (e.g. 3-13) and some data on rate of removal of scale from strip which is more concerned with dissolution of oxides. On the other hand it was considered likely that a suitable rate equation could be developed from experimental data by using conventional reaction kinetic theory as the system was relatively simple. Details of the experimental programme and results are given in Section 3.3 et seq.

3.2 Experimental work on iron ore leaching

A series of laboratory batch leaching tests were performed on a low grade iron ore from Northamptonshire, which was chosen as a result of the discussion in Section 2.2.

3.2.1 Iron Ore

Stewarts and Lloyds (Minerals) Ltd. supplied a large batch of Northants ironstone, which had the following analysis:

Fe_2O_3	56.5	% wt.
FeO	0.26	% wt.
Al_2O_3	6.3	% wt.
SiO_2	9.4	% wt.
CaO	3.5	% wt.
MgO	0.5	% wt.
H_2O	8.0	% wt.
S	0.06	% wt.
P_2O_5	1.39	% wt.
L.O.I	12.3	% wt.
	98.21	

Ore analysis is a very complex technique which requires considerable expertise to obtain even a reasonably accurate answer. This is partly on account of the complicated chemical structure in which the individual oxides are combined together, as high molecular weight hydrated aluminosilicates for example. Another reason is the widely differing analysis of different parts of an ore body, and even between adjacent lumps of ore. A fairly wide spread of results may be anticipated therefore.

For the experimental work the ore was stored in the laboratory (which tended to reduce the "H_2O" figure), and was crushed, ground and sieved to four particle size ranges for the initial experimentation:

- $\frac{1}{4}$ inch + 5 mesh (or -7 mm + 3 mm.)
- 5 + 25 mesh (or -3 mm + 700 micron)
- 25 + 75 mesh (or -700 micron + 200 micron)
- 75 mesh (or -200 micron)

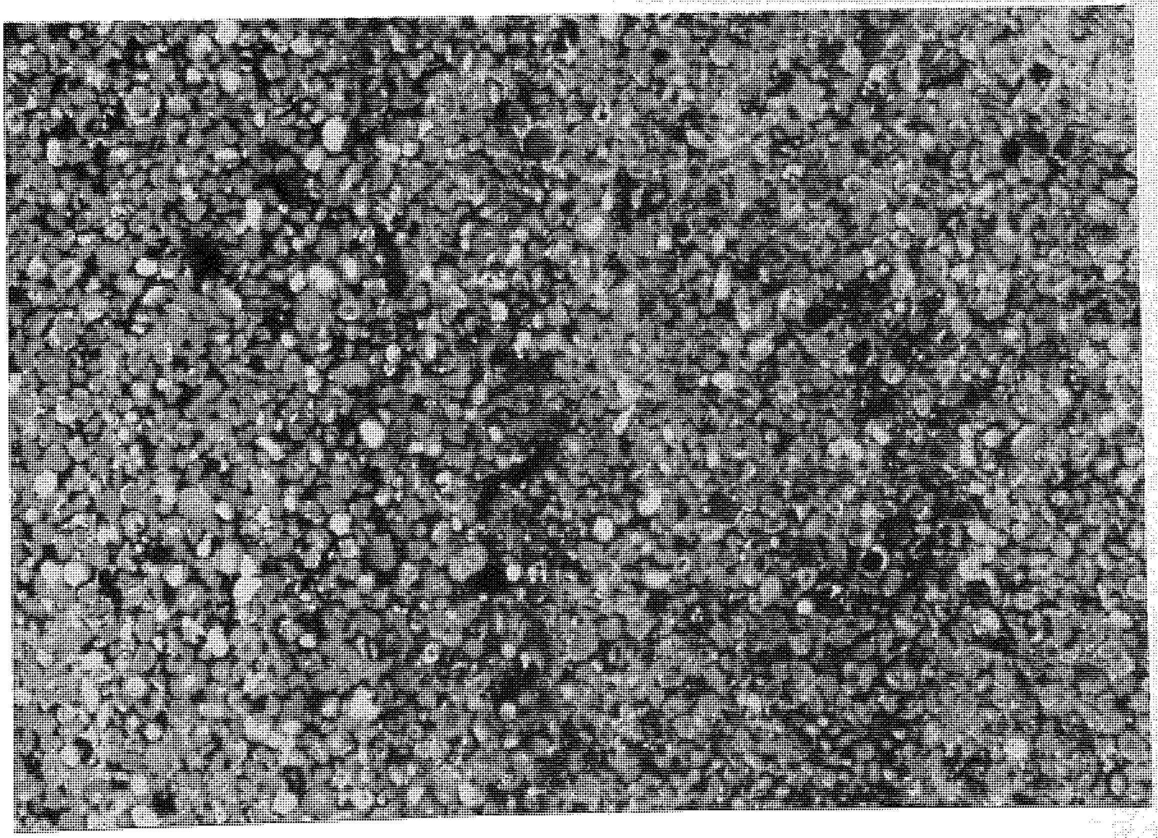
Prior to the leaching experiments, the free water content of the ore was determined to a constant weight at 110°C, and found to be 3.8% weight average. This figure appears reasonable as the natural figure of 8.0% weight would be expected to reduce in a laboratory. A corrected analysis then became:

Fe_2O_3	60.3	% wt.	) Fe 42.4% wt.
FeO	0.3	% wt.	)
Al_2O_3	6.7	% wt.	
SiO_2	10.0	% wt.	
CaO	3.7	% wt.	
MgO	0.5	% wt.	
H_2O	3.8	% wt.	
S	0.1	% wt.	
P_2O_5	1.5	% wt.	
L.O.I	13.1	% wt.	
	100.0		

The ore sample provided by Stewarts and Lloyds (Minerals) Ltd., was taken from a mine near Corby, Northamptonshire where the iron ore exists in a series of oolitic rocks to which the name Main (or Great) Oolitic Series is given. The structure is made up generally of 0.1 to 0.6 mm ooliths (oval "lumps") of chamosite (iron aluminosilicates) and limonite (hydrated ferric oxide) in a matrix of siderite (impure iron carbonate) with sometimes calcite and/or chamosite. (See 3-7, 3-8 and Section 2.2.1 also). By comparing analyses and other information given in (3-7) and (3-8) with the analysis of the ore received from Stewarts and Lloyds and used the experiments, it was concluded that the experimental ore consists of a weathered i.e. oxidised, oolitic ore with an original matrix of siderite and hematite which had been substantially oxidised to limonite. The ooliths consist mainly of carbonates

Iron Ore

as supplied



Thin section of Ore
Magnified x11 diam.
(transmitted light)
N.B.White parts are
perforations

Plate 3.1

and/or their oxidation products (chamosite/goethite) in a groundmass of limonite and hematite. See Plate 3.1 .

3.2.2 Experimental programme

A programme of experimental work was carried out to investigate the parameters listed in Section 3.1. These were studied within specified limits chosen by reference to other work (see Appendix 1 and Section 2) and practical limitations.

Temperature:	$90^\circ C$ to constant boiling maximum ($108^\circ C$). This was chosen to give maximum extraction and minimum residence time without requiring pressure.
Time:	Up to two hours or until complete extraction occurred.
Particle size:	As wide a range as possible conducive to handling problems.
Acid concentration:	Constant boiling point acid (20% wt.) was chosen to facilitate acid recycling, water removal and HCl gas recycling. A higher concentration was also used for comparison.
Acid excess:	The effect of excess acid over that required for stoichiometric dissolution of soluble constituents was investigated.
Pressure:	Pressure would be necessary for leaching at temperatures greater than azeotropic ($108^\circ C$). This was not investigated due to practical difficulties.
Pre-roasting conditions:	The effect of roasting the ore in air at various temperatures was investigated.

3.2.3 Methods

3.2.3.1 Experimental

The same basic method was employed for all the experiments. The apparatus is shown diagrammatically in Figure 3.1. The correct quantity of aqueous hydrochloric acid was brought to reaction temperature in the flask. 100 g. of ore of the required size fraction was added via a side arm. The resulting drop in temperature was compensated by the initial heat of reaction which resulted in temperature control to ± 2°C. After the required reaction time the experiment was stopped. Two methods were employed. The first was to turn off the heat, and filter the mixture under vacuum as quickly as possible, washing the residue with water. (Experiments1-36). Due to the resultant values of iron extracted (see discussion later) a different technique was employed for the remainder of the experiments. This second technique "froze" the reaction, by adding a large constant quantity of cold water via the condenser, which considerably diluted the acid and reduced the temperature. The reaction mixture was then filtered and washed with water as above. The residue was dried to constant weight at 110°C, and for some of the experiments the filtrate was titrated for ferric iron with iodine and thiosulphate. The titration was carried out on at least two samples of the filtrate to ensure reproduceability.

3.2.3.2 Mathematical

(a) Stoichiometric acid requirements.

The ore is made up of a complex mixture of oxide minerals as discussed in Section 2.2, and 3.2.5.8. The minerals may be assumed to behave as individual metal oxides

Apparatus for Ore Leaching Experiments

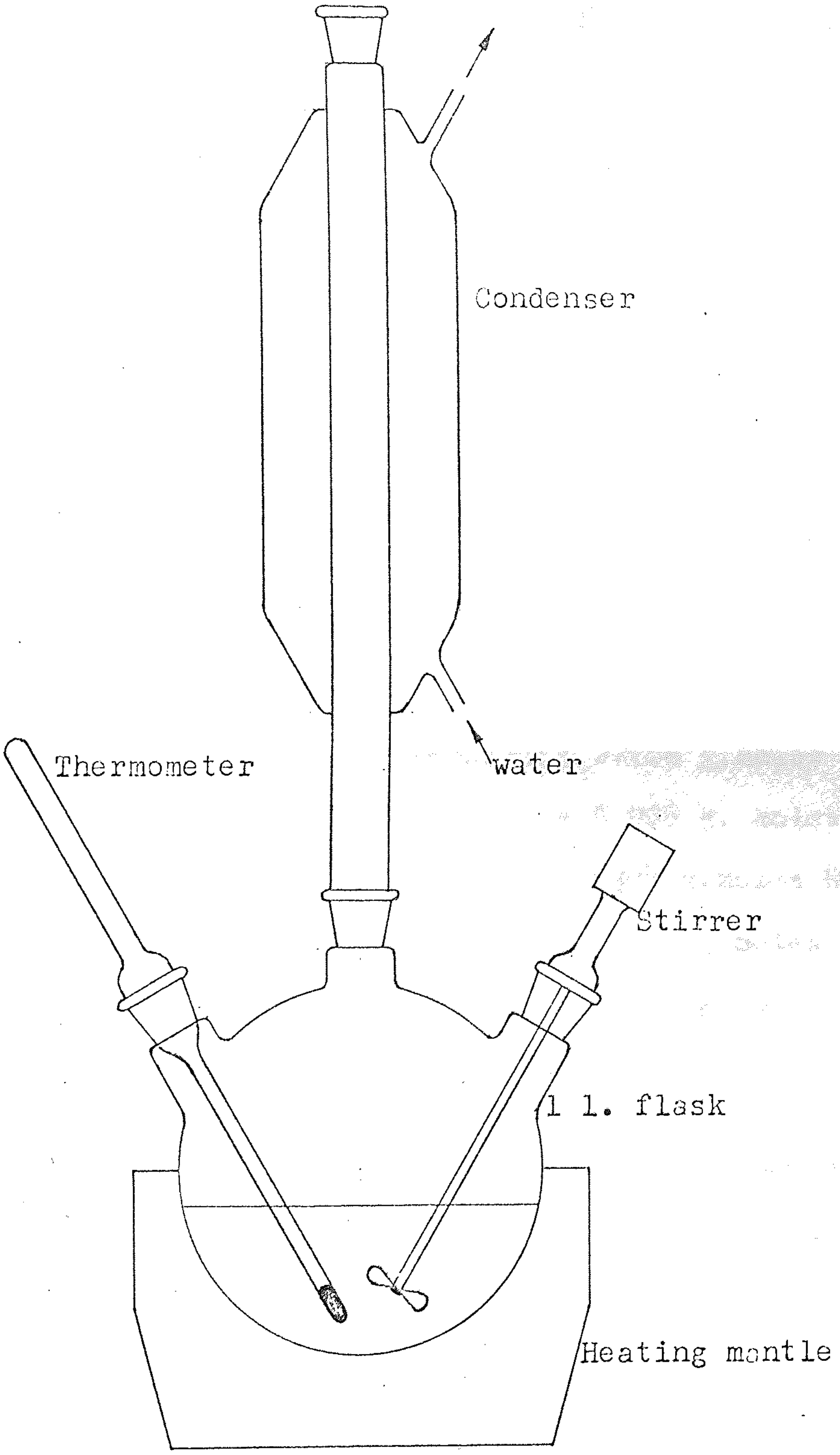


Figure 3.1

as far as stoichiometry is concerned and these react thus:

$$Fe_2O_3 + 6\ HCl \rightarrow 2\ FeCl_3 + 3H_2O$$

$$FeO + 2\ HCl \rightarrow FeCl_2 + H_2O$$

$$Al_2O_3 + 6\ HCl \rightarrow 2\ AlCl_3 + 3H_2O$$

$$CaO + 2\ HCl \rightarrow CaCl_2 + H_2O$$

$$MgO + 2\ HCl \rightarrow MgCl_2 + H_2O$$

Sulphur probably existed as sulphide which reacted to give H_2S. As the quantity involved was so small, it was neglected. P_2O_5 probably existed as complex phosphate (e.g. collophane) which may be assumed not to react.

Each mole of Fe_2O_3 and Al_2O_3 reacted with 6 moles of HCl and each mole of FeO, CaO and MgO reacted with 2 moles of HCl.

In 100 g. ore there were:

60.3 g.Fe_2O_3= 0.3776 g.moles requiring 2.266 g.moles HCl

0.3 g.FeO = 0.0042 g.moles requiring 0.008 g. moles HCl

6.7 g.Al_2O_3= 0.0657 g.moles requiring 0.394 g.moles HCl

3.7 g.CaO = 0.0660 g.moles requiring 0.132 g.moles HCl

0.5 g.MgO = 0.0124 g.moles requiring 0.025 g.moles HCl

Total 2.825

2.825 g. moles HCl were required for complete dissolution of the soluble portion of 100 g. ore = 103.0 g. HCl. Constant boiling point acid was 20.2% wt. HCl which had a density of 1.0980 gm/ml at 20°C (App.II). The stoichiometric 20.2% wt. aqueous HCl requirement for 100g. ore was therefore 509.9 g. or 464.4 mls. For 30% wt. HCl, density 1.1493 gm/ml at 20°C (App.II) this was 343.3 g or 298.7 mls. Acid strength was checked by standard acid/alkali titration prior to experimentation.

(b) Post-reaction analysis.

For the purpose of calculating extraction efficiency, it was assumed that the proportion of each soluble constituent of the ore was extracted to the same extent. Verification of this assumption was sought by titration for ferric iron.

The first method of mass-balance analysis employed the following technique:

Of the initial ore, 10.0% wt. may be considered insoluble (SiO_2)

3.8% wt. was "free" water

13.1% wt. was "combined" water

73.1% wt. may be considered soluble

The associated "free" and "combined" water may be assumed to be uniformly distributed throughout the ore. After leaching the residue was washed and dried at 110°C, and would have the following composition:

10.0% wt. of initial ore as SiO_2

13.1% wt. of unreacted ore as "combined" H_2O

Remainder of residue would be unreacted soluble ore.

Example:

100.0 ore were leached and 40.0 g remained after drying.

This 40 g was made up:

10.0% wt. of initial ore as SiO_2 = 10.0 g.

13.1% wt. of unreacted ore as combined H_2O = 5.24 g.

Remainder, = unreacted solubles = 40.0 -(10.0 + 5.24)g

= 24.76 g.

Of the initial ore, 73.1% wt., or 73.1 g, were soluble constituents, and the extraction efficiency therefore was

$$\frac{73.1 - 24.76}{73.1} \times 100\%$$

$$= 66.1\%.$$

The second method of analysis was titration of ferric chloride in the filtrate after leaching, filtering and washing. A number of methods were described in the literature, involving either reduction of ferric ions to ferrous, or oxidation of ferrous to ferric. Since over 99.5% wt. of the iron was in the ferric state to start with, a reduction method was chosen, which was also thought less susceptible to side-reactions with the chemicals employed. Iodide ions were used as the reducing agent, titrating with thiosulphate with starch as indicator. The mechanism was:

$$2\,Fe^{+++} + 3I^{-} \rightarrow 2\,Fe^{++} + I_3^{-}$$

$$I_3^{-} + 2S_2O_3^{--} \rightarrow 3I^{-} + S_4O_6^{--}$$

A measured volume of filtrate was titrated against molar (IN) thiosulphate solution, scaled up to the full volume of filtrate, and hence total quantity of ferric ions in the solution was found. The percentage dissolution of iron was then calculated.

3.2.4 Results

The results from the experiments are presented in tabular form below (Table 3.1). All experiments started with 100.0 g. ore and followed the method described in Section 3.2.3.

Table 3.1

Iron Ore Leaching - Experimental Results

100 g ore were reacted in each experiment

Exp. No.	Time Mins	Temp. °C	Weight after (1)	Extn. % (2)	Titn. mls. (3)	Fe^{+++} gms. (4)	Extn. % (5)
Stoichiometric acid, 20% wt., particle size 200-700 micron							
1	5	91	53.2	50.4	246.5	13.8	32.5
2	15	91	40.7	65.3	302.4	16.9	39.8
3	30	91	38.2	68.3	322.2	18.0	42.4
4	45	91	36.6	70.2	331.5	18.5	43.6
5	60	91	35.8	71.1	333.7	18.6	43.6
6	75	91	35.4	71.8	343.4	19.2	45.3
7	5	98	49.1	55.3			
8	15	98	38.2	68.3			
9	30	98	34.9	72.2			
10	45	98	33.1	74.3			
11	60	98	32.0	75.6			
12	75	98	31.4	76.4			
13	5	104	46.1	58.9			
14	15	104	36.2	70.6			
15	30	104	31.5	76.2			
16	45	104	29.0	79.2			
17	60	104	28.5	80.4			
18	75	104	28.0	80.4			
10% excess acid, 20% wt., particle size 200-700 micron							
19	5	91	50.3	53.9			
20	15	91	38.2	68.3			
21	30	91	36.0	70.9			
22	45	91	34.6	72.5			
23	60	91	33.9	73.4			
24	75	91	33.6	73.7			
20% excess acid, 20% wt., particle size 200-700 micron							
25	5	91	47.9	56.7			
26	15	91	36.0	70.9			
27	30	91	33.8	73.5			
28	45	91	32.6	74.9			
29	60	91	32.2	75.4			
30	75	91	31.8	75.9			
30% excess acid, 20% wt., particle size 200-700 micron							
31	5	91	46.0	59.0			
32	15	91	34.0	73.3			
33	30	91	32.0	75.6			
34	45	91	31.4	76.4			
35	60	91	31.0	76.8			
36	75	91	30.5	77.4			

Table 3.1 continued

Exp. No.	Time Mins	Temp. °C	Weight after (1)	Extn. % (2)	Titn. mls (3)	Fe^{+++} gms. (4)	Extn. % (5)
20% excess acid, 20% wt., particle size 200-700 micron							
37	10	95	37.5	69.1	496.0	27.7	65.3
38	20	95	29.9	78.1	593.6	33.2	78.3
39	30	95	26.7	81.9	632.5	35.3	83.2
40	40	95	21.7	87.9	660.8	36.9	87.0
20% excess acid, 20% wt., particle size 700-3000 micron							
41	5	95	69.4	31.2	232.2	13.0	30.7
42	10	95	49.3	55.1	404.2	22.6	53.3
43	15	95	49.9	54.4	455.0	25.4	59.9
44	20	95	46.2	58.8	437.5	24.4	57.5
45	30	95	43.7	61.7	494.5	27.6	65.1
46	45	95	34.9	72.2	535.5	29.9	70.5
20% excess acid, 20% wt., particle size 3-7 mm							
47	5	95	73.0	26.9	196.9	11.0	25.9
48	10	95	61.4	40.7	339.0	18.9	44.6
49	15	95	57.4	45.4	362.1	20.2	47.6
50	20	95	55.9	47.2	374.0	20.9	49.3
51	30	95	44.3	61.0	496.3	27.7	65.3
52	45	95	36.6	70.2	580.8	32.4	76.4
20% excess acid, 30% wt., particle size 200-700 micron							
53	5	95	25.1	83.8	687.7	38.4	90.5
54	10	95	32.1	75.5	660.6	36.9	87.0
55	15	95	27.6	80.9	673.2	37.6	88.7
56	20	95	22.2	87.3	735.4	41.1	96.9
57	30	95	20.4	89.4	664.2	37.1	87.5
58	45	95	31.3	76.5	645.9	36.1	85.1
20% excess acid, 30% wt., particle size 700-3000 micron							
59	5	95	51.3	52.7	397.9	22.2	52.3
60	10	95	47.6	57.1	441.5	24.7	58.2
61	15	95	38.2	68.3	520.4	29.1	68.6
62	20	95	34.5	72.7	559.7	31.3	73.8
63	30	95	30.9	76.9	578.7	32.3	76.2
64	45	95	31.2	76.6	624.5	34.9	82.3
20% excess acid, 30% wt., particle size 3-7mm							
65	5	95	61.4	40.7	338.6	18.9	44.6
66	10	95	51.3	52.7	449.4	25.1	59.2
67	20	95	47.4	57.3	451.4	25.2	59.4
68	30	95	42.5	63.2	491.8	27.5	64.8
69	45	95	33.0	74.5	580.8	32.4	76.4

Notes
(1) Weight of dried filter cake after leaching
(2) Extraction, wt. %, based on mass balance
(3) Scaled-up titration of filtrate, mls 1N thiosulphate
(4) Fe+++ content of filtrate, gms
(5) Extraction, wt. %, based on titration

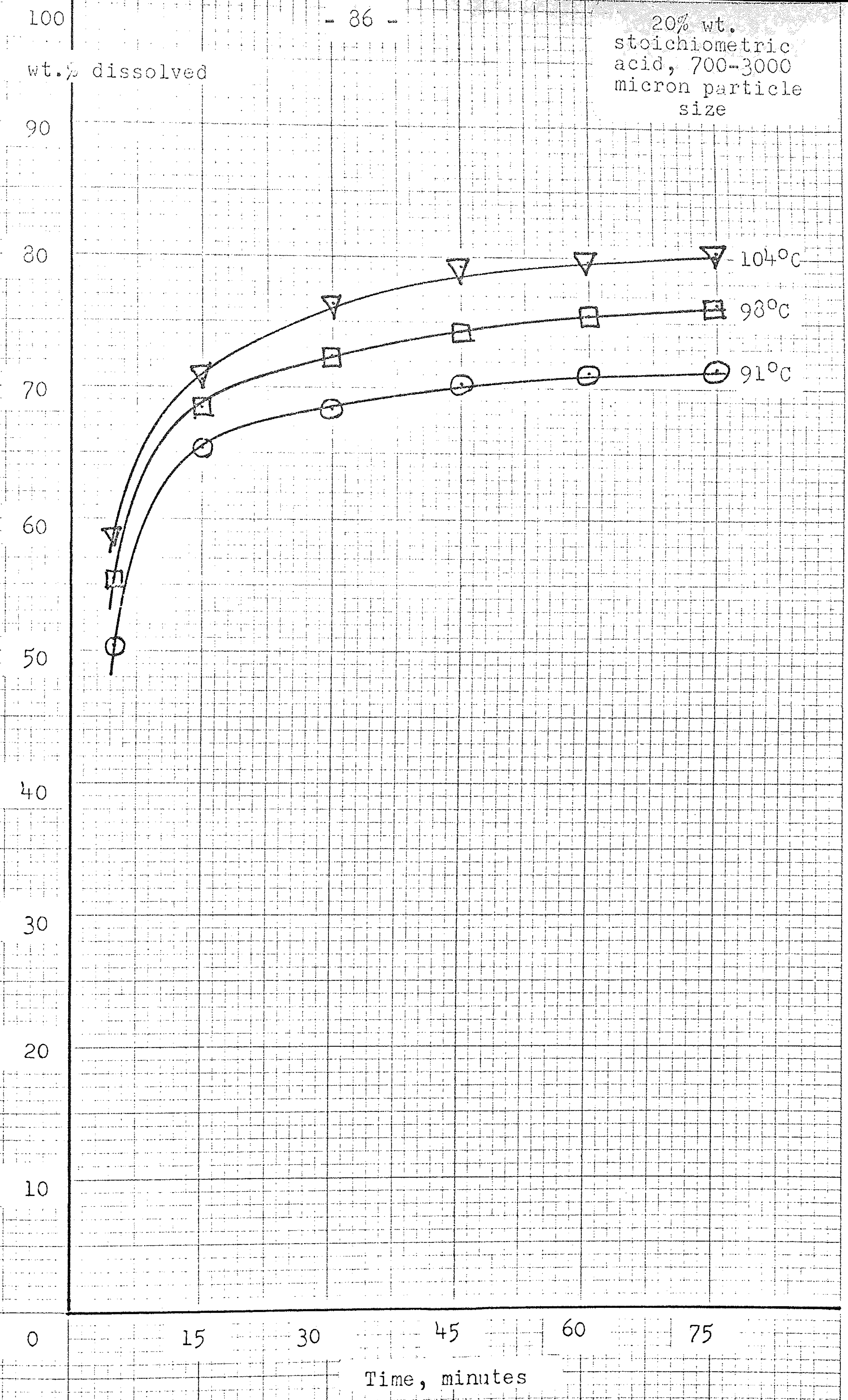

100
wt.% dissolved
90
80
70
60
50
40
30
20
10
0
15
30
45
60
75
Time, minutes
20% wt. stoichiometric acid, 700-3000 micron particle size
104°C
98°C
91°C

Figure 3.2

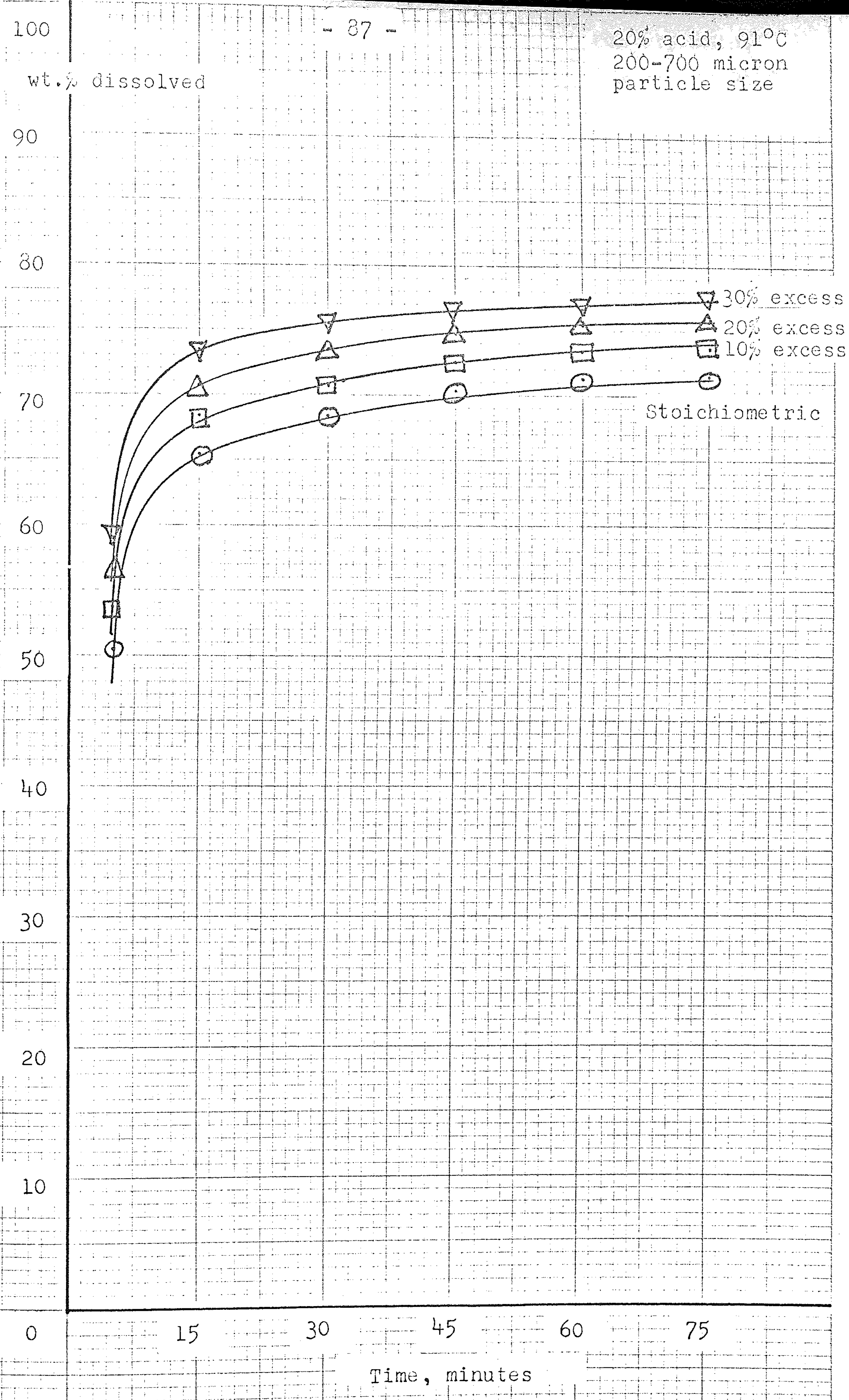

100
wt.% dissolved
90
80
70
60
50
40
30
20
10
0
15
30
45
60
75
Time, minutes
20% acid, 91°C
200-700 micron
particle size
30% excess
20% excess
10% excess
Stoichiometric

Figure 3.3

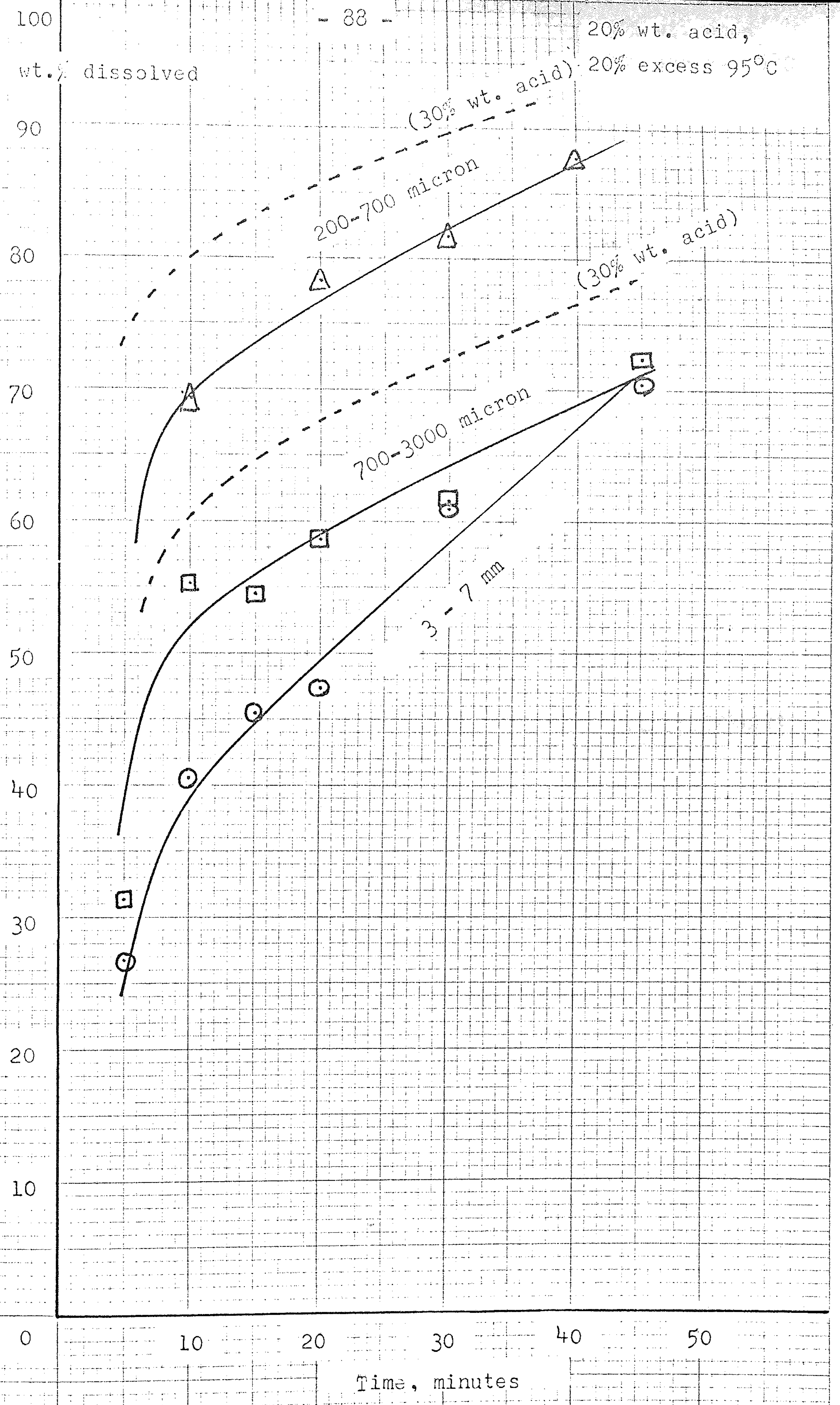

100
wt.% dissolved
90
80
70
60
50
40
30
20
10
0
20% wt. acid,
20% excess 95°C
(30% wt. acid)
200-700 micron
(30% wt. acid)
700-3000 micron
3 - 7 mm
10
20
30
40
50
Time, minutes

Figure 3.4

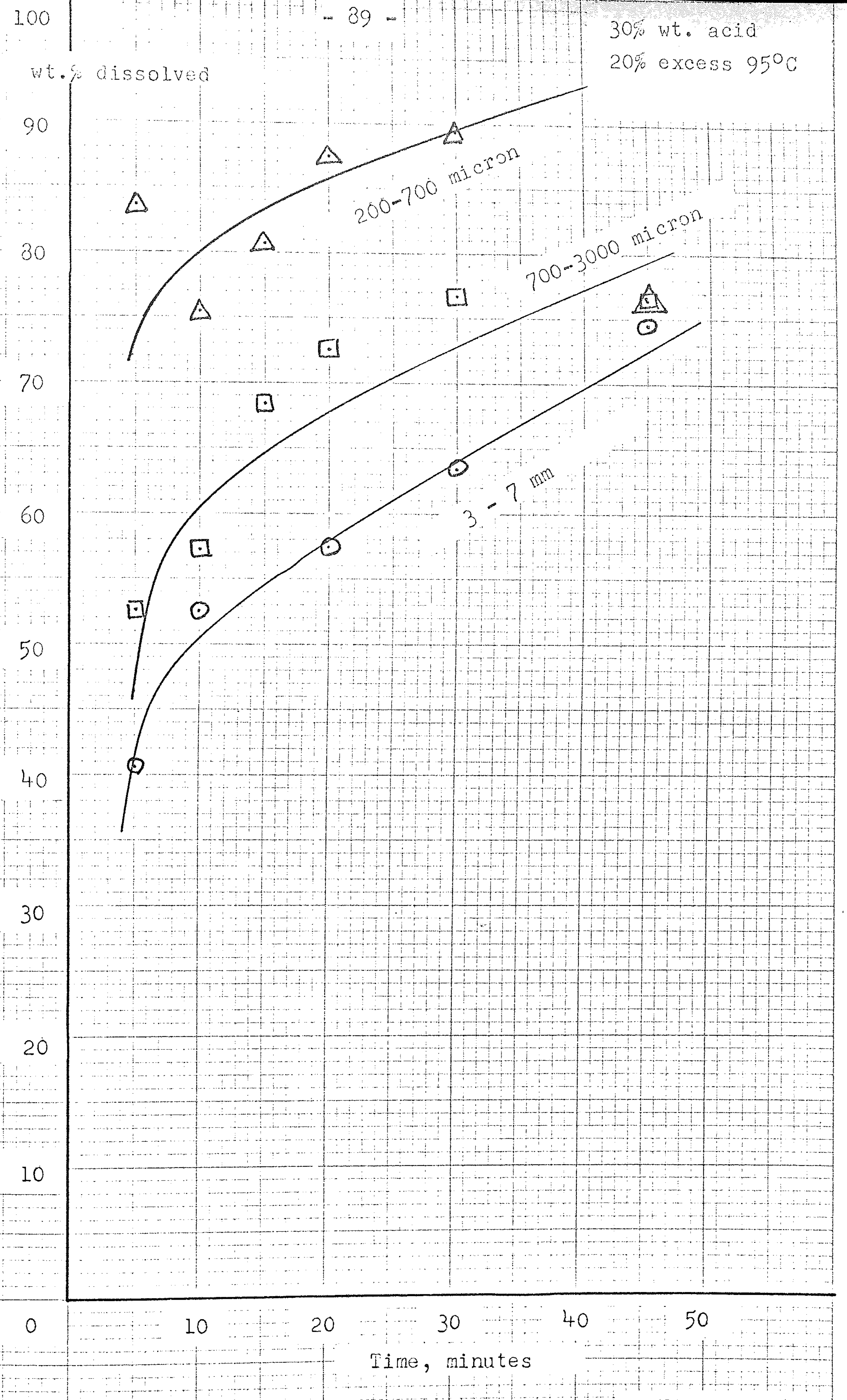

30% wt. acid
20% excess 95°C
wt.% dissolved
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
Time, minutes
200-700 micron
700-3000 micron
3 - 7 mm

Figure 3.5

3.2.5 Discussion of results

3.2.5.1 Experiments 1-36

The first group of 36 experiments investigated the effects of temperature and excess acid on extraction efficiency; and the results are represented graphically in Figures 3.2 and 3.3. (taken from Table 3.1). The results showed a considerable discrepancy between extraction as measured by mass balance, and by titration for ferric iron. The maximum extraction from the graphs appeared to be 75-80% instead of the expected 100%. Since in subsequent experiments (see following section), close agreement was found between both methods of analysis as well as an asymptotic approach to 100% extraction, an explanation was necessary.

The only difference between this set of experiments and the later ones lay in the technique of stopping the reaction which was discussed in Section 3.2.3.1. Since the extraction yield by titration of filtrate for experiments 1 to 6 was considerably below the extraction yield by mass balance, and both techniques were considered to give reliable results under normal circumstances, then some iron was apparently retained by the filter cake. A possible mechanism to explain this was adsorption of ferric chloride or a chlorinated ferric chloride complex onto the ore particles. In ref. 1-1, reference was made to physical adsorption of ferric chloride on silica gel, and on naturally occurring alumino-silicates. One of the standard text books on ore analysis (3-9) warns of the difficulties of adsorption of many elements on silica hydrogel during analysis for silicon, and these cannot be removed by prolonged washing. Gravenor et al. (1-5) also discussed the question of silica or aluminosilica dissolution, concluding that if care was not taken to prevent this considerable loss of chlorides as iron or acid would result; but the mechanism by which this was supposed to occur was not made clear. References have been found to complex ion formation $FeCl_4^-$ (3-10 a and b), which occurs in strong acid solution only; and while this may occur under the conditions of experimentation, was not thought to contribute significantly to the adsorption. The mechanism was therefore considered to be pure physical adsorption either on the unreacted ore particles and/or on a silica hydrogel caused by strong acid attack. Practically, the difficulty may be overcome by washing the residue with hot concentrated HCl followed by water. This might effectively be carried out by employing a two stage leaching operation.

3.2.5.2 Experiments 37 onwards

Subsequent experiments showed the expected approach to 100% extraction; and also gave very close agreement between yield by mass balance and yield by titration. This was considered to be due to no adsorption taking place as a result of stopping the reaction by adding cold water but the mechanism is not understood. Averaging the results made the yield by titration 2.5% above the yield by mass balance, or 1.5% if experiments 53-58 are discounted. From this it might be concluded that the iron tended to dissolve to a slightly greater extent than the other soluble constituents. As the difference of 2.5% was the same for initial extraction yields as final overall values, each ore constituent apparently dissolved at the same rate.

3.2.5.3 Other experiments

A number of experiments were carried on large ore particles of 25-50 mm., suspending them in hot 20% wt. hydrochloric acid without agitation. A very rapid initial reaction occurred with evolution of gas thought to be carbon dioxide from carbonate breakdown. This quickly subsided and was followed by very slow disintegration of the particle's surface layers, with clear indications by visual refraction changes, of concentration gradients at the surface. This slow reaction continued for up to an hour appearing to gradually get slower and the ore surface became much lighter in appearance. Subsequent examination of the washed and dried sample showed a well defined "skin", 1-3 mm. thick of "sticky" reacted siliceous material which readily broke away. This apparently hindered reaction. The siliceous material had a grain size of around 250-500 microns. Visual examination of the ore indicated also a grain size of around 200-600 microns.

3.2.5.4 Temperature effect

The effect of temperature was investigated in experiments 1 to 18, the results of which are depicted graphically in Figure 3.2. While the actual results from these experiments were thought to be misleading for reasons discussed in the previous section 3.2.5.1, it was considered likely that the results gave an approximate indication of the effect of temperature, which appeared to be minimal on the initially high rate of reaction and thereafter did not appear to affect the rate of extraction significantly. It is clear however that as the temperature was increased, the rate and degree of extraction increased also. The optimisation of time (i.e. reactor volume effectively) and temperature is considered later. It may also be concluded that chemical reaction was not the rate limiting step, as otherwise the temperature effect would be much more pronounced (see later section on kinetics). It is thought unlikely that temperatures in excess of around 100°C would justify the extra cost of heat and pressure equipment, although further experimentation is needed to justify this.

3.2.5.5 Excess acid effect

The affect of different percentages of excess acid over stoichiometric requirements was investigated in experiments 19 to 36 and results are shown in Figure 3.3. Again the experimental difficulties discussed earlier made the actual results erroneous, but the effect of acid excess on rate and degree of extraction appeared to be relatively marginal and not as great as the effect of temperature. The quantity of acid present for dissolution therefore can be controlled to give the particular pH of leach liquor necessary for subsequent treatment.

3.2.5.6 Particle size fffect

Initially three ranges of particle size were employed: 7000-3000 micron (+5 mesh), 3000-700 micron (-5 + 25 mesh) and 700-200 micron (-25 + 75 mesh). The effect of these three size ranges is shown in Figure 3.4 for 20% wt. acid (experiments 37 to 52) and in Figure 3.5 for 30% wt. acid (experiments 53 to 69).

The graphs show that the rate of reaction is inversely proportional to particle size and that the increase in extraction is much more marked for the smallest size range than for the other two ranges. An increased extraction for smaller particle sizes would be expected due to their greater surface area. It was observed that the larger particles quickly broke down under the agitation employed in the experiments into a "sand" like material, and this is shown in Figure 3.4 when the lines converge for the two largest size ranges, which was taken to indicate that the ultimate natural grain size may be nearer the 200-700 micron particle size range. In spite of the dubious results of the first 36 experinents (see above), particle size had a more profound effect on rate and degree of extraction than either temperature, acid excess and to a lesser extent acid concentration. This is interesting as it agrees with Peters et al. (see section 3.1 and 3.2.5.8) work on deriving a mathematical model for uranium ore extraction.

3.2.5.7 Acid concentration effect

The series of experiments investigating the effect of particle size was carried out for two acid concentrations, 20% wt. and 30% wt. which are compared in Figure 3.4. The higher concentration acid improved extraction by 5-20%, with maximum improvement occurring during initial reaction, and for the middle size range (700-3000 micron), and therefore indicated a driving force effect which is shown later to be probably diffusional. It may not however be advantageous to employ the higher 30% wt. acid as recycling this concentration may prove more difficult than constant boiling point acid when either acid or water may be distilled to preserve balances.

3.2.5.8 Kinetics

It is clear from all the experimental results that initially the rate of reaction is very fast indeed; a substantial part of the overall extraction being completed in under 7-8 minutes. This figure appears to be the same for all experiments using 20% wt. acid regardless of other conditions. For 30% wt. acid this time for the initial very fast reaction falls to around 4 minutes. This effect is best demonstrated by plotting the extraction efficiency vs. time graphs as two straight lines (Figure 3.6); an acceptable fit is obtained with the majority of the data. This might be taken as evidence of a zero or pseudo zero order reaction either in series or in parallel.

Conventional reaction analysis was performed in a similar way to that carried out for metallic iron dissolution (section 3.3.4) in an attempt to find a rate equation. This was not successful. It was however possible to show that ash layer diffusion was probably the rate controlling step, by plotting a graph of fraction of iron unconverted (1-X) versus fraction of total time required (t/T). Different shaped curves are obtained for different rate controlling steps for which Levenspiel (3-6) has derived equations and plotted graphs. These are shown below for chemical reaction controlling (C), film diffusion controlling (FD), and ash layer diffusion controlling (AD). This technique is also discussed in section 3.3.4.

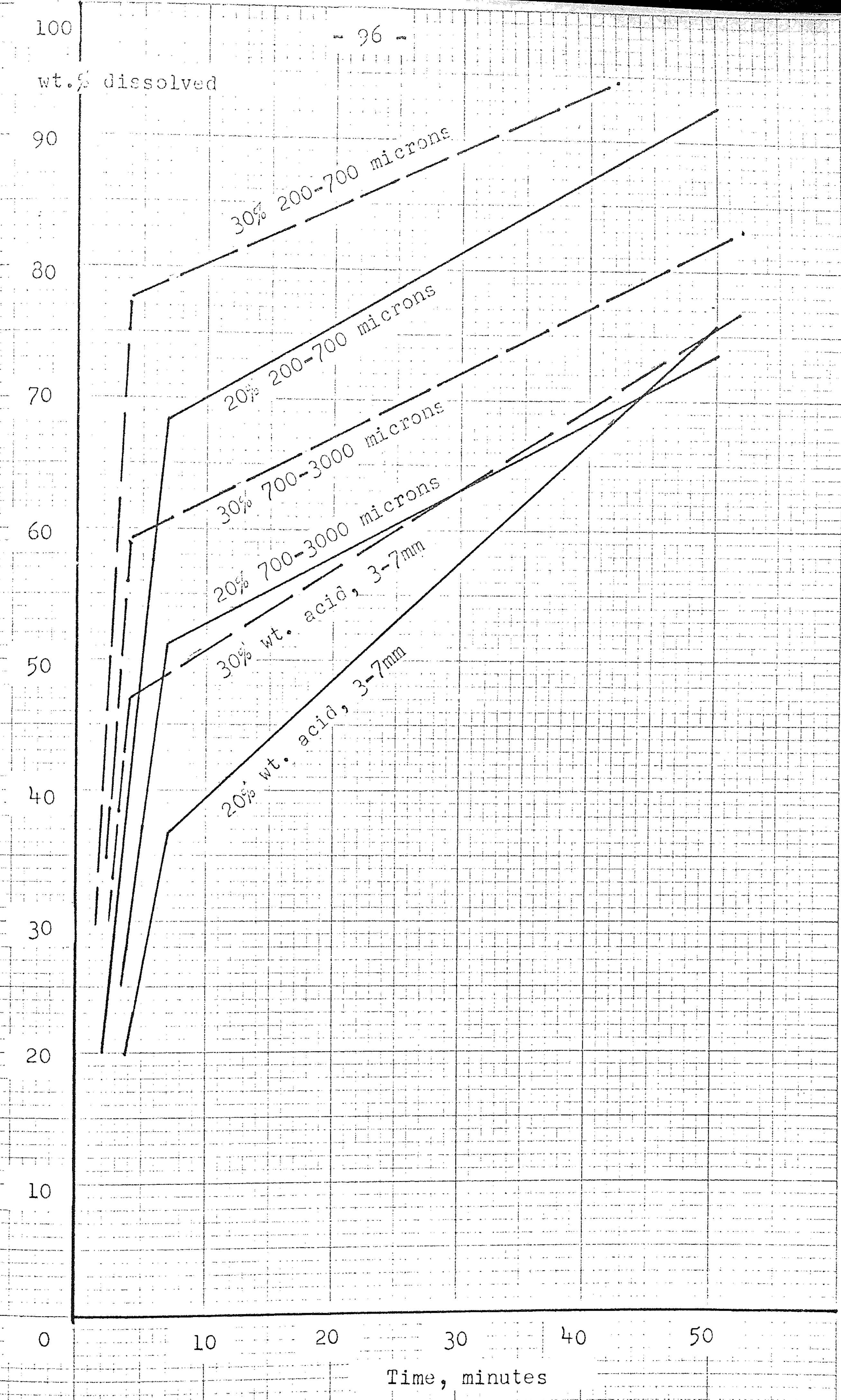
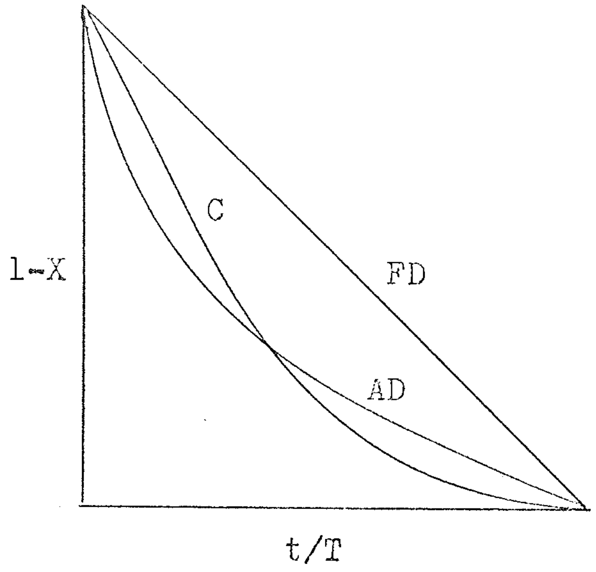

wt.% dissolved
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
Time, minutes
30% 200-700 microns
20% 200-700 microns
30% 700-3000 microns
20% 700-3000 microns
30% wt. acid, 3-7mm
20% wt. acid, 3-7mm

Figure 2.6



The results from experiments using 20% wt. acid for three different size ranges were treated in this way, Table 3.2, to give Figure 3.7A. The shape of the graph appeared to be shaped like the curve for ash diffusion controlled, which was emphasised and thereby confirmed by superimposing a"mirror image" about the 45^o line through the origin in the sector containing the data - Figure 3.7B. The conclusion that the reaction is ash layer diffusion controlled is supported by the temperature and excess acid effects, and by observations on the behaviour of a large lump or ore, all of which is reported above.

It is very likely that the reaction mechanism is a combination of series and parallel reactions which cannot be formulated. However the following set of equations should give an idea of the possible complexity:

$Fe_2O_3 . H_2O + 6 HCl \rightarrow 2FeCl_3 + 4H_2O$
Goethite (3-8)

$Al_2O_3 . 2SiO_2 . 2H_2O + 6HCl \rightarrow 2AlCl_3 + 2SiO_2 + 5H_2O$
Kaolinite (3-8)

$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
Carbonate (3-8)

Table 3.2

20% wt. acid, 20% excess, 95°C

Exp. No.	X (1)	1-X (2)	t (3)	T (4)	t/T	Particle size
37	0.69	0.31	10	70	0.143	200-700 microns
38	0.78	0.22	20	70	0.286	
39	0.82	0.18	30	70	0.429	
40	0.88	0.12	40	70	0.571	
41	0.31	0.69	5	105	0.048	700-3000 microns
42	0.55	0.45	10	105	0.095	
43	0.54	0.46	15	105	0.144	
44	0.59	0.41	20	105	0.192	
45	0.62	0.38	30	105	0.288	
46	0.72	0.28	45	105	0.432	
47	0.27	0.73	5	85	0.059	3-7 mm
48	0.41	0.59	10	85	0.118	
49	0.45	0.55	15	85	0.177	
50	0.47	0.53	20	85	0.236	
51	0.61	0.39	30	85	0.353	
52	0.70	0.30	45	85	0.530	

Notes:(1) X = fraction reacted

(2) fraction unreacted

(3) time

(4) total time by extrapolation

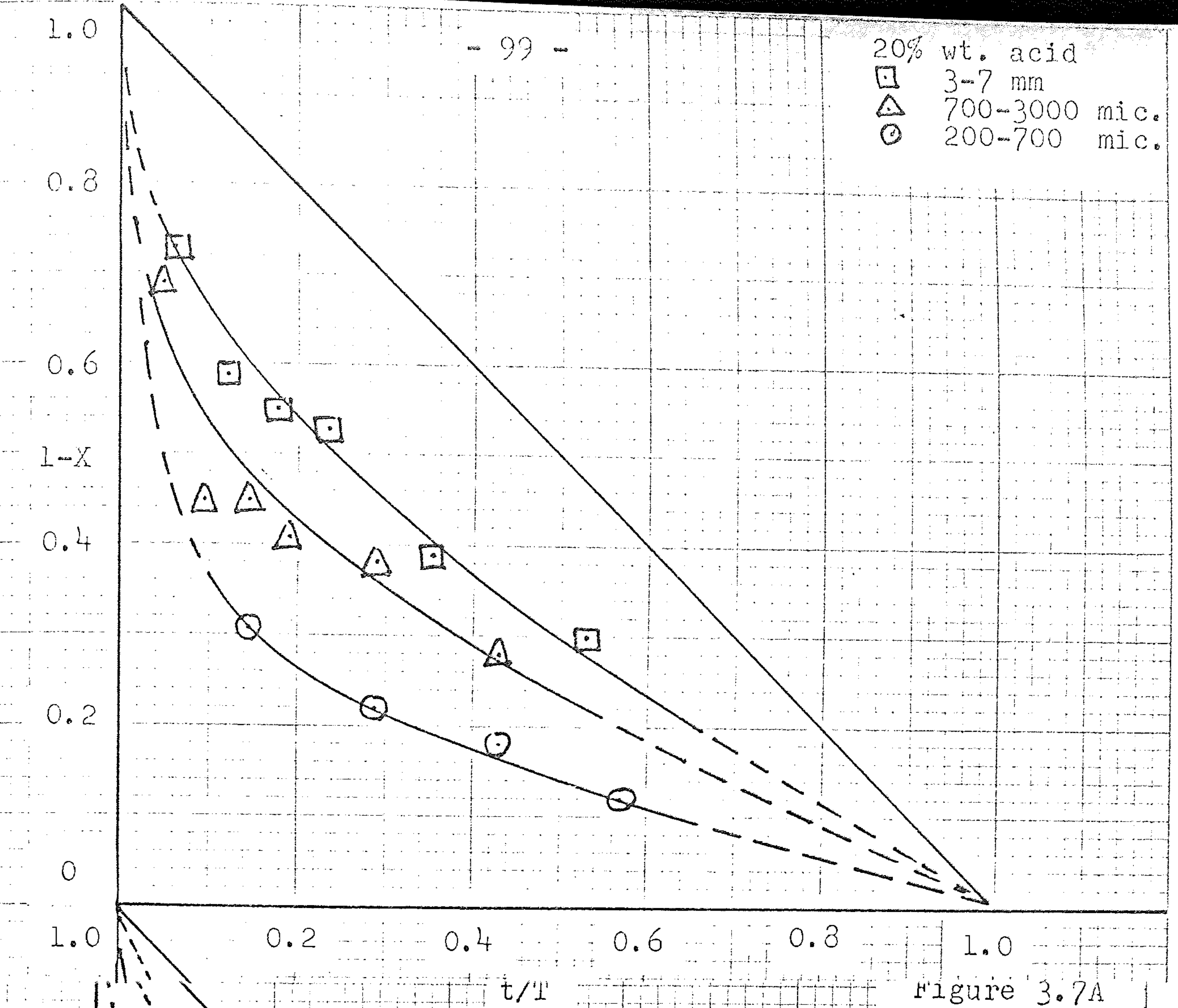


Figure 3.7A

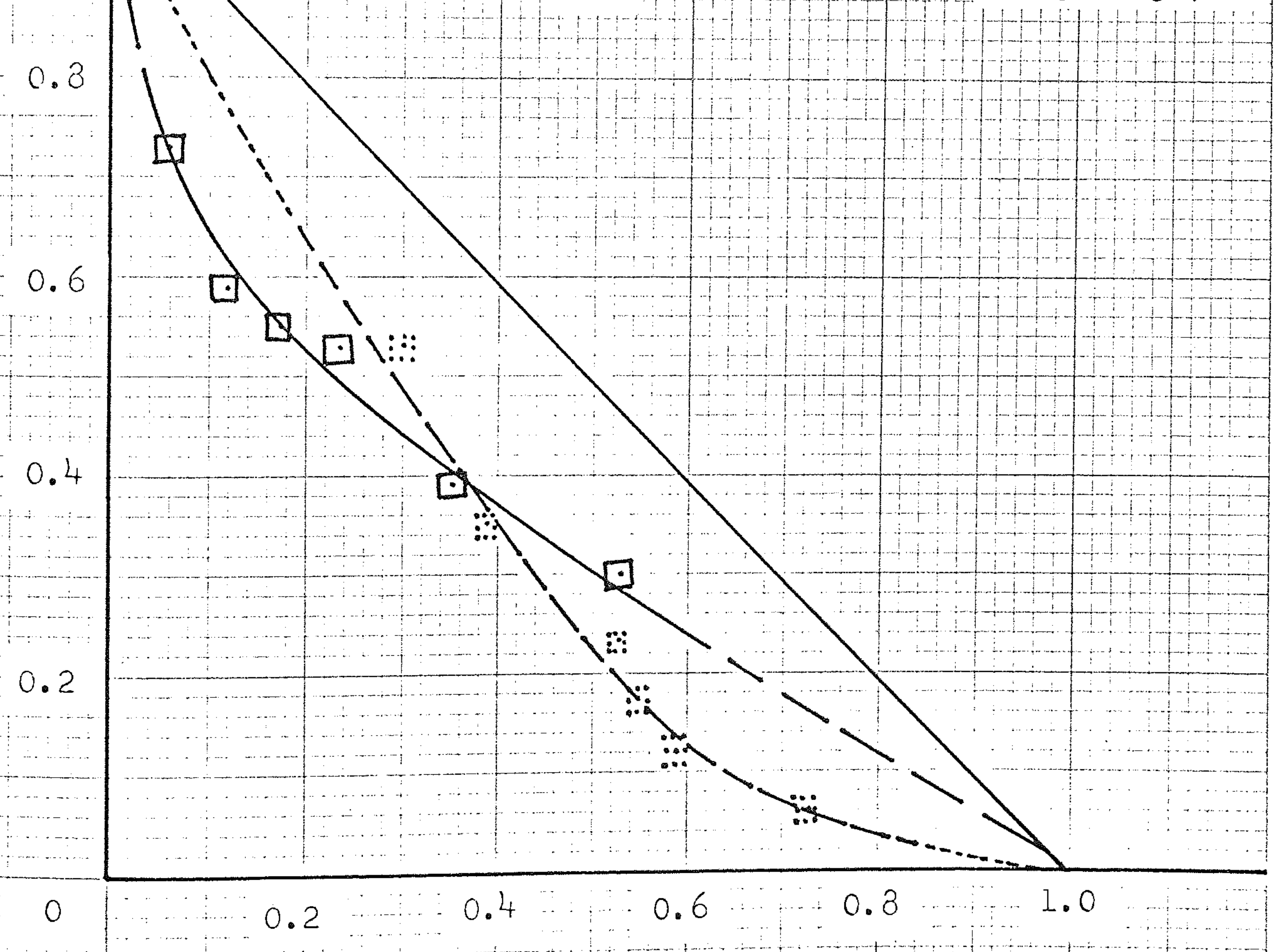


Figure 3.7B

$$\underset{\text{Collophane (3-8)}}{Ca_3(PO_4)_2} + 6HCl \rightarrow 3CaCl_2 + 2H_3PO_4 \text{ (?)}$$

$$\underset{\text{typical Chamosite (3-8)}}{(Al_2O_3.Fe_2O_3).(FeO.MgO)_2.(SiO_2)_2.2H_2O} + 20HCl$$

$$\rightarrow 2FeCl_3 + 2FeCl_2 + 2AlCl_3$$

$$+ 2MgCl_2 + 2SiO_2 + 12H_2O$$

These are a few of the typical minerals likely to be found in the type of ore employed in the experimentation. The mechanism of each reaction is likely to include both series and parallel reactions, particularly for chamositic minerals and similar.

Modelling difficulties such as these have led to different approaches: Peters et al. (3-4) considered the rate limiting step as diffusional and derived an equation for fraction unleached, I:

$$I = \left(1 - \frac{2DCi}{\gamma R_o} . t\right)^{\frac{3}{2}}$$

where D = diffusivity

Ci = concentration at liquid-solid interface

γ = specific gravity

R_o = initial particle radius

t = time

based on the assumptions that the particles were very small and of negligible volume, and the surroundings behaved as a rigid non-moving medium. This equation gave good agreement with experimental results obtained from leaching uranium. The form of the leaching curve so obtained was similar to those obtained in the experimental work reported here. In spite of this similarity however, his equation had a number of drawbacks in the nature of the ore used in the experiments being substantially different, and in the assumptions made in deriving the equation theoretically. The equivalent equation for the classical boundary layer theory was:

$$I = \left(1 - \frac{DCi}{\gamma . Ro . h} \right)^{3}$$

where h = film thickness

Peter's claimed that his equation gave a better correlation than the boundary layer model, but no other comparisons with alternatives were made, and he specifically disclaimed his model as the only one valid.

The development of a new theory and model to account for the limited experimental results on iron ore leaching reported herein is considered to at least constitute a PhD.topic in its own right and it is not possible therefore to be included here. An equation has however been derived empirically from the results obtained from the later experiments when adsorption of ferric chloride did not occur (experiments 1-36, see Section 3.2.5.1):

$$X = 0.005\ t + 6.9 . H^{0.5} . \left(\frac{1}{\log r} \right)^{1.6}$$

where X = fraction of iron leached

t = time of reaction, minutes

H = fractional acid concentration by weight

r = mean particle size, microns.

This was obtained by considering the extraction curves as two straight lines, as discussed at the beginning of this section; ignoring the initial very fast reaction; and deriving an equation for the subsequent reaction line based on y = mx + c where c is the "constant" and is considered a function of reaction parameters. As the initial fast reaction is ignored, the equation is only applicable for $t > 8$, and at 95°C and employing 20% excess acid as the results were obtained under these conditions. Incorporation of temperature and excess acid effects from the earlier experiments (numbers 1-36) gives:

$$X = 0.005\, t + 7.0 .\, H^{0.5} .\, \left(\frac{1}{(\log r)}\right)^{1.6} .\, (E)^{0.2} .\, \left(\frac{T}{(100)}\right) . \quad \text{(Eqn. 3.1)}$$

where E = measure of acid excess; for 10% excess

$E = 1.1$; 20%, $E = 1.2$ etc.

T = temperature, °C.

It is unlikely that the accuracy is better than ± 5%, which is probably sufficient for initial design purposes. There is however much scope for improvement. It is worth noting that for every 10 minute increase in time of reaction, the extraction increases by 5%.

3.2.5.9 Pretreatment

A number of experiments were carried out into the effect of roasting the ore before leaching. Ore was roasted at 200, 400, 600 and 800°C for 1, 2 and 4 hours, allowed to cool, then leached under the same conditions as the other experiments (numbers 37 on). The results are given in Table 3.3 and plotted graphically in Figures 3.8 and 3.9. The calculation of percentage extraction was based on the mass balance method described in Section 3.2.3.2 B, but with allowance made for the reduced "loss on ignition" value when using roasted ores.

It can be seen from Figures 3.8 and 3.9 percentage extraction appears to increase slightly with roasting temperatures, but the time roasting does not have any effect. The validity of these results is considered doubtful due mainly to the possible different effects on the different

Table 3.3

Effect of Roasting Ore Prior to Leaching

Conditions: 20% wt. acid, 20% excess acid, 95°C,
200-700 microns particle size.

Exp.	Roasting			Leaching				Extn.
No.	Temp. °C	Time hrs.	Wt. loss %	Time mins	Wt. bef. g	Wt. aft. g	Wt. loss g	wt. %
70	-	-	-	5	50	34.97	15.03	30.5
71	-	-	-	10	50	27.09	22.91	49.3
72	-	-	-	30	50	23.73	26.27	57.3
73	200	1	3.87	10	50	24.17	25.83	57.8
74	200	2	4.28	5	50	33.22	16.78	37.0
75	200	2	4.28	10	50	23.89	26.11	58.5
76	200	2	4.28	30	50	21.59	28.41	63.8
77	200	4	4.42	10	50	23.05	26.95	60.4
78	400	1	13.05	10	50	20.86	29.14	65.6
79	400	2	13.05	5	50	24.23	25.77	57.8
80	400	2	13.05	10	50	20.47	29.53	66.5
81	400	2	13.05	30	50	18.29	31.71	71.5
82	400	4	13.25	10	50	20.34	29.66	66.8
83	600	1	13.85	10	50	19.31	30.69	69.2
84	600	2	14.22	5	50	26.69	23.31	52.2
85	600	2	14.22	10	50	19.25	30.75	69.3
86	600	2	14.22	30	50	16.19	33.81	76.4
87	600	4	14.47	10	50	19.07	30.93	69.8
88	800	2	14.80	5	50	32.92	17.08	38.0
89	800	2	14.80	10	50	20.71	29.29	66.3
90	800	2	14.80	30	50	17.92	32.38	73.1

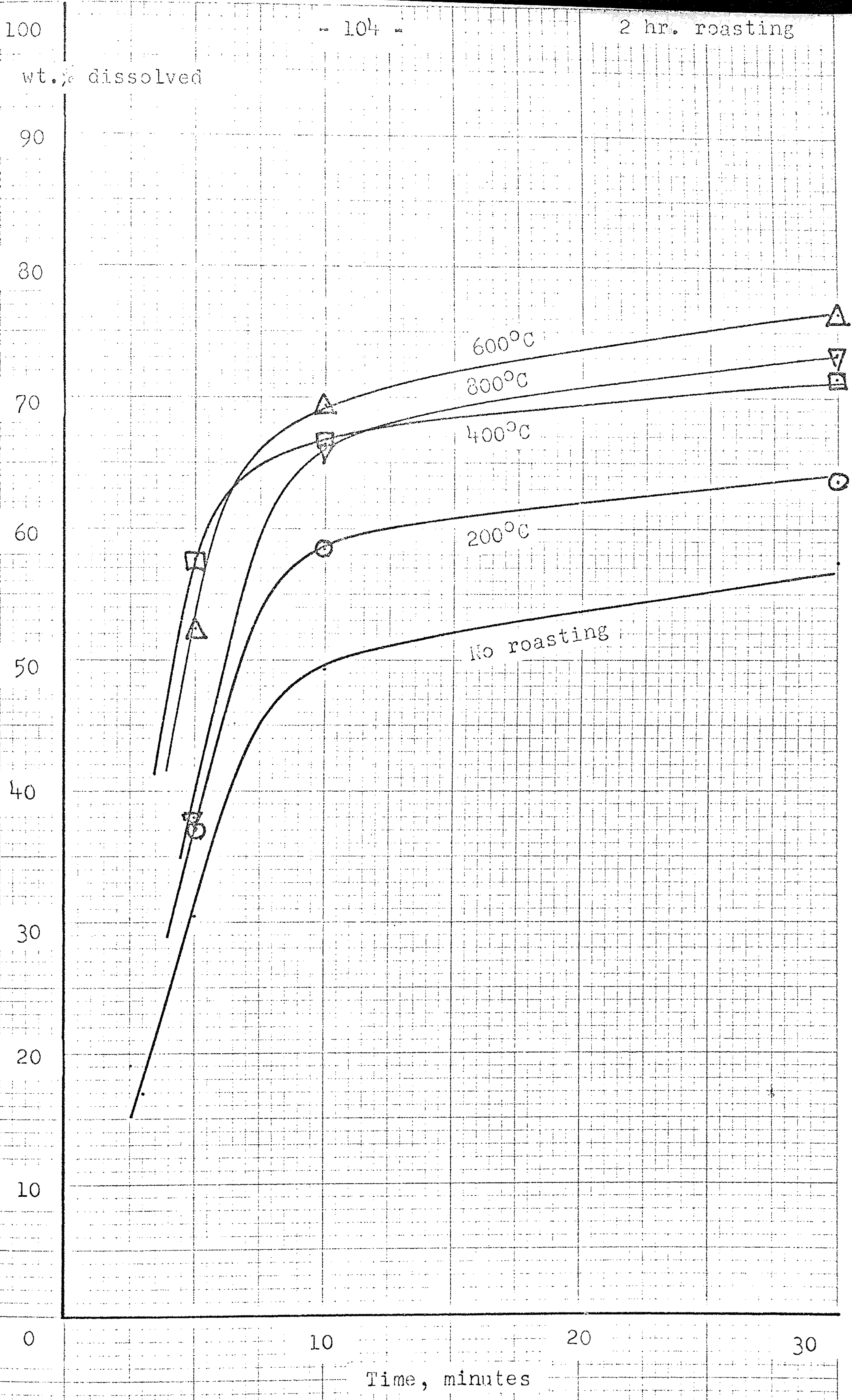

2 hr. roasting
wt.% dissolved
100
90
80
70
60
50
40
30
20
10
0
10
20
30
Time, minutes
600°C
800°C
400°C
200°C
No roasting

Figure 3.8

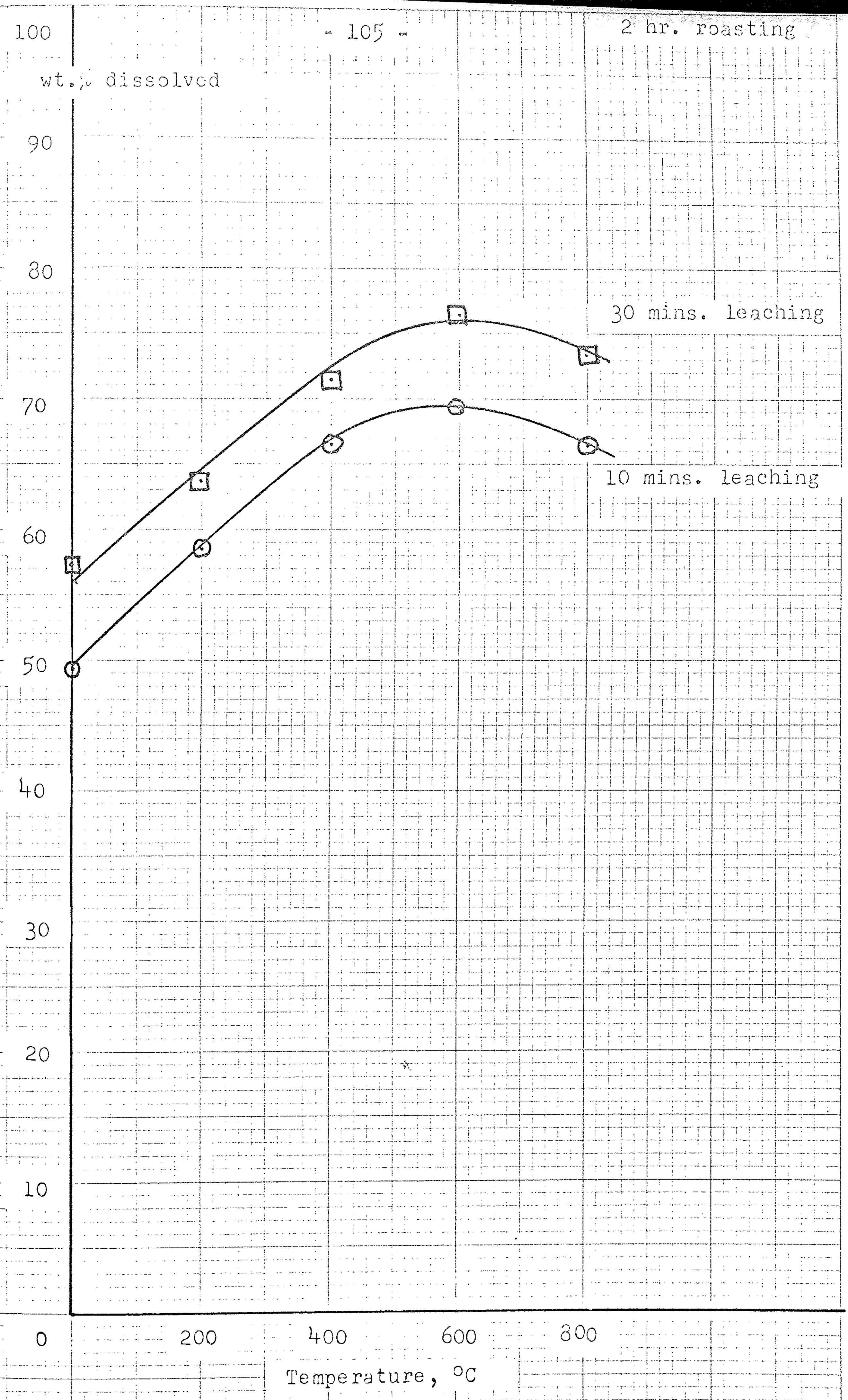

2 hr. roasting
wt.% dissolved
100
90
80
70
60
50
40
30
20
10
0
200
400
600
800
Temperature, °C
30 mins. leaching
10 mins. leaching

Figure 3.9

ore constituents (which deserves attention as advantages may be obtained), and partly to the method of analysis of results, which may tend to emphasise the roasting effect. In the previous experiments, any possible error in the assumptions relating to water and L.O.I. would probably have had a constant effect on the results, which is not the case for these experiments.

Apart from these considerations, it is unlikely that the extra capital and operating cost of a roasting kiln would repay the small savings from reducing the time for leaching, unless distinct advantages in selective leaching were also found. This is clearly an area where further work is necessary.

3.2.6 Application to design of an ore leaching system

The following design is based on the results from relatively few experiments already reported with only one ore, and cannot therefore be taken as representative of all low grade ores, or even those arising in Northamptonshire. A comprehensive programme of experimentation on different ores would be a useful exercise, and further detailed experimentation would be required on the range of ores likely to be fed to a commercial process. It is considered likely however that the results obtained above give a good qualitative indication of the reaction of siliceous iron ores, and in the absence of any other information will be used as the basis for design of the leaching reaction system. The optimisation of this system requires considerably more information than is at present known, but there are a number of techniques available in which, for example, the minimum amount of experimentation may be statistically planned to provide all the necessary data for optimisation. Even this approach may prove difficult due to wide mineralogical variations of ore bodies, with consequent changes in both chemical and physical conditions. It is important therefore that any proposed design should be as flexible as possible.

3.2.6.1 Operating conditions

The following conditions were specified as a basis for initial reactor design:

20% wt. HCl	$H = 0.20$
Stoichiometric acid	$E = 1.0$
100°C	$T = 100$
200-800 micron particle size	$r = 500$
95% conversion	$X = 0.95$
Ore composition as quoted	

The empirical extraction equation 3.1, derived in Section 3.2.5.8:

$$X = 0.005t + 7.0.H^{0.5}.E^{0.2}.\frac{T}{100}.\left(\frac{1}{(\log r)}\right)^{1.6}$$

gives the time required for reaction, t, as 60 minutes

Constant boiling point acid was specified for ease of recycling.

Stoichiometric acid was specified as this will give a slight excess after 95% dissolution and help prevent premature hydrolysis.

The temperature of 100°C was arbitrarily chosen.

Particle size range of 200-800 microns was considered to give maximum extraction without the necessity of breaking down individual grains which would require more power. The ore was generally found to be amenable to crushing to particle sizes above the natural grain size.

95% conversion was specified as a realistic maximum obtainable, as the extraction "curve" is likely to be asymptotic to 100%, and the straight line relationship invalid above this figure. A high conversion was chosen at the expense of residence time as it is unlikely that this will affect direct costs significantly, and will reduce indirect costs by giving a more efficient extraction. (The question of "impurity" separation, and purification as marketable by-products arises which is discussed later).

The ore composition as employed in the experiments was specified as the data related to that ore.

3.2.6.2 Throughput

The quantity of ore required to produce 350,000 tons p.a. iron powder was calculated with the following information and assumptions:

42.4% wt. Fe

95% conversion

5% loss of iron through the process

It should be pointed out that the figure quoted for iron content is high compared to the average figure for Northamptonshire ironstone which is 30-35% Fe. The throughput and related figures may therefore need adjusting for different feedstocks.

<u>Ore feed</u> = 914,650 long tons p.y.
= 114.331 long tons per hour (8000 hours/yr.)
= 116,165 kg per hour

This contains (49,254 kg/hr Fe)
70,048 kg/hr Fe_2O_3
348 kg/hr FeO
7,783 kg/hr Al_2O_3

11,617	kg/hr SiO_2
4,298	kg/hr CaO
581	kg/hr MgO
4,414	kg/hr H_2O
116	kg/hr S
1,742	kg/hr P_2O_5
15,218	kg/hr LOI

Acid

From section 3.2.3.2, 100 g. ore require 103.0 g HCl for stoichiometric dissolution, therefore

119,650	kg/hr HCl is required
= 598,250	kg/hr 20% wt. HCl, made up of 119,650 kg HCl plus 478,600 kg H_2O.

Residue

95% of the soluble constituents react, leaving

3,502	kg/hr Fe_2O_3
21	kg/hr FeO
467	kg/hr Al_2O_3
11,617	kg/hr SiO_2 (unreacted)
258	kg/hr CaO
35	kg/hr MgO
700	kg/hr H_2O *
7	kg/hr S (assumed lost as H_2S)
105	kg/hr P_2O_5 (assumed hydrolysed to H_3PO_4)
2,181	kg/hr LOI *
Total: 18,893	kg/hr

* assumed distributed uniformly throughout ore.

This represents silica with 23% impurities. It is worth noting that substantial quantities of sand for glassmaking are purified by HCl leaching. (3-3)

Solution

The solution from the reactor has the following composition:

(46,791	kg/hr Fe)		
66,546	kg/hr Fe_2O_3	as $FeCl_3$ =	135,172 kg/hr
327	kg/hr FeO	as $FeCl_2$ =	415 kg/hr
7,316	kg/hr Al_2O_3	as $AlCl_3$ =	19,140 kg/hr
4,040	kg/hr CaO	as $CaCl_2$ =	7,996 kg/hr
546	kg/hr MgO	as $MgCl_2$ =	1,290 kg/hr
109	kg/hr S	as H_2S =	116 kg/hr
1,637	kg/hr P_2O_5	as H_3PO_4 =	2,260 kg/hr
522,942	kg/hr H_2O		522,942 kg/hr
6,191	kg/hr HCl		6,191 kg/hr
		Total =	695,522 kg/hr

This corresponds to a 19.4% wt. solution of ferric chloride, or 19.4 g. $FeCl_3$/100 g solution or approximately 213.8 g. $FeCl_3$/1 solution.

The outline system is shown in Figures 3.10A and B in the following section. Practically, the "fresh" acid fed to the acid wash would be recycled acid from subsequent purification steps, and would probably contain recycled ferric chloride and some impurities. This is discussed in Section 4. The waste solids would be expected to be wet, and contain at least an equal quantity of water, which in terms of the mass balance above, would be subtracted from the water in the solution "out." The water wash is not likely to be 100% efficient and some loss of iron and acid is likely. Other sources (see Section 2 and references 1-1 and 1-2) indicate that these losses are not high and in later economic analysis (Section 8) may be assumed to be 1% HCl and 1% Fe (as $FeCl_3$) based on leaching reactor feed. The water balance over the whole process is likely to be one of the more critical areas which will require considerable attention in optomising the various process steps. The problem is discussed again in Section 4 in connection with purification processes, and also in Section 6 when mass balances are constructed. A sensitivity analysis by calculation was performed using batches of wash water equivalent to the unreacted solids residue, using one, two or three mixer-settler stages and assumptions as to slurry solids content after settling/filtration of 50% and 33%. The results are tabulated in Table 3.4 and assume 100% stage efficiency. It can be seen that thorough washing is necessary to reduce total chloride loss to below 1%.

The volumetric throughput is approximately $5.95 \times 10^8 cm^3/hr$ or 595 m^3/hr using an average density of 1.2 g/cm^3. For a residence time of 60 minutes (previous section), the total volume of the leaching reactor is 595 m^3.

3.2.6.3 Design

Table 3.5B outlines all possible arrangements in principle of liquid-solid contacting devices. These are explored methodically by considering equipment initially. Under the highly corrosive conditions specified, as few moving parts and internals as possible will minimise both capital and operating (maintenance) costs and give best economy of scale. The simplest construction would utilise

Table 3.4

Effects of Different Parameters on Residue Washing Efficiency

	Percentage loss of total chloride as HCl	
	solid content of washed slurry	
	50 %	33 %
No washing	2.716	3.622
18893 kg/hr water total		
in 1 stage	1.358	3.622
in 2 stages	1.207	3.475
in 3 stages	1.148	3.420
37786 kg/hr water total		
in 1 stage	0.905	2.716
in 2 stages	0.679	2.417
in 3 stages	0.587	2.295
56679 kg/hr water total		
in 1 stage	0.679	2.173
in 2 stages	0.435	1.776
in 3 stages	0.340	1.612
75572 kg/hr water total		
in 1 stage	0.543	1.810
in 2 stages	0.302	1.358
in 3 stages	0.214	1.173
94465 kg/hr water total		
in 1 stage	0.453	1.552
in 2 stages	0.222	1.073
in 3 stages	0.143	0.880

Table 3.5

Morphology of Liquid-Solid Reactors

A) Analysis of individual functions:

Motion 'in' of reagents
Entry device for reagents
Distribution of reagents
Energy transfer
Reaction equilibria)
)
Reaction kinetics) Reaction zone
)
Reaction energy transfer)
Separation of reagents/products
Exit device for products
Motion 'out' of products

For a hydrometallurgical acid leaching operation this list may be amplified:

Motion of water 'in'
" " acid "
" " solid "
Entry device for water
" " " acid
" " " solid
Distribution of water
" " acid
" " solid
Energy transfer to liquid phase
" " " solid "
Transport of acid through liquid bulk
" " " " " laminar layer
" " " " solid
" " product through solid
" " " " liquid laminar layer

Table 3.5 continued

Transport of product through liquid

Reaction equilibrium in/at solid

" kinetics

" energy transfer to/from solid

" " " " liquid

Liquid separation from solid

Solid " " liquid

(Gas separation)

Liquid exit device

Solid " "

Liquid motion 'out'

Solid " "

B) Classification by relative phase movements:

Equipment	Liquid phase	Solid phase	Example
Static	Static	Static	Batch
"	"	Moving	Batch
"	Moving	Static	Fixed bed
"	"	Moving	Tubular
Moving	Static	Static	
"	"	Moving	
"	Moving	Static	
"	"	Moving	Stirred tank

Equipment is defined as anything that does not react, but is in contact with the reactants.

This mode of analysis is particularly useful because:

1) There are no constraints imposed by restricting choice to specific available reactors,

2) Every possible system is studied and is quite general,

3) New arrangements and/or designs may be produced.

no internal motion devices at all. A static solid phase may either be large/massive lumps of ore when the ash layer that quickly forms would prevent effective reaction and thus be unsatisfactory; or relatively small particles in either a "fixed" bed or fluidized bed. It is difficult to visualize the stable existence of a fixed bed of small particles and a fluidized bed is likely to require such careful control of particle size to prevent loss of unreacted ore particles as to be uneconomic. This latter possibility is an interesting notion which is considered to deserve further attention. Finally, for the continuous process that is being considered, a moving liquid phase is necessary as this carries the reaction products to subsequent process steps. Three types of reactor may be considered to fit the requirements: tubular reactor, multistage continuously stirred tank reactor (CSTR), and Pachuca tank. The tubular reaction would feed acid and ore slurry cocurrently through a pipe or tube under suitable turbulent conditions to ensure mixing and suspension. A C.S.T.R. would probably require four stages to avoid by-passing, with acid and ore again co-current, and air agitation. (Multistage counter current operation is not included due to greater complexity and hence higher cost with no obvious advantages). The Pachuca tank is well known in the hydrometallurgical copper extraction industry. It is essentially a single stage C.S.T.R. or batch reactor with a vertical internal tube in the centre through which air is blown to circulate and mix the reagents. This may also be used as a multiple unit although there is no evidence of such use.

The reaction system is shown in block diagram form in Figure 3.10A. Fresh ore is fed to the main leaching reactor, probably as a slurry, where it reacts with acid recycled from subsequent purification stages. The reactor products are aqueous impure ferric chloride, and solid residue. While this residue appears to tend to absorb ferric chloride (see Section 3.2.5.1), dilution of the slurry prior to water washing has been found on laboratory experimentation to overcome this problem. The reactor products are settled therefore and the concentrated settled solids diluted with fresh water prior to water washing. The wash water will contain ferric chloride etc. and is sent forward to the purification step, with the main stream.

An alternative scheme is shown in Figure 3.10B for washing the leach residue with acid prior to water washing if the problem of ferric chloride adsorption proves this necessary.

The tubular reactor appeared interesting but is very dependent on suitably reliable pumps, and C.S.T.R.'s may therefore be more attractive and cheaper. With the system under investigation, it is not possible to offer further details of a C.S.T.R. or Pachuca tank system without laboratory experimentation to specify stage behaviour or geometry. A schematic outline of both systems is shown in Figure 3.11. A tentative design of a tubular reactor is however included as this is fundamentally simpler. Materials of construction requirements are likely to be similar to those for scrap leaching. Separate acid and ore slurry feeds are specified in the design, which would either require separation of acid and water in the hydrolysis recycle liquor, Iron ore leaching system

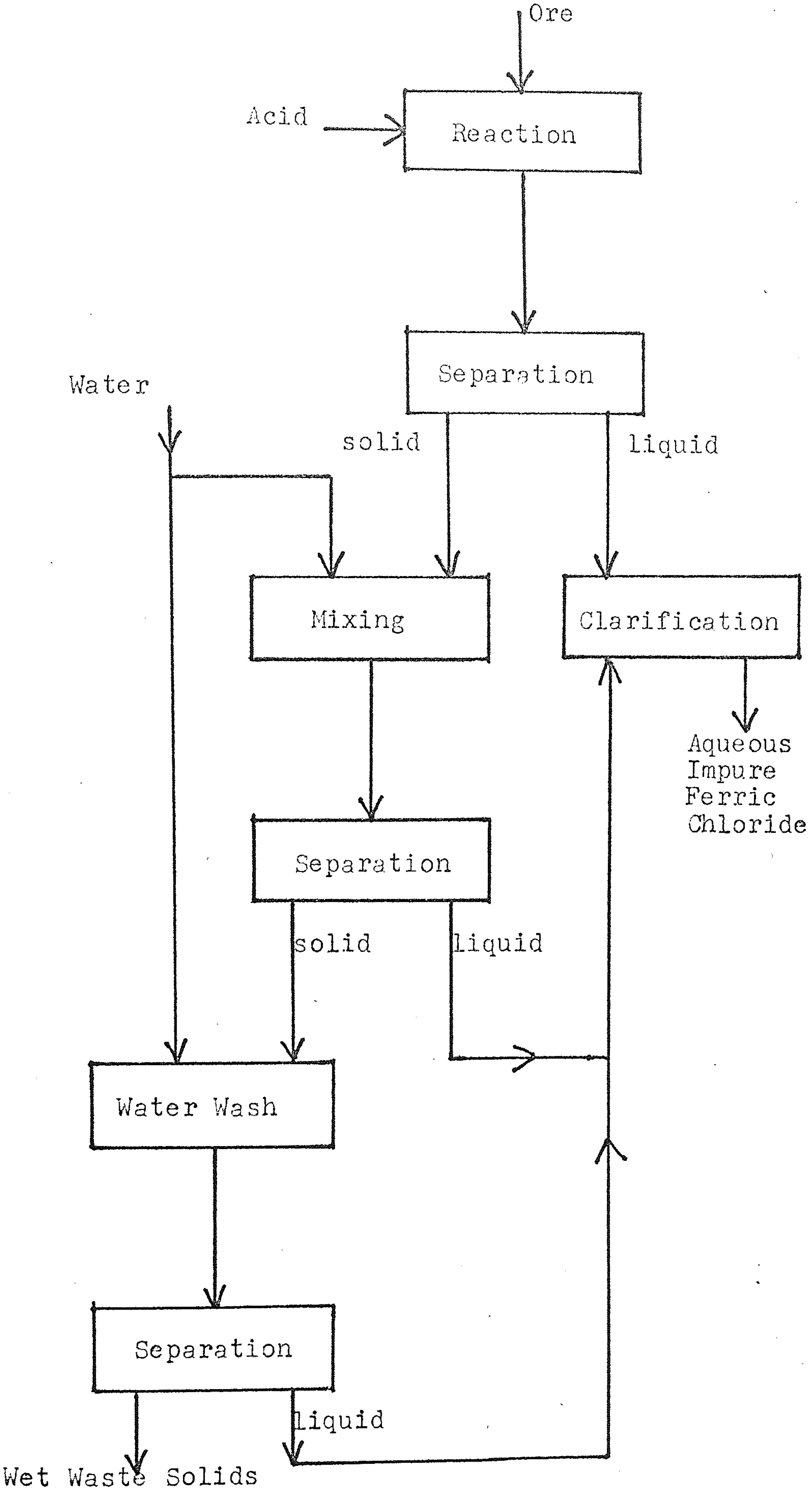


Figure 3.10A

Alternative iron ore leaching system

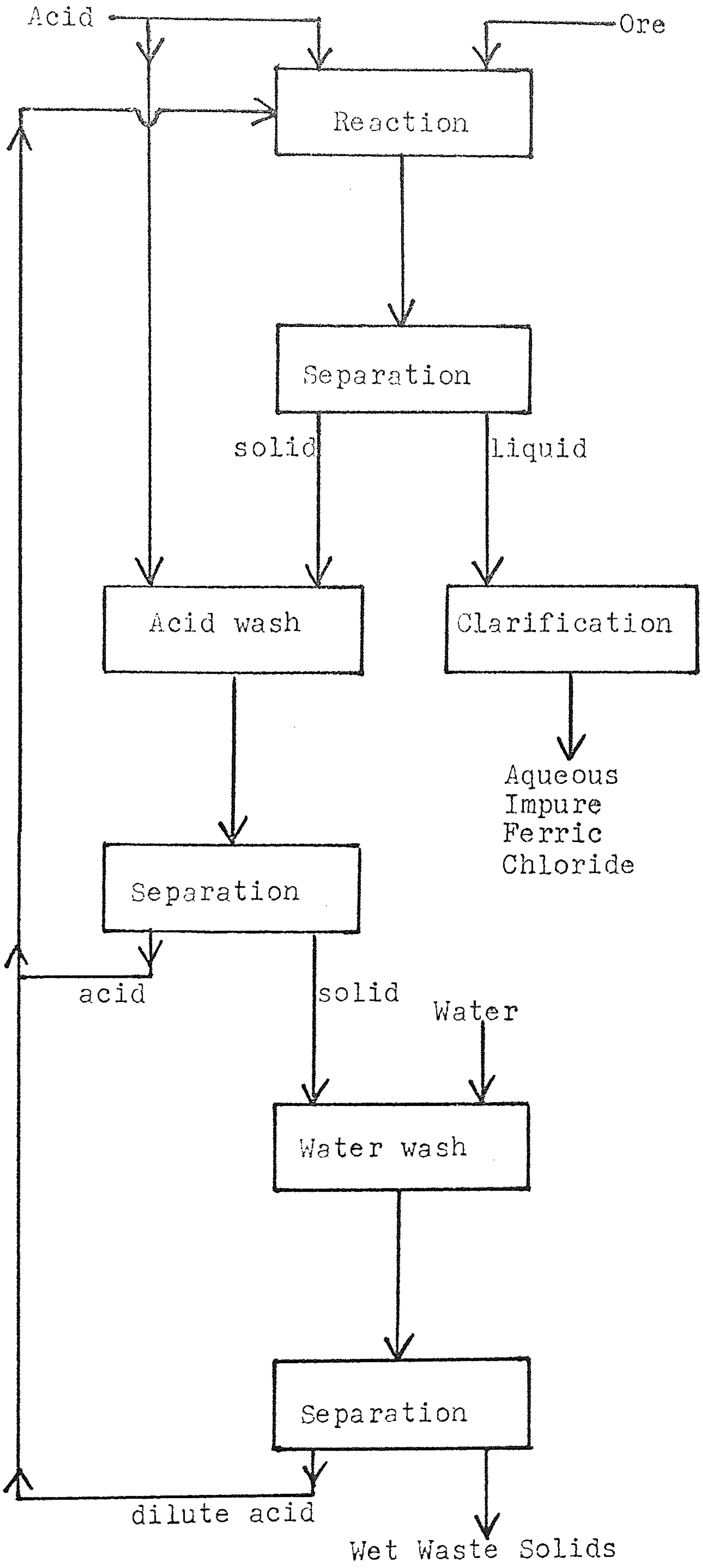
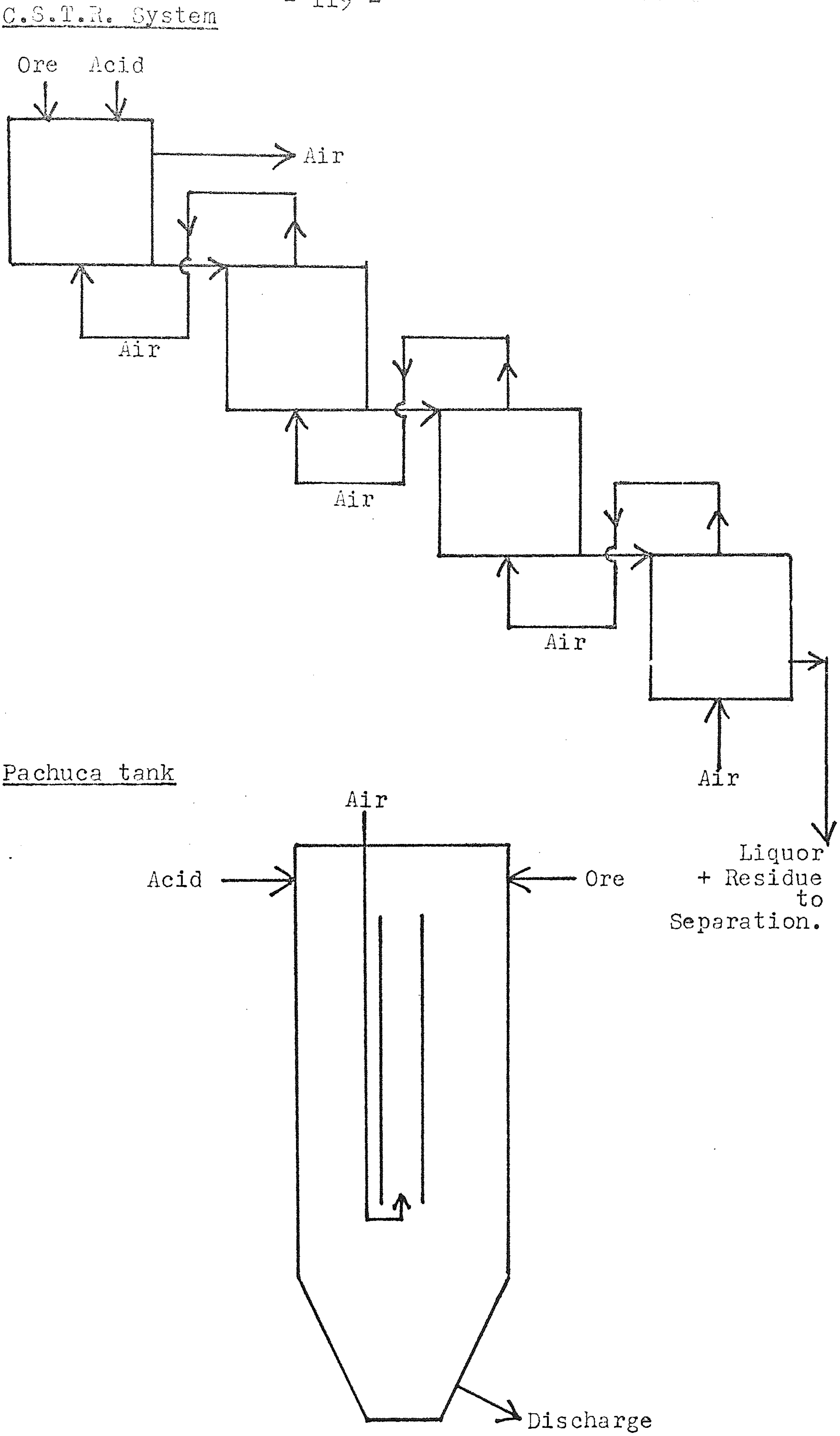


Figure 3.10B



C.S.T.R. System

Pachuca tank

Figure 3.11

or a different method of ore and acid feed. This may prove an additional disadvantage and requires investigation.

Adequate mixing of solid and liquid should result from employing conditions of turbulent flow in the reactor. This required a knowledge of the rheological properties of reacting slurries, which again is a far reaching problem of considerable depth and beyond the scope of this dissertation. It was assumed therefore for simplicity, that a minimum Reynolds number of 10,000 would ensure turbulence (around 3,000 is adequate for "normal" fluids). Also simple arithmetic means of varying physical properties were used.

$$\text{Reynolds number, Re} = \frac{d.\rho.v}{\mu}$$

where d = pipe diameter, cm
v = slurry velocity, cm/sec.
ρ = average slurry density, g/cm^3
μ = average slurry viscosity; g/cm.sec.

It is important also to ensure that the particles remain in suspension, and while ensuring turbulent flow it is also necessary for the velocity of the slurry in the reactor to be higher than the terminal falling velocity of the largest particle likely to be encountered. An expression for the terminal falling velocity, u, is given by Coulson and Richardson (3-14) as:

$$u^2 = 3\, d^1 g \left(\frac{\rho s - \rho}{\rho}\right)$$

where u = terminal falling velocity, cm/sec.
d^1 = particle diameter, cm
g = gravitational constant, cm/sec^2
ρs = solid density, g/cm^3
ρ = fluid density, g/cm^3

This applies to spherical particles under the conditions applicable in this design. The largest particle likely to be encountered is assumed to be 1 mm or 0.1 cm, and the fluid density assumed to be 1.2 g/cm^3 (averaged over the reactor). The ore density is 5 g./cm^3.

$$u^2 = 3.0.1.\ 981.\ \left(\frac{5 - 1.2}{1.2}\right)$$

$$= 934$$

$$\text{and } u = 30.6 \text{ cm/sec.}$$

(As the reaction proceeds the particles are likely to decrease in size to a maximum of 0.5 mm, when the terminal velocity is 21.6 cm/sec). A slurry velocity of 40 cm/sec was arbitrarily selected. The volumetric throughput of the reactor was found to be 5.95 x 10^8 cm^3/hr in section 3.2.6.2 or 1.65 x 10^5 cm^3/sec, which gives the cross sectional area of the reactor as 4140 cm^2. For a circular reactor this corresponds to a diameter of 72.5 cm, and for a square reactor a side of 65 cm. The length of a square reactor is therefore $\frac{5.95 \times 10^8}{4140}$ cm = 1440 metres.

$$\text{The Reynolds number} = \frac{\rho . v . d}{\mu}$$

$$= \frac{1.2.\ 40.\ 65(\text{or}72.5)}{0.03}$$

$$= 104{,}000$$

which is well inside the turbulent region. The value of μ, viscosity, was found experimentally, and is the mean of approximately inlet and outlet values. If subsequent work shows that the velocity may be cut to 20 cm/sec, for example, then the reactor length is reduced proportionately.

The power required for pumping the acid and ore slurry when the reactor discharge is at the same level as the pump was calculated theoretically as 1.8 H.P. Assuming 50% pump efficiency this would require 3½ H.P. If a spiral reactor is considered, 10 diameters high, then the theoretical priming power becomes 18 H.P. which drops to 1.8 H.P. if the discharge is at the same level as the pump.

There are a number of ways of constructing a reactor 0.65 m. square and 1440 m. long, which include a horizontal baffled tank or a spiral. Dead spaces and arrangements that include upward flow of slurry should be avoided to prevent problems of pump failure or blockage and consequent cleaning difficulties.

The analysis of a general liquid-solid reactor, Table 3.5A has been applied to this problem to complete the reactor specification and is summarised in Table 3.6. The overall reaction system flow diagram is shown in Figure 3.12.

Details of a possible four stage C.S.T.R. (or Pachuca tank) system, are included for completion. This would possibly consist of four tanks each 150 m^3 capacity, for example 5 x 5 x 6 m. Acid would be pumped to the first tank and mixed with ore at a controlled feed rate. Interstage transfer may either use pumps or gravity. Stirring or mixing could usefully employ air from the ferric oxide drying stage, which would help maintain a water balance and also recover the heat. The air may either be fed to each stage in parallel or in series, and it would be necessary to cool and/or scrub the outlet air to remove acid fumes. An outline specification is given for this system in Table 3.7 based on Table 3.5A.

3.2.7 Conclusions

A reaction system has been designed to leach

Table 3.6

Tubular Reactor Specification

1. Motion of water 'in'	Pumped
2. " " acid "	
3. " " solid "	Pumped as slurry
4. Entry device for water	Piped and valve
5. " " " acid	
6. " " " solid	
7. Distribution of water	Mixing by Turbulence
8. " " acid	
9. " " solid	
10. Energy transfer to liquid phase	Preheat
11. " " " solid "	Preheat slurry if necessary
12. Transport of acid through liquid bulk	Mixing by turbulence
13. " " " " liquid laminar layer	
14. " " " through solid	
15. " " product through solid	
16. " " " " liquid laminar layer	
17. " " product through liquid	
18. Reaction equilibria	Goes to completion
19. " kinetics	See text
20. " energy transfer to/from solid	Heat of reaction absorbed by system, Interstage heat transfer if necessary
21. " " " to/from liquid	
22. Liquid separation from solid	After reaction
23. Solid " " liquid	
24. Gas separation	None
25. Liquid exit device	With 26, pipe and valve to separator

Table 3.6 continued

26. Solid exit device : With 25, pipe and valve to separator

27. Liquid motion 'out' :) Together, from
)
28. Solid " " :) initial pumping

29. Gas " " : None

Leaching system flow diagram

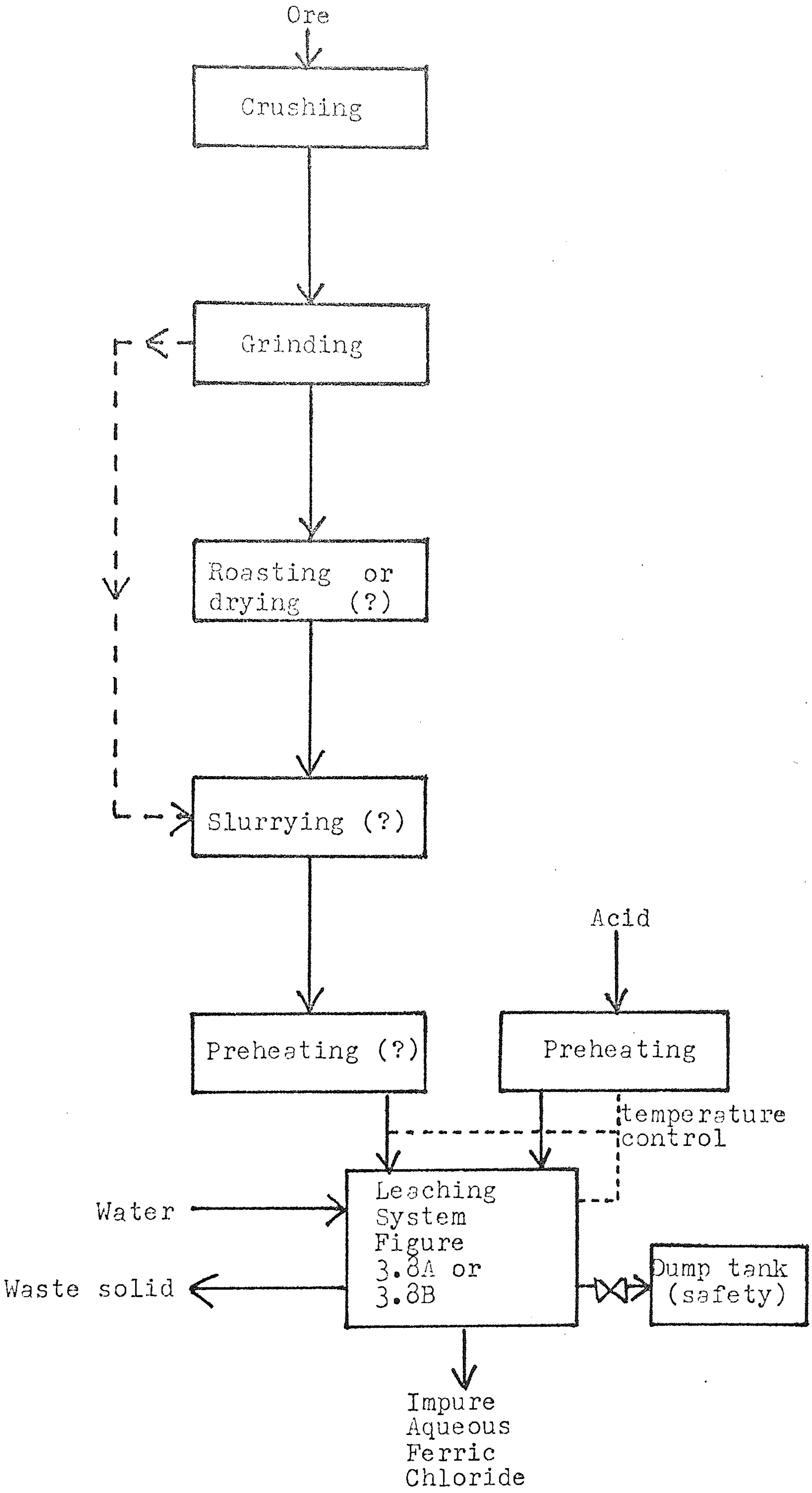


Figure 3.12 .

Table 3.7

C.S.T.R. Specification

1.	Motion of water 'in'	Pumped
2.	" " acid "	
3.	" " solid "	Hopper/gravity
4.	Entry device for water	Valve
5.	" " " acid	
6.	" " " solid	Shutter valve/screw
7.	Distribution of water	Air agitation
8.	" " acid	
9.	" " solid	
10.	Energy transfer to liquid phase	Preheat and air
11.	" " " solid "	From liquid
12.	Transport of acid through liquid bulk	Mixing
13.	" " " " liquid laminar layer	
14.	" " " through solid	
15.	" " product through solid	
16.	" " " " liquid laminar layer	
17.	" " product through liquid	
18.	Reaction equilibria	Goes to completion
19.	" kinetics	See text
20.	" energy transfer to/from solid	Heat of reaction absorbed by system, Interstage heat transfer if necessary
21.	" " " to/from liquid	
22.	Liquid separation from solid	Gravity, inside and after reactor
23.	Solid " " liquid	
24.	Gas separation	Disentrainers, coolers driers

Table 3.7 continued

25. Liquid exit device : Weir and/or pump

26. Solid " " : Mechanical

27. Liquid motion 'out' : Gravity/weir

28. Solid " " : Pumped or gravity

29. Gas " " : Gas pressure

116,165 kg/hr low grade iron ore with hydrochloric acid as the first stage of a process to produce 350,000 tons p.y. iron powder.

There are many aspects of an ore leaching reactor which are difficult, if not impossible, to take account of in designing a suitable system. This is perhaps why empirical designs are so common. An attempt has been made above to identify important features of leaching low grade iron ore and relate these to a practical situation, although it is patently clear that a vast amount of work remains to be done. Some of the more significant areas have been delineated and are summarised at the end of this dissertation.

3.3 Experimental work on leaching of scrap iron

Since scrap iron occurs in sizes ranging from borings to large sheets or bales, it was considered unreasonable to perform laboratory experiments on this scale. Therefore small samples of mild steel rod and strip were employed. It was appreciated that nonferrous and non-metallic impurities are frequently present in scrap metal (see Section 2.2) which may affect the reaction and/or make recovery an attractive economic proposition, and is explored later.

3.3.1 Mild steel

The analyses of the rod and strip employed in the experiments were:

	Rod % wt.	Strip % wt.
Carbon	0.87	0.12
Silicon	Trace	Trace
Sulphur	0.022	0.24
Phosphorus	0.006	0.057
Manganese	0.32	1.2
Iron	to 100%	to 100%

The sample sizes were kept as constant as possible at:

Strip: 6.35 cm. long x 1.27 cm. wide x 0.165 cm. thick

Rod: 6.35 cm. long x 0.635 cm. diameter

except for stoichiometric acid experiments when the following size was used:

Strip: 2.54 cm. long x 1.91 cm. wide x 0.165 cm. thick

3.3.2 Experimental programme

The programme followed similar lines to that employed for ore extraction (Section 3.2.2) and the following parameters were investigated:

Temperature: 65°C to 108°C which is the maximum obtainable with constant boiling point acid.

Time: Up to three hours to allow for complete dissolution of the sample.

Acid excess: Both substantial excess acid, and stoichiometric acid conditions were used.

Type of iron: Two samples were used as mentioned above - high and low carbon steel.

Acid concentration: Constant boiling, 20% wt. acid was used.

Pressure: Pressure was not employed to raise the temperature above 108°C.

Surface condition: The following surface conditions were investigated:

1) pickled in cold acid for 4 hours
2) cleaned with emery paper to a bright finish
3) rusted in warm moist air
4) rusted in moist air then smeared with a thin film of grease.

3.3.3 Method

The apparatus was similar to that employed for iron ore leaching and is shown in Figure 3.13. For those experiments involving a substantial excess of acid, several samples were treated at the same time, and each sample was removed from the reaction flask after the correct time interval. This

Apparatus for Iron Dissolution Experiments

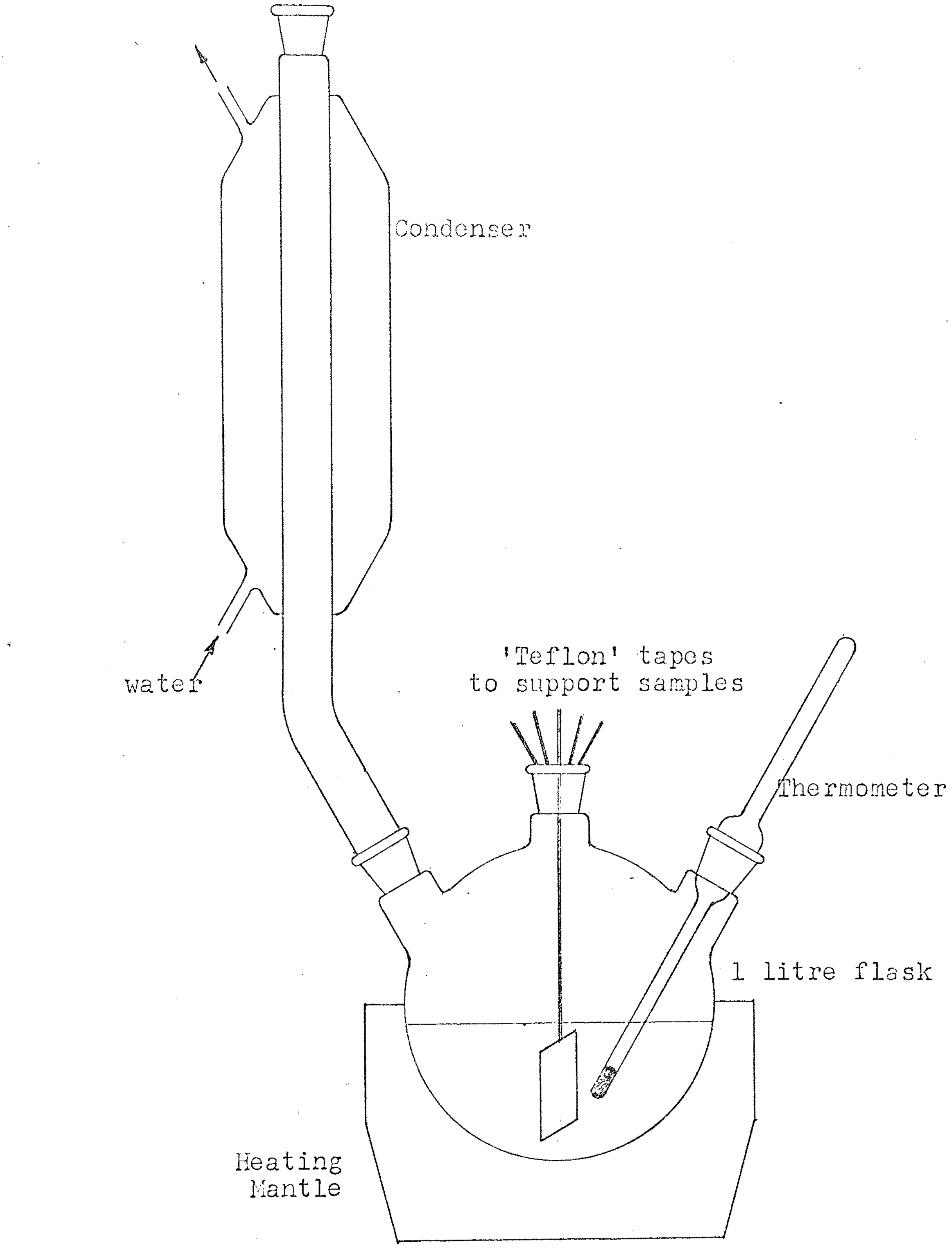


Figure 3.13

considerably reduced the amount of experimentation and was thought not to affect the validity of the results as about four times the amount of acid required for complete dissolution of all the samples was used. Agitation was not considered necessary on account of the rapid evolution of hydrogen from the surface of the metal effectively stirring the liquid. One sample at a time was reacted for those experiments requiring stoichiometric acid conditions.

A considerable amount of attention was given to sample preparation. Each sample was cleaned with emery cloth to a bright finish and then weighed. After heating the acid to the required temperature, a batch of five prepared samples was suspended with "teflon" tape (see Figure 3.13) from the centre neck of the flask and held in place with a rubber bung. A sample was easily withdrawn when necessary by removing the bung, and extracting the necessary sample, leaving the others in the acid. This was then washed in water, dried carefully and reweighed, taking care to minimise surface oxidation. Temperature was maintained at ±1°C and timing to ±10 seconds.

20% wt. HCl, constant boiling point acid, was used throughout these experiments. This was made up by diluting concentrated (38% wt.) acid with distilled water and accurately adjusting the strength by reference to standard acid/alkali titration.

The reaction between iron and acid is given as:

$Fe + 2HCl \rightarrow Fe\,Cl_2 + H_2$ (Appendix II)

and from the approximate molecular weights:

56 gms. Fe react with 73 gms. HCl

or 10 gms. Fe (approximate weight of strip sample)

require 13.1 gms. HCl

and 15 gms. Fe (approximate weight of rod sample)
require 19.6 gms. HCl

This is equivalent to 65.4 gms. and 98.1 gms. of 20% wt. acid respectively. The actual quantity of acid used was 1250 mls. in a 21 flask in each set of excess acid experiments. For the stoichometric acid series of investigations, smaller strip samples of approximately 6 gms. were employed, using a 250 ml flask and 40 gms. 20% wt. HCl, the stoichiometrically correct quantity being used to 0.1 gm. The results were obtained by direct reference to weight loss and/or surface area as the system is much simpler than for iron ore extraction and is discussed more fully later.

3.3.4 Results

The results are presented in tabular form in Table 3.8, and graphically in Figures 3.14 to 3.20. The chemical and physical properties, and thermodynamics of the relevant systems are included in Appendix II.

The first experiments were carried out with excess acid to investigate the effect of temperature and different types of iron. The graphs of percentage dissolution versus time, Figures 3.14 and 3.16 , indicated that the strip samples dissolved faster than the rod samples, but when the weight loss was related to apparent surface area, Figures 3.15 and 3.17 , the difference was considerably reduced. After preliminary analysis of results with excess acid, strip samples were dissolved in stoichiometric quantities of acid to develop a model on which to base reactor design.

While the weight loss per unit surface area was apparently similar for both types of iron, it was noted that the strip samples dissolved uniformly and cleanly at an

Metallic Iron Leaching - Experimental Results

Table 3.8

Exp. No.	Time Mins	Temp. °C	Weight before	Dimensions before (1)	Weight after	Dimensions after	Loss gms.	Loss %	A.S.A. cm^2 (2)	Loss g/cm^2
Excess acid, strip samples										
91	15	80	10.102	6.35x1.27	9.141	6.35x1.27x0.150	0.961	9.5	18.52	0.0519
92	30	80	9.500	6.43x1.27	7.714	6.35x1.14x0.117	1.786	18.8	17.55	0.1026
93	60	80	9.831	6.48x1.27	6.251	6.12x1.19x0.089	3.580	36.4	17.48	0.2054
94	90	80	9.822	6.35x1.27	4.655	6.10x1.17x0.069	5.167	52.7	16.97	0.3046
95	120	80	9.814	6.38x1.27	3.226	6.15x1.02x0.051	6.588	67.0	15.94	0.4123
96	150	80	9.511	6.35x1.27	1.620	6.10x1.02x0.038	7.890	83.0	15.68	0.5022
97	15	90	9.708	6.35x1.27	7.871	6.30x1.27x0.127	1.836	18.9	17.94	0.1025
98	30	90	10.138	6.35x1.27	6.534	6.35x1.27x0.117	3.604	35.5	18.26	0.1976
99	45	90	10.387	6.35x1.27	4.727	6.10x1.27x0.086	5.660	54.6	17.74	0.3193
100	60	90	9.752	6.22x1.27	2.804	6.10x1.02x0.064	6.948	71.2	15.81	0.4402
101	75	90	11.303	6.48x1.27	1.865	5.97x1,02x0.041	9.438	83.4	15.87	0.5937
102	10	100	10.984	6.48x1.32	8.448	6.40x1.27x0.127	2.536	23.1	18.97	0.1336
103	20	100	10.438	6.60x1.27	5.938	6.48x1.22x0.114	4.500	43.0	18.45	0.2434
104	25	100	11.069	6.48x1.35	5.270	6.35x1.27x0.102	5.800	52.5	18.84	0.3077
105	30	100	11.483	6.48x1.40	4.746	6.10x0.76x0.079	6.737	58.6	18.97	0.3550
106	40	100	10.021	6.60x1.22	2.488	6.30x1.02x0.053	7.533	75.1	16.13	0.4681
107	10	105.5	10.925	6.35x1.27	7.292	6.30x1.27x0.127	3.633	33.2	18.26	0.1984
108	20	105.5	10.504	6.35x1.27	4.844	5.84x1.27x0.089	5.660	53.9	17.35	0.3255
109	25	105.5	10.041	6.35x1.27	3.535	5.97x1.12x0.074	6.513	64.8	16.52	0.3937
110	30	105.5	9.757	6.30x1.27	2.380	6.10x1.02x0.038	7.377	75.6	16.84	0.4387
111	35	105.5	9.883	6.30x1.27	1.588	5.84x1.02x0.038	8.295	85.0	15.42	0.5379

Table 3.8 continued

Exp. No.	Time Mins	Temp. ^{o}C	Weight before	Dimensions before (1)	Weight after	Dimensions after	Loss gms.	Loss %	A.S.A. cm^2 (2)	Loss g/cm^2
Excess acid, rod samples										
112	15	65	14.368	6.15	13.851	6.10x0.622	0.517	3.5	12.70	0.0408
113	60	65	15.118	6.35	12.627	6.22x0.597	2.491	16.5	12.76	0.1953
114	90	65	14.737	6.20	11.228	6.10x0.572	3.501	23.8	12.22	0.2868
115	120	65	14.823	6.30	10.333	6.10x0.551	4.990	30.2	12.11	0.4123
116	165	65	15.572	6.48	8.893	6.35x0.538	6.679	42.9	12.37	0.5394
117	15	80	14.725	6.27	13.400	6.22x0.610	1.326	9.0	12.82	0.1035
118	30	80	14.625	6.20	12.028	6.10x0.584	2.597	17.7	12.35	0.2099
119	60	80	15.255	6.48	10.325	6.35x0.533	4.930	32.3	12.32	0.3999
120	90	80	15.203	6.40	8.583	6.10x0.518	6.620	43.5	11.87	0.5580
121	120	80	14.914	6.35	6.646	6.15x0.467	8.268	55.5	11.35	0.7285
122	15	90	15.396	6.35	12.584	6.30x0.589	2.811	18.3	12.74	0.2201
123	30	90	14.274	6.10	9.653	6.10x0.559	4.621	32.4	11.99	0.3860
124	45	90	14.892	6.22	8.419	6.10x0.538	6.472	43.5	11.90	0.5437
125	60	90	15.240	6.48	7.217	6.35x0.531	8.023	52.6	12.28	0.6526
126	75	90	14.911	6.22	5.692	5.84x0.483	9.218	61.7	11.14	0.8293
127	10	100	15.277	6.35	12.757	6.30x0.589	2.520	16.5	12.75	0.1976
128	20	100	15.189	6.22	10.604	6.10x0.556	4.585	30.2	11.45	0.3999
129	25	100	15.348	6.22	9.948	6.10x0.536	5.400	35.2	11.90	0.4526
130	30	100	15.979	6.60	9.689	6.35x0.531	6.310	39.5	12.41	0.5084
131	49	100	15.545	6.48	7.140	6.30x0.480	8.405	54.1	11.73	0.7177

Table 3.8 continued

Exp. No.	Time Mins	Temp. ^{o}C	Weight before	Dimensions before (1)	Weight after	Dimensions after	Loss gms.	Loss %	A.S.A. cm^2(2)	Loss g/cm^2
132	10	105.5	15.624	6.35	12.305	6.30x0.582	3.319	21.2	12.66	0.2620
133	20	105.5	14.880	6.22	9.384	5.84x0.531	5.542	37.2	11.61	0.4759
134	25	105.5	15.399	6.35	8.736	5.97x0.508	6.663	43.3	11.61	0.5751
135	30	105.5	15.564	6.60	7.684	6.10x0.483	7.880	50.6	11.86	0.6650
140	40	105.5	14.667	6.22	4.384	5.84x0.406	10.283	70.1	10.37	0.9920
Stoichiometric acid, strip samples										
141	15	80	5.678	1.78x2.51	5.225	1.78x2.46x0.152	0.452	8.0	10.21	0.0443
142	30	80	5.828	1.78x2.51	5.343	1.78x2.51x0.147	0.485	8.3	10.28	0.0468
143	45	80	5.839	1.80x2.54	4.520	1.78x2.49x0.132	1.319	22.6	10.28	0.1287
144	75	80	5.989	1.91x2.51	3.863	1.85x2.36x0.119	2.135	35.5	10.41	0.2046
145	90	80	6.406	2.01x2.54	3.506	1.93x2.46x0.107	2.820	44.0	11.10	0.2542
146	10	90	6.980	2.03x2.74	6.422	2.03x2.72x0.152	0.558	8.0	10.28	0.0543
147	30	90	6.150	1.96x2.54	4.588	1.88x2.44x0.132	1.612	25.4	10.86	0.1488
148	50	90	6.047	1.88x2.54	3.560	1.78x2.49x0.109	2.187	41.7	10.39	0.2100
149	80	90	6.335	2.03x2.54	2.740	1.88x2.31x0.091	3.590	56.8	10.65	0.3364
150	15	100	6.122	1.85x2.59	4.560	1.85x2.54x0.130	1.562	25.5	10.81	0.1449
151	25	100	6.348	1.96x2.54	3.866	1.93x2.49x0.112	2.479	39.4	11.01	0.2248
152	35	100	6.556	2.03x2.54	3.280	1.98x2.39x0.097	3.277	50.0	11.07	0.2961
153	45	100	6.405	2.03x2.54	2.533	1.83x2.39x0.081	3.871	60.5	10.63	0.3643
154	10	105.5	5.860	1.85x2.54	4.532	1.83x2.46x0.135	1.328	22.7	10.52	0.1263
155	20	105.5	6.281	1.96x2.54	3.862	1.88x2.51x0.114	2.420	38.5	10.94	0.2209
156	30	105.5	5.988	1.88x2.54	2.796	1.80x2.34x0.091	3.192	53.3	10.10	0.3162
157	40	105.5	5.923	1.80x2.54	2.296	1.78x2.31x0.081	3.627	61.2	9.74	0.3720
158	50	105.5	6.080	1.91x2.44	1.804	1.73x2.39x0.066	4.280	70.3	9.75	0.4387

Table 3.8 continued

Exp. No.	Time Mins	Temp. °C	Weight before	Surface Condition	Weight after	Loss gms.	Loss %
Excess acid, strip samples, surface effects							
159	2	100	9.617)	Pickled	(9.239	0.378	3.9
160	5	100	10.696)		(9.378	1.318	12.3
161	2	100	10.820)	Emery cleaned	(10.419	0.401	3.7
162	5	100	10.727)		(9.544	1.183	11.0
163	2	100	9.381)	Rusted	(9.066	0.314	3.4
164	5	100	10.269)		(9.192	1.079	10.5
165	2	100	10.227)	Rusted and greasy	(9.972	0.255	2.5
166	5	100	10.017)		(9.073	0.994	9.3

Notes: (1) Strip samples were of constant initial thickness 0.165 cm, and rod samples of constant initial diameter 0.634 cm.

(2) Average surface area

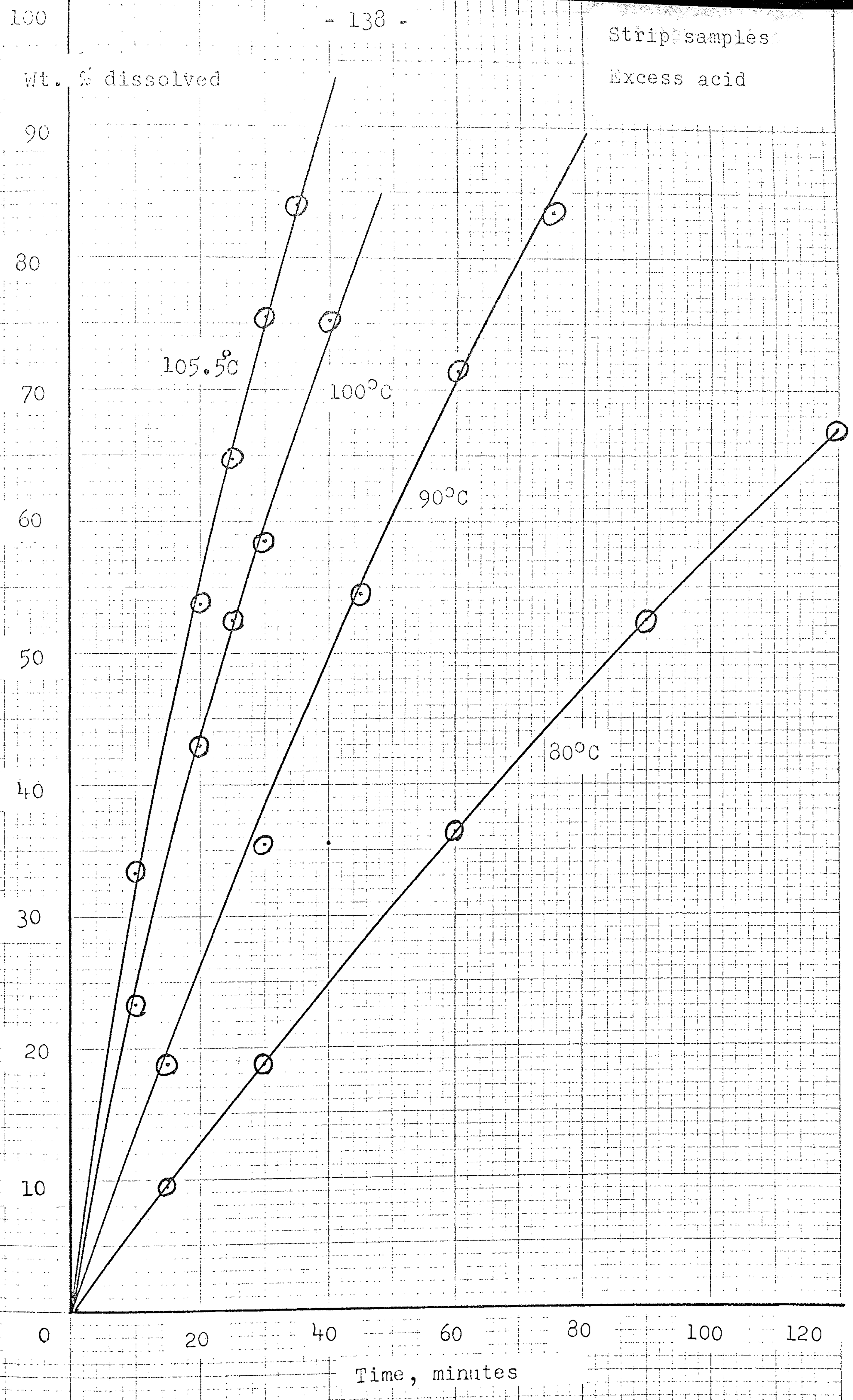

Strip samples
Excess acid
Wt. % dissolved
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
120
Time, minutes
105.5°C
100°C
90°C
80°C

Figure 3.14

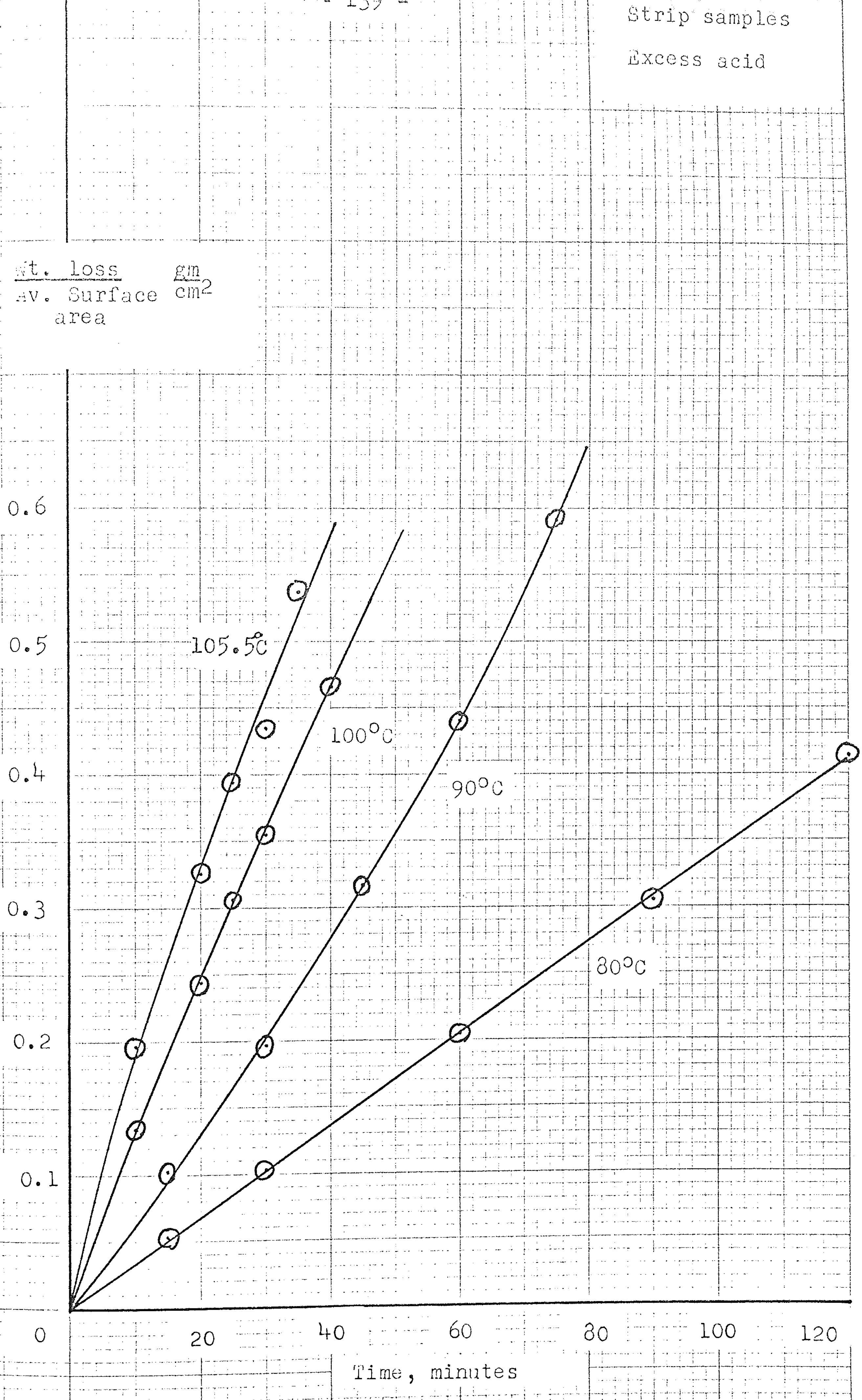

Strip samples
Excess acid
Wt. loss / Av. Surface area gm/cm2
0.6
0.5
0.4
0.3
0.2
0.1
0
20
40
60
80
100
120
Time, minutes
105.5°C
100°C
90°C
80°C

Figure 3.15

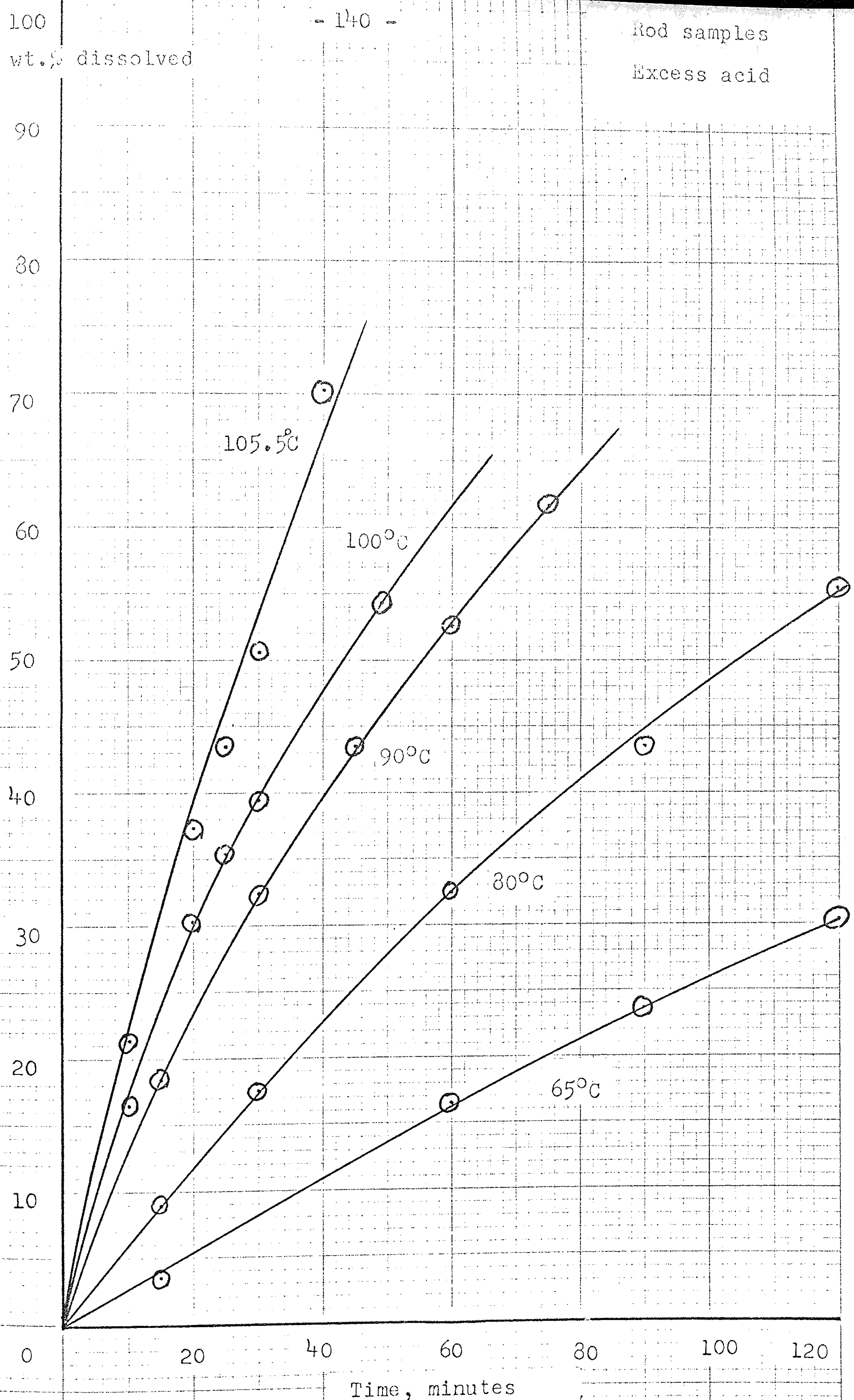

Rod samples
Excess acid
100
wt.% dissolved
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
120
Time, minutes
105.5°C
100°C
90°C
80°C
65°C

Figure 3.16

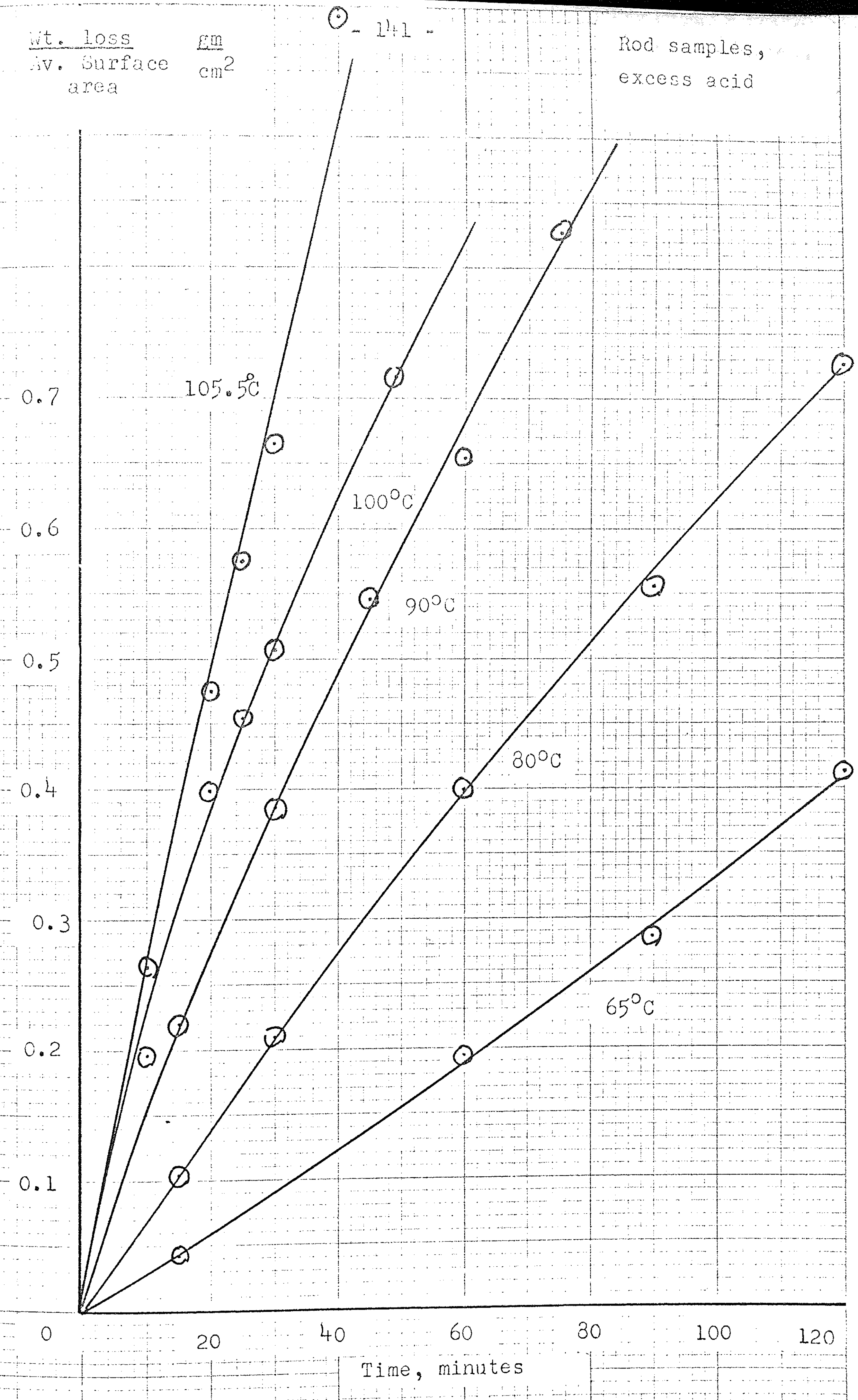

Wt. loss / Av. Surface area
gm / cm^2
Rod samples, excess acid
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
20
40
60
80
100
120
Time, minutes
105.5°C
100°C
90°C
80°C
65°C

Figure 3.17

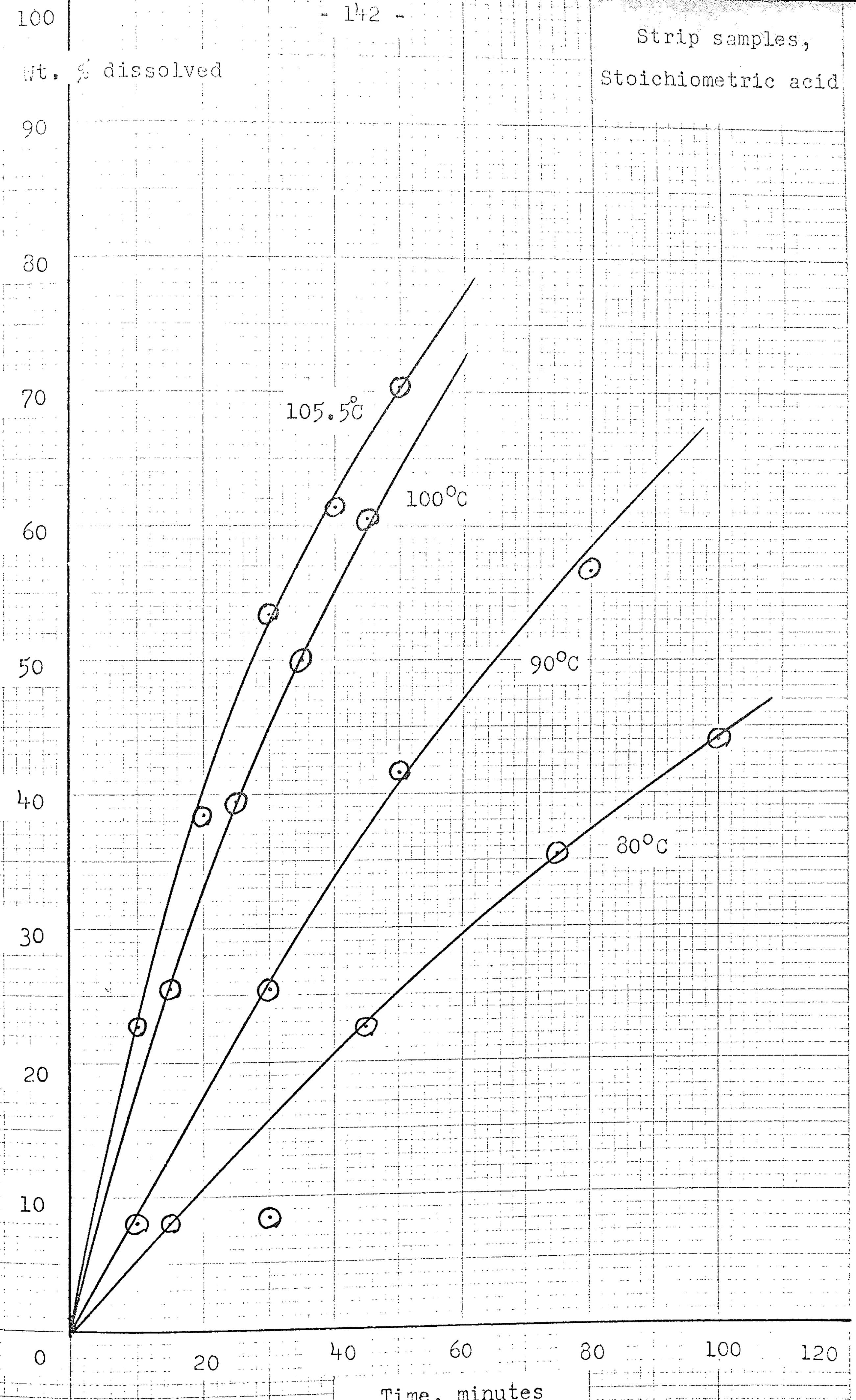

100
Wt. % dissolved
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
120
Time, minutes
Strip samples,
Stoichiometric acid
105.5°C
100°C
90°C
80°C

Figure 3.18

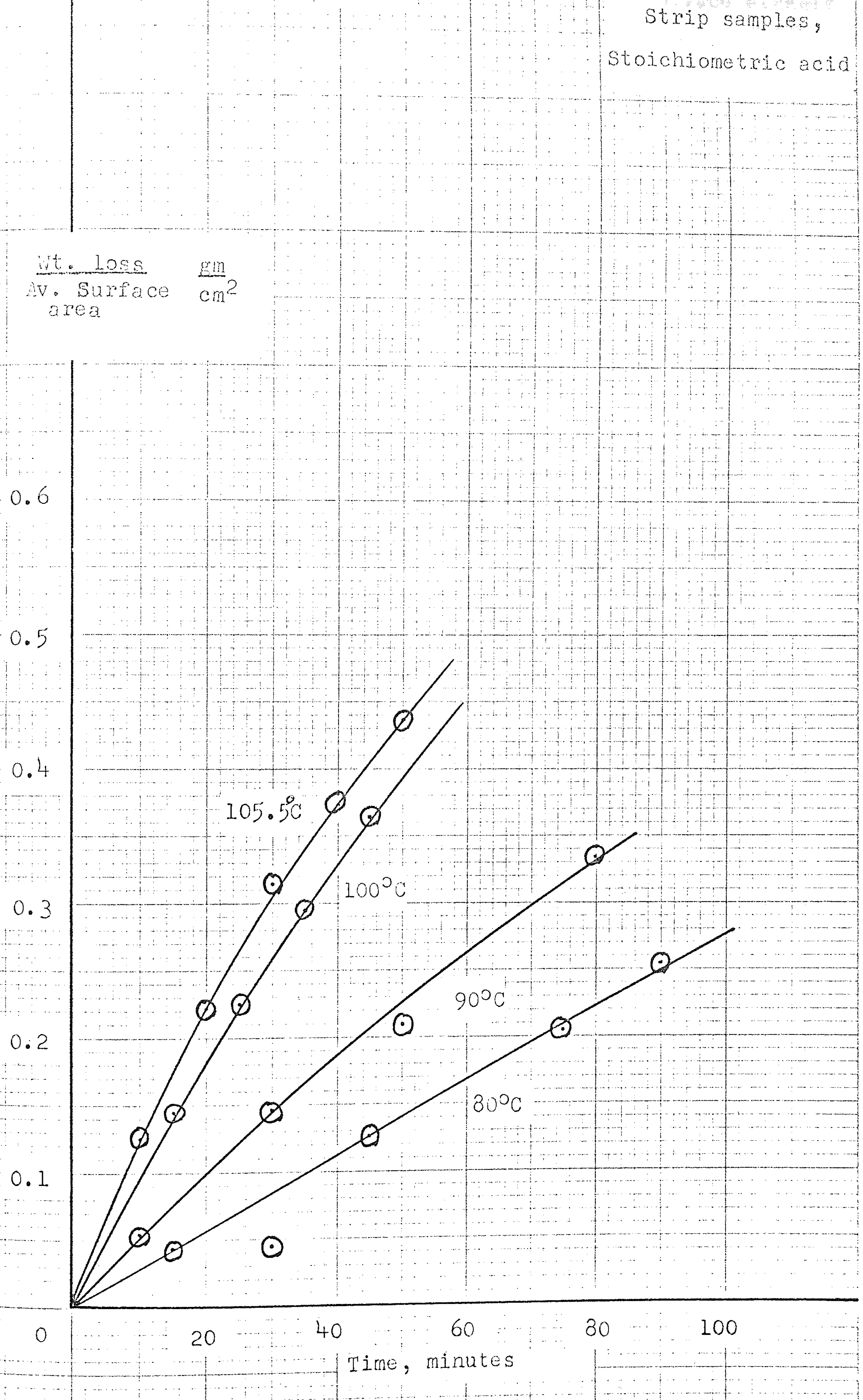

Strip samples,
Stoichiometric acid
Wt. loss / Av. Surface area gm/cm^2
0.6
0.5
0.4
0.3
0.2
0.1
0
20
40
60
80
100
Time, minutes
105.5°C
100°C
90°C
80°C

Figure 3.19

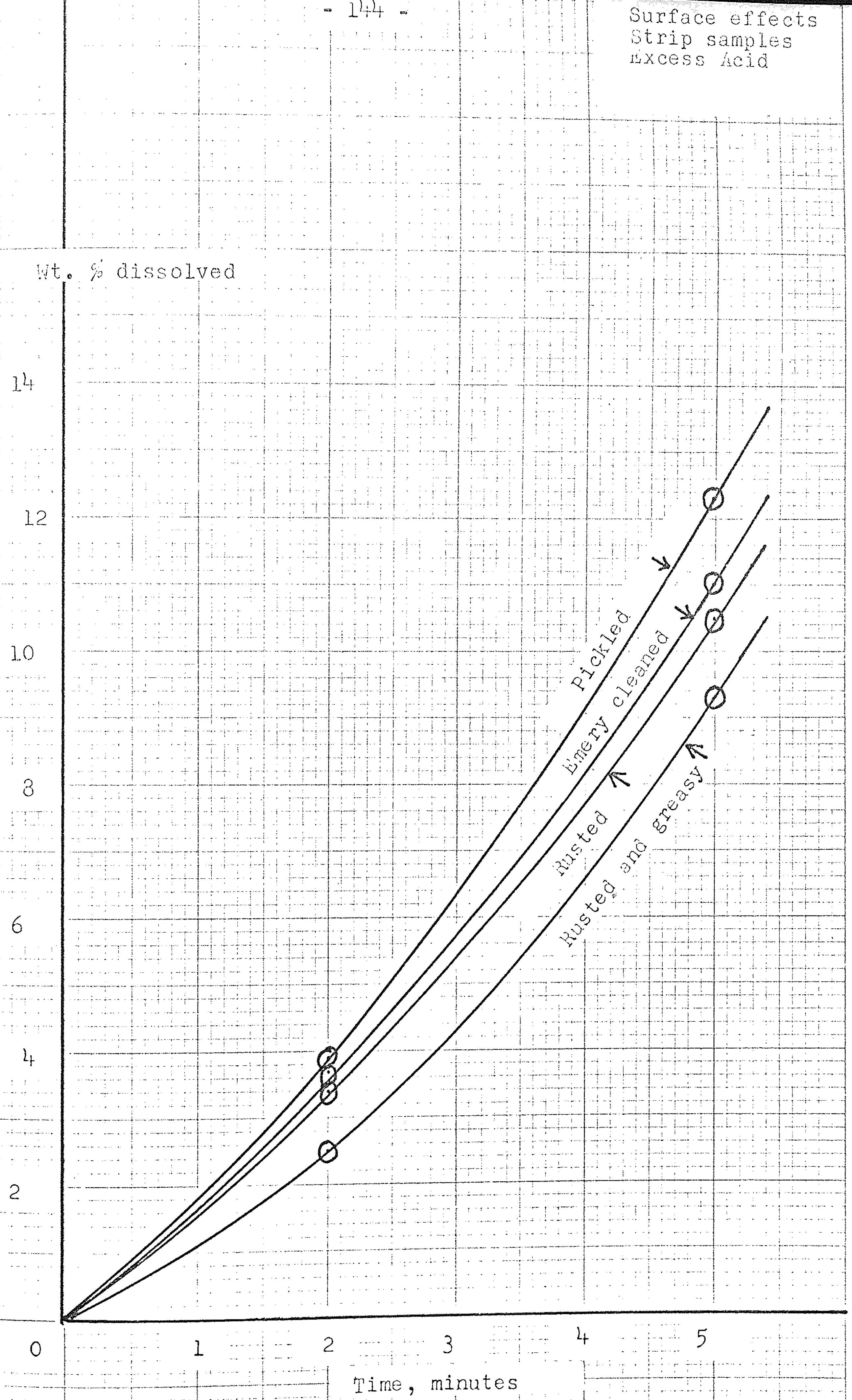

Surface effects
Strip samples
Excess Acid
Wt. % dissolved
14
12
10
8
6
4
2
0
1
2
3
4
5
Time, minutes
Pickled
Emery cleaned
Rusted
Rusted and greasy

Figure 3.20

approximately constant surface area, whereas the high carbon rod dissolved very unevenly, the ends particularly became very jagged. A coating of what was thought to be insoluble black carbon built up on the rod surface and also discoloured the solution, but this did not appear to affect the dissolution reaction significantly. Subsequent analysis indicated that this "ash" layer might tend to hinder reaction, although it is thought that hydrogen evolution may effectively break this layer up. As a wide range in composition of irons and steels is likely to be encountered in practice, an investigation of the behaviour of various types of ferrous metals and alloys would be necessary.

In a heterogeneous system involving solids, there are two basic conventional theories - particles of unchanging size, and particles of reducing size finally disappearing (3-6). The latter situation exists in this investigation and there are three essential steps that take place:

(1) Diffusion of reactant (HCl) through the film surrounding the particle to the solid surface.

(2) Chemical reaction of iron and acid.

(3) Diffusion of reaction products through the film back into the main body of liquid.

In the reaction under investigation, there was the added complication of evolution of hydrogen which may affect steps (1) and (3) by hindering or aiding diffusion. Levenspiel (3-6) has derived equations for the two situations of diffusion control or chemical reaction control which are:

For film diffusion controlling:

$$\frac{t}{T} = 1 - \left(\frac{r}{R}\right)^3 = X \qquad \text{(Eqn. 3.2)}$$

and for chemical reaction controlling:

$$\frac{t}{T} = 1 - \frac{r}{R} = 1 - (1 - X)^{\frac{1}{3}} \quad \text{(Eqn. 3.3)}$$

where t = time

T = total time for complete reaction

r = thickness (radius) of sample after time t.

R = original thickness of sample

X = mass fraction of material reacted in time t.

Equations 3.2 and 3.3 may be represented graphically in Figure 3.21A and B respectively.

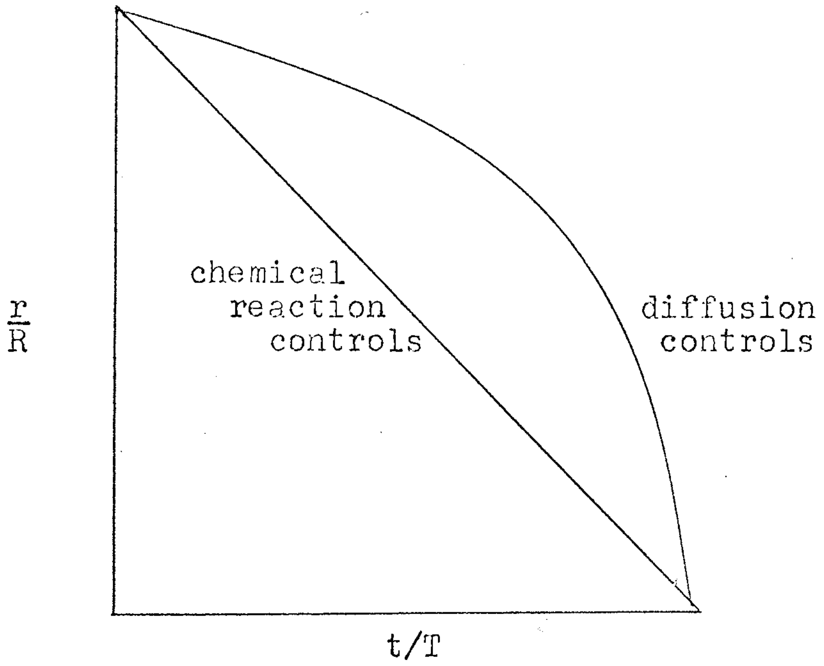


Figure 3.21A

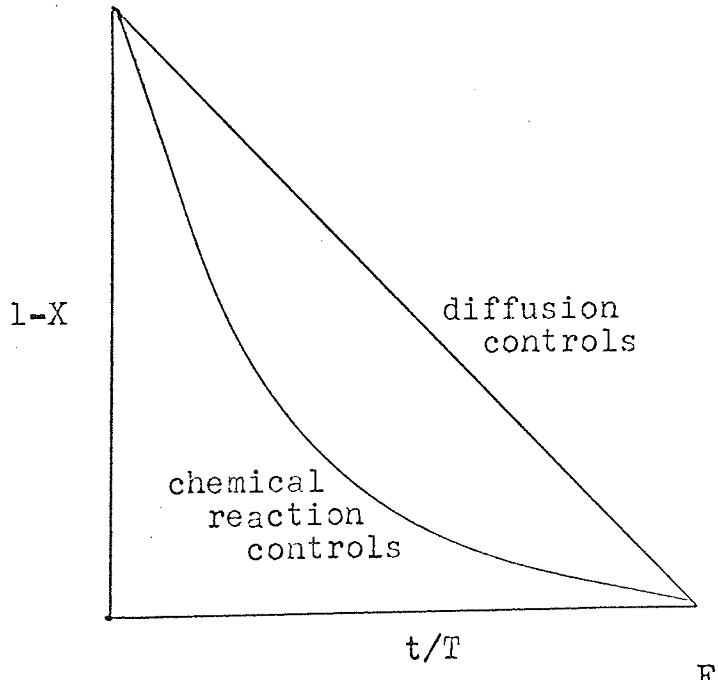


Figure 3.21B

Based on the above theory similar graphs were plotted from the data in Table 3.9 (derived from Table 3.8) and these are reproduced in Figure 3.22. Only one temperature, 100°C was taken as representative of the range studied, and each of the three systems investigated was included. The shape of these graphs indicated that chemical reaction was probably the controlling step. The deviation in the upper graph of the rod sample which might be taken as indication of ash diffusion controlling, was thought to be due to the layer of insoluble carbon that built up and hindered diffusion of acid and ferrous chloride.

The rate of reaction may be expressed generally as (3-6):

$$- r = - \frac{dC}{dt} = k'.C^n \qquad \text{(Eqn. 3.4)}$$

where r = rate of reaction

C = concentration

t = time

k = reaction rate constant

n = order of reaction

If $n = 0$, a zero order reaction,

$$- r = - \frac{dC}{dt} = k'$$

integration gives:

$$C_{initial} - C = C_{initial} .X = kt$$

where X = fraction reacted

If $n = 1$, a first order reaction,

equation 3.4 integrates to:

$$- \ln \left(\frac{C}{C_{initial}}\right) = - \ln (1 - X) = k'. t \qquad \text{(Eqn. 3.5)}$$

TABLE 3.9

Expt. No.	Time t mins.	Total Time T mins.	Thickness initial	Thickness final	X	$\frac{t}{T}$	$\frac{r}{R}$	1-X
Strip samples, excess adid								
102	10	60	0.165	0.127	0.23	0.17	0.77	0.77
103	20	"	"	0.114	0.43	0.33	0.69	0.57
104	25	"	"	0.102	0.53	0.42	0.62	0.47
105	30	"	"	0.079	0.59	0.50	0.48	0.41
106	40	"	"	0.053	0.75	0.67	0.32	0.25
Rod samples, excess acid								
127	10	130	0.634	0.589	0.16	0.08	0.93	0.84
128	20	"	"	0.556	0.30	0.15	0.88	0.70
129	25	"	"	0.536	0.35	0.19	0.85	0.65
130	30	"	"	0.531	0.40	0.23	0.84	0.60
131	49	"	"	0.480	0.54	0.64	0.76	0.46
Strip samples, stoichiometric acid								
150	15	100	0.165	0.130	0.26	0.15	0.79	0.74
151	25	"	"	0.112	0.39	0.25	0.68	0.61
152	35	"	"	0.097	0.50	0.35	0.59	0.50
153	45	"	"	0.081	0.61	0.45	0.49	0.39

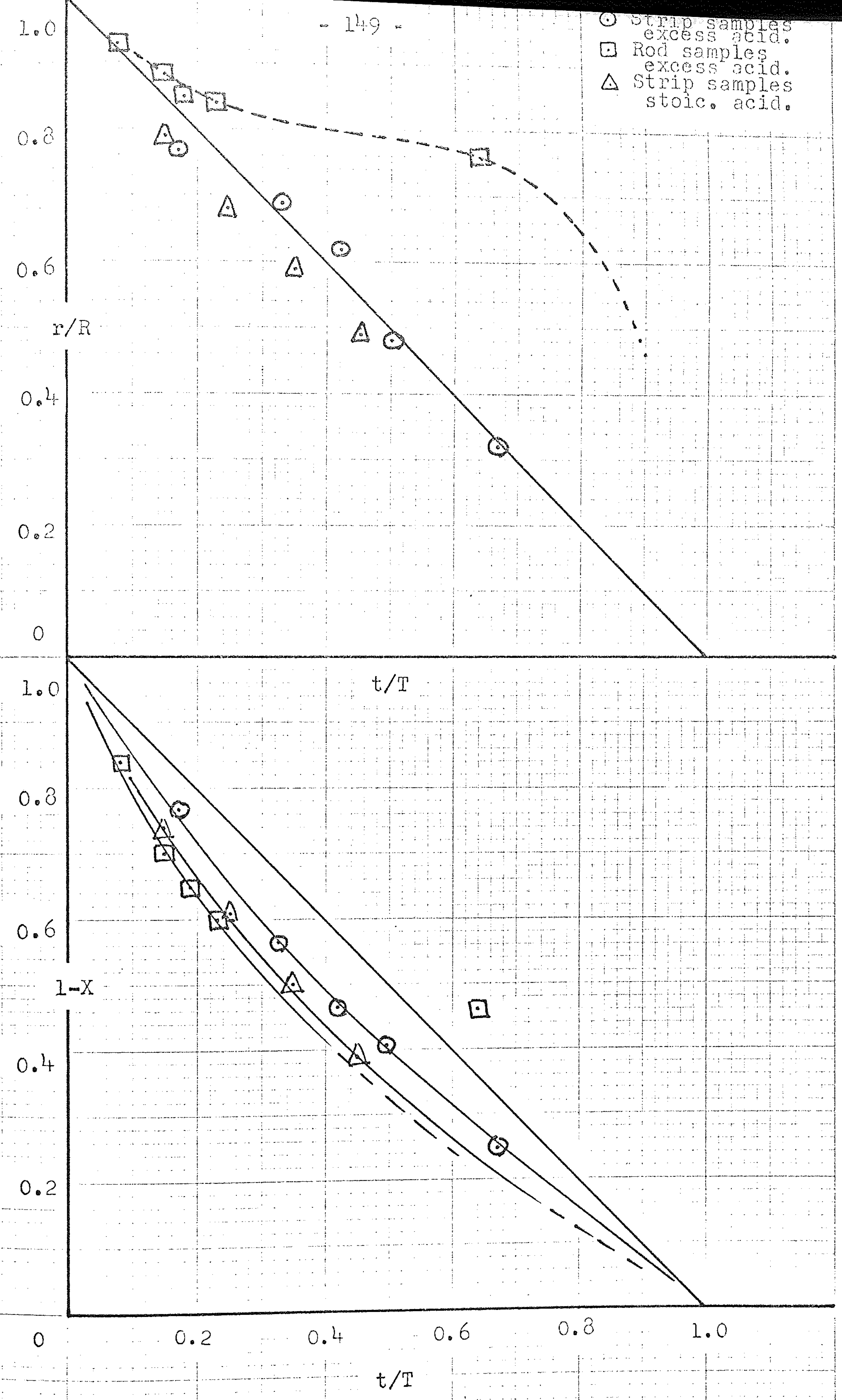

⊙ Strip samples excess acid.
⊡ Rod samples excess acid.
△ Strip samples stoic. acid.
r/R
1.0
0.8
0.6
0.4
0.2
0
t/T
1-X
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
t/T

Figure 3-22

and if $n \neq 1$, a fractional, second, third, or fourth order reaction, integration of equation 3.4 gives:

$$C_{\text{initial}}^{1-n} \cdot \left((1-X)^{1-n} - 1 \right) = (n-1)\, K't$$

The curve of the extraction lines for stoichiometric acid in Figures 3.18 and 3.19 indicated that the reaction was not zero order but a higher order. The graphs for excess acid were near straight lines, Figures 3.14 to 3.17, particularly when average surface area was included, Figures 3.15 and 3.17, as would be expected if the rate of reaction was dependant on acid concentration, which did not change appreciably in those experiments.

Since reaction with stoichiometric acid approaches the conditions likely to be found in an industrial process, the subsequent analysis is based on those results. A first order reaction was assumed initially, and a graph plotted of $- \ln (1-X)$ versus t, Figure 3.23, from results in Table 3.10. Straight lines were obtained, although there was a little scatter on the 80°C points, which was considered due to experimental error. Further values of n were therefore not tried as this first order approximation was considered acceptable. The gradient of the lines of Figure 3.23, gives the reaction rate constant, k' (from Equation 3.5):

0.0060	min^{-1}	at	80°C
0.0105	min^{-1}	at	90°C
0.0198	min^{-1}	at	100°C
0.0243	min^{-1}	at	105.5°C

The activation energy was found by plotting a graph of ln k' versus $1/T^{o}K$, Figure 3.24. As a straight line was obtained Arrhenius law, $k' = A.e^{-E/RT}$, was considered

TABLE 3.10

Expt. No.	Temp. °C	X	1-X	Time mins.	$\frac{1}{1-X}$	-ln(1-X)
141	80	0.080	0.920	15	1.09	0.0862
142	"	0.083	0.917	30	1.09	0.0862
143	"	0.226	0.774	45	1.29	0.2546
144	"	0.355	0.645	75	1.55	0.4383
145	"	0.440	0.560	90	1.79	0.5822
146	90	0.080	0.920	10	1.09	0.0862
147	"	0.254	0.746	30	1.34	0.2927
148	"	0.417	0.583	50	1.72	0.5423
149	"	0.568	0.432	80	2.31	0.8372
150	100	0.255	0.745	15	1.34	0.2942
151	"	0.394	0.606	25	1.65	0.5008
152	"	0.500	0.500	35	2.00	0.6931
153	"	0.605	0.395	45	2.53	0.9290
154	105.5	0.227	0.773	10	1.29	0.2546
155	"	0.385	0.615	20	1.63	0.4886
156	"	0.533	0.467	30	2.14	0.7608
157	"	0.612	0.388	40	2.58	0.9478
158	"	0.703	0.297	50	3.37	1.2149

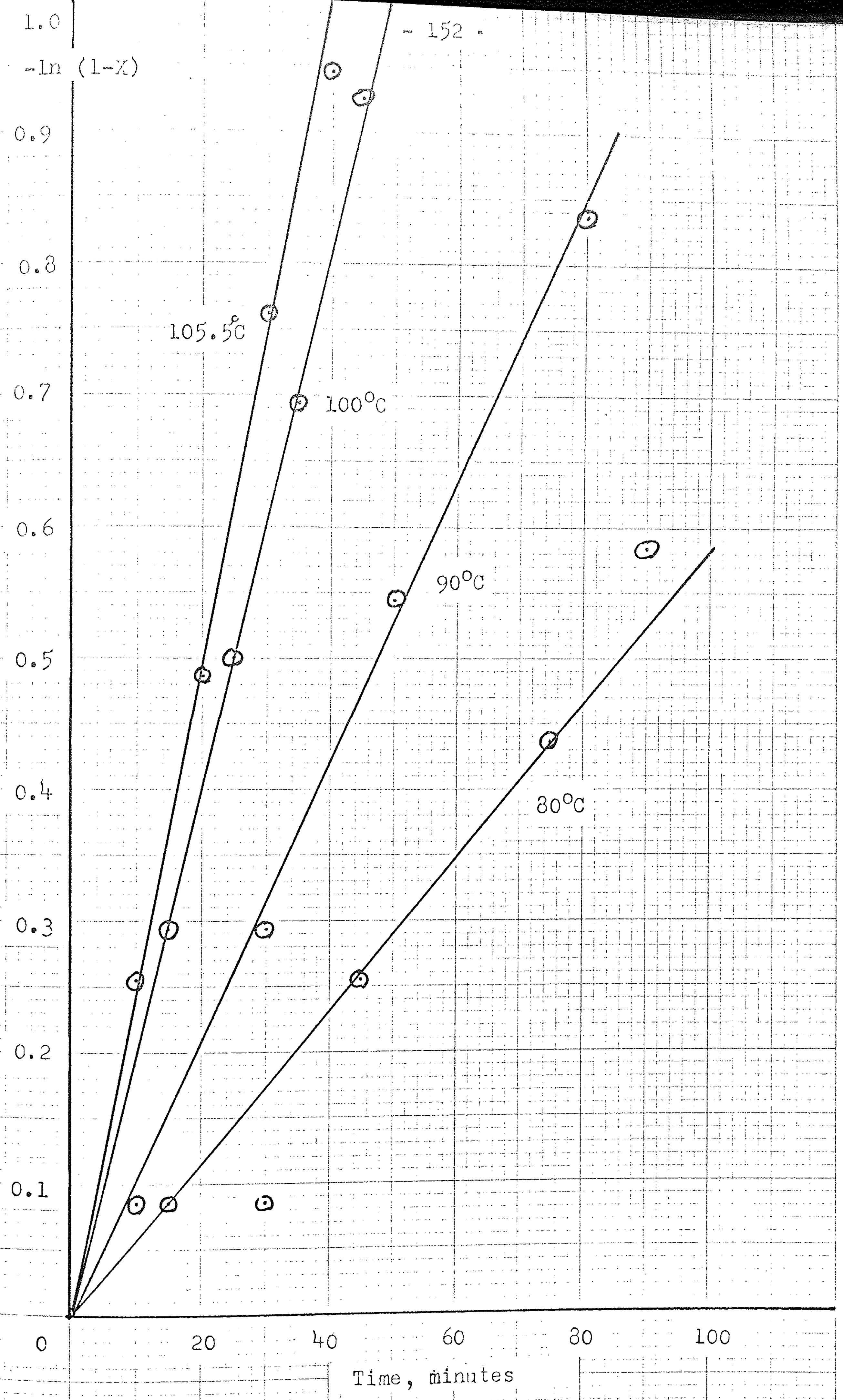

1.0
-ln (1-X)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
105.5°C
100°C
90°C
80°C
20
40
60
80
100
Time, minutes

Figure 3-23

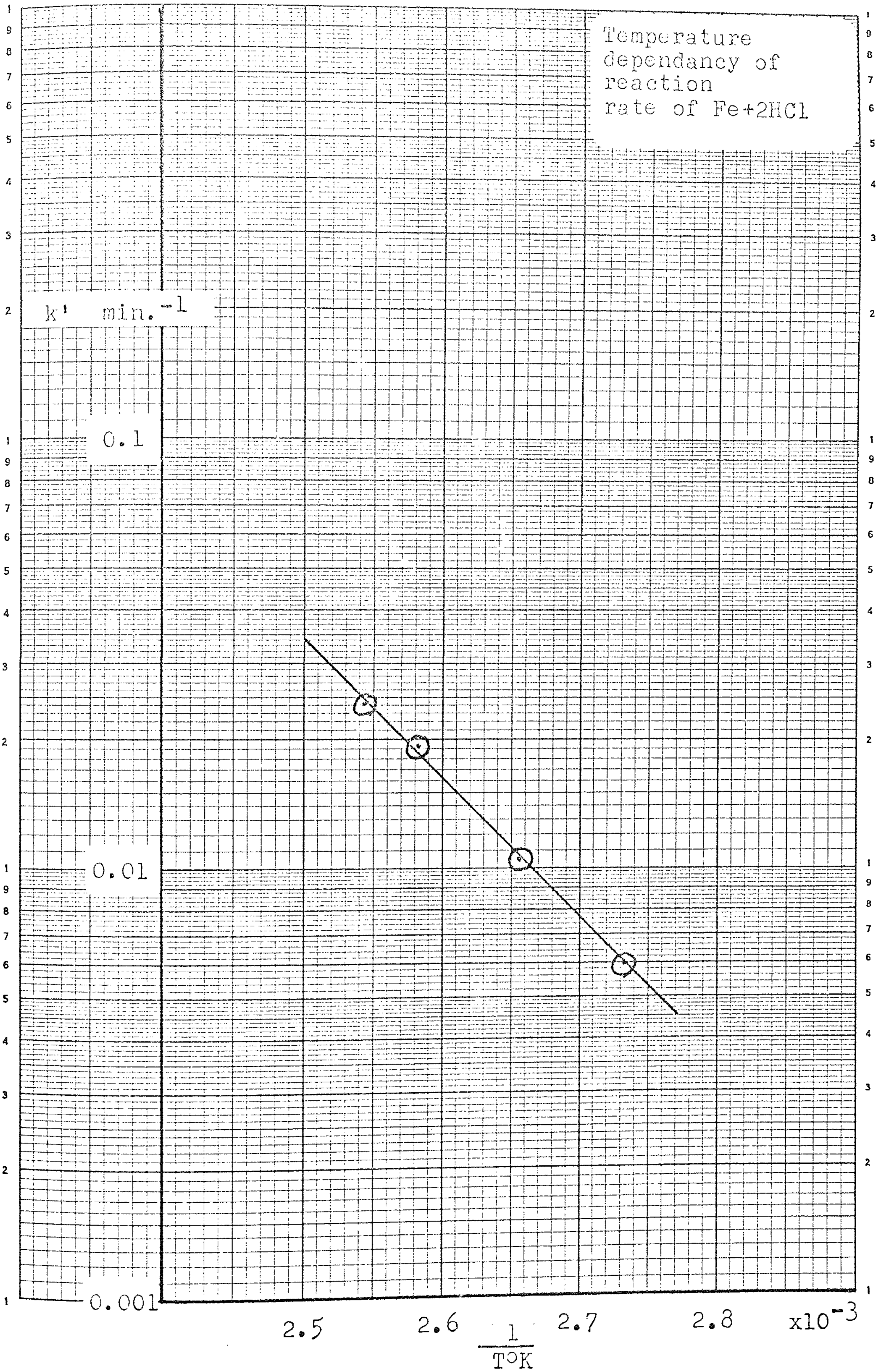

Temperature dependancy of reaction rate of Fe+2HCl
k' min.$^{-1}$
0.1
0.01
0.001
2.5
2.6
2.7
2.8
x10^{-3}
$\frac{1}{T^{o}K}$

Figure 3.24

to hold;

where A = constant
E = activation energy
R = gas constant
T = temperature, °K.

The slope of the line in Figure 3.24 was found algebraically:

$$\frac{\ln\left(k1'/k'_2\right)}{\left(\frac{1}{T_2} - \frac{1}{T1}\right)} = \frac{E}{R}$$

using the upper and lower values of k', from which E was found to be 14550 cals/ g mole Fe. Levenspiel (3-6) states that reactions with a high activation energy (above 10,000 cals/g mole) are usually held to be chemical reaction controlling which supports the earlier conclusions.

The reaction between iron and hydrochloric acid is a heterogeneous system involving liquid and solid phases (gas also, but this is considered later), and the rate of reaction would be expected to be a function of surface area as well as concentration of iron or acid. Some difficulty was encountered in relating surface area to concentration, but the following theory has been satisfactorily developed to form the basis of a continuous reaction system. In order to keep the model simple, it was necessary to make the following assumptions.

1) The average surface area of the metal is constant during the course of the reaction.
2) The fluid phase density is constant.
3) The volume occupied by the solid phase is constant.
4) The temperature is constant.

(In practical terms these assumptions will tend to overdesign the reactor).

The nomenclature is:

t = time, minutes

s = surface area of metal exposed to acid, cm^2

V = volume of liquid, $cm3$

a = $\frac{s}{V}$, surface area of metal per unit volume of liquid, $\frac{cm^2}{cm3}$

C = concentration of acid, g. moles/cm^3

Consider the change in acid concentration between t and t + dt:

$$\text{Input} - \text{Output} = \text{Accumulation}$$

$$0 - (-r).s.dt = V\left(\left(C + \frac{dC}{dt}.\, dt\right) - C\right)$$

where (-r) is the rate of disappearance of acid per unit surface area of exposed metal.

Hence,

$$-\frac{dC}{dt} = (-r).\,\frac{s}{V}$$

$$= (-r).a$$

Experimentally, $(-r) = k.C$ (from eqn.3.4)

and therefore $-\frac{dC}{dt} = k.C.a$ (Eqn. 3.6)

where k is the reaction rate constant.

Integration gives:

$$-\int_{C_{\text{initial}}}^{C} \frac{dC}{C} = k.a.\int_0^t dt$$

or $$\ln \frac{C_{\text{initial}}}{C} = (k.a).t \qquad \text{(Eqn.3.7)}$$

which gives the time for reaction to any specified extent.

Units are important.

$(-r)$: $\frac{\text{g moles}}{\text{min. cm}^2}$

$(-ra)$: $\frac{\text{g moles}}{\text{min. cm}^3}$

k : $\frac{\text{cm}}{\text{min}}$

ka : $\frac{1}{\text{min}}$

Alternatively the change in mass of metal may be considered.

From stoichiometry,

$$-dN_A = -2\ dN_M$$

where N = number of g moles of component in the system. (A- acid, M- metal)

$$\text{or } -\frac{dN_A}{V} = -2\ \frac{dN_M}{V}$$

$$\text{since } \frac{N_A}{V} = C$$

$$-2\ \frac{d(N_M/\ V)}{dt} = -\frac{dC}{dt} = k.a.C.$$

rearrangement gives:

$$-\frac{d\ N_M}{dt} \cdot \frac{1}{V} = \frac{k}{2} \cdot \frac{s}{V} \cdot C.$$

$$\text{or } -\frac{1}{S} \cdot \frac{dN_M}{dt} = \frac{k}{2} \cdot C$$

Under stoichiometric conditions,

$$N_{A}\text{ initial} = 2\ N_M\text{ initial}$$

$$(N_{A\text{ initial}} - N_A) = 2\ (N_{M\text{ initial}} - N_M)$$

$$\text{hence } N_A = 2\ N_M$$

$$\text{and therefore } -\frac{1}{S} \cdot \frac{dN_M}{dt} = \frac{k}{2} \cdot 2 \cdot \frac{N_M}{V}$$

$$\text{or } -\frac{dN_M}{dt} = k.\frac{s}{V}.\ N_M$$

$$= k.a. N_M \qquad \text{(Eqn. 3.8)}$$

which may be compared with equation 3.6

The experimentally determined reaction rate constants, k', are related to the theoretically derived constant k by:

$$k' = k\ a$$

$$\text{or } k = \frac{k'}{a}$$

which gave the following values of k, cm^3/cm^2. min.:

2.21×10^{-2} at $80^\circ C$

3.67×10^{-2} at $90^\circ C$

6.82×10^{-2} at $100^\circ C$

9.02×10^{-2} at $105.5^\circ C$

By Arrhenius' law,

$$k = ko.e^{-E/RT}$$

from which ko was found to be $2.136 \times 10^6 \frac{cm^3}{cm^2.\ min}$

and the rate equation became:

$$-r.a = -\frac{dC}{dt} = 2.136 \times 10^6.\ e^{-7323/T}.C.a \quad \frac{g.\ moles}{cm^3.\ min}$$

(Eqn. 3.9)

It must be emphasized that the object of this work was to produce a viable design for a reaction system, and the above theory and model, although sufficient for this purpose, is not the only one, nor necessarily the best. For example the model could include changes in area during reaction by considering the change in volume or mass, or thickness of sheet, as reaction proceeds. Allowance could be made for different shapes, weight/area characteristics, and wide size ranges of commercial scrap. There is a considerable amount of interesting and worthwhile work to be done in this field.

3.3.5 Discussion of results and application to reactor design

The reaction between iron and hydrochloric acid in stoichiometric proportions has been found to be a first order reaction, with chemical reaction controlling the overall rate of reaction, which is:

$$-r.a = 2.136 \times 10^6 . e^{\frac{-7323}{T}} . C.a. \ \frac{g.\ moles}{cm^3.\ min}$$

This exploratory experimentation has indicated that two factors appear to be significant in designing a reaction system - surface area and temperature.

The surface area to weight ratio of commercially available blended scrap metal may be taken as constant, in the absence of any other information, and shearing machines to increase this surface area appreciably are likely to be very expensive both in capital and operating costs. In certain areas however borings, having a high surface area to weight ratio, may be encountered. The cheapest form of scrap normally available in bulk is destructor grade (see Section 2.2.2) which is usually in bales of about three cubic feet, of a fairly high surface area per unit mass. Higher grades of scrap iron tend to have reducing surface areas per unit mass as the grade improves and cost increases. The reactor system should therefore be capable of handling baled destructor scrap with a high proportion of non-iron and non-metal inclusions, as well as higher grades of scrap.

In order to obtain a high rate of dissolution a high temperature is necessary. The maximum temperature obtained in the experimentation was 105.5°C but a commercial sized reactor may use higher temperatures by operating at elevated pressures, and 110°C is proposed. This has the advantages of higher rates of reaction, and pressure a little above atmospheric which will tend to keep oxygen out of the system,and at the same time not introduce difficulties into a reactor loading mechanism. Low temperature heat is relatively inexpensive, but costs more as the temperature rises. Pressure follows a similar pattern, but only significantly affects the capital cost of equipment. A detailed economic optomisation study of the reactor system would be interesting and worthwhile, but is unfortunately beyond the scope of this dissertation.

A preliminary morphological analysis of liquid-solid reactors has been carried out (3-12) which has been summarised in Table 3.6, Section 3.2. Due to the high corrosivity of the reactor contents it is important to keep the basic design as simple as possible with as few moving parts as possible. This is best achieved by stationary "equipment", stationary solid phase, and moving liquid phase.

Design details and calculations are presented in the following sections.

3.3.5.1 Throughput

The process employing scrap iron as feedstock was outlined in Section 2.9, and manufactures 50,000 tons per year iron powder. Allowing an overall loss of 10% on feed for actual losses and feedstock impurities, and including the loss of ferric oxide in the purification step equivalent to one third of the iron throughput, then 82,500 tons per year scrap iron have to be reacted.

Annual throughput of Fe	82500 tons
Hourly " " (8000 hrs./year)	10.31 tons
or	23100.0 lbs.
or	10478 kg.
or	10.478×10^6 g.

The following reaction takes place:

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

Molecular weights: 55.85 72.92 $\longrightarrow$ 126.76 2.016 (Appendix II)

which gives:

Hourly throughput of HCl	13.681×10^6g
" " " HCl solution (20% wt.)	68.405×10^6g
" production of H_2	0.378×10^6g
" " " $FeCl_2$	23.781×10^6g

The volumetric throughputs may be calculated from densities of iron, 7.5 g/cm^3; aqueous ferrous chloride + 20% wt. hydrochloric acid, 1.1 g/cm^3 (approximate as no accurate information is available); hydrogen, 0.1060 g/l. at 120°C and 1.7 atm. (3-1):

Volumetric hourly throughput of Fe	1.397×10^6 cm^3
" " " " HCl soln.	62.186×10^6 cm^3
" " " " H_2	3566.0×10^6 cm^3

3.3.5.2 Residence time

A rate equation was derived in Section 3.3.4 which integrated to:

$$k.a.t = \ln \frac{C_{\text{initial}}}{C}$$

$$\text{or} \quad t = \frac{1}{k.a} \cdot \ln \frac{C_{\text{initial}}}{C}$$

where t = time for reaction, minutes

k = reaction rate constant, $\frac{cm}{min}$

a = surface area of metal per unit volume of solution, $\frac{cm^2}{cm^3}$

C = acid concentration

At 110°C, the chosen operating temperature, k = 0.126 cm/min. 'a' was 0.27 cm^{-1} for the experimental work and was assumed constant in the theoretical derivation. It is thought that 'a' may vary between 0.1 and 0.5 cm^{-1} for different types of scrap metal, and that a cautious value of 0.2 cm^{-1} is reasonable in the absence of accurate information. The concentration ratio is taken as 20 from discussion in Section 4. The time for reaction, t, is:

$$t = \frac{1}{0.126 \times 0.2} \log_e 20 \text{ minutes}$$

$$= 118.9 \text{ minutes}$$

As the leaching reaction is chemical reaction controlling, the residence time, and hence volume also, will double approximately for each 10°C drop in temperature.

3.3.5.3 Temperature

From the thermodynamic information in the Appendix, the reaction

$$Fe_{(S)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_2\ (g)$$

is exothermic, H = 20,3000 cals/g. mole $FeCl_2$.

While it may be necessary to provide localised cooling near the reactor inlet, control of acid inlet temperature based on reactor outlet temperature is thought to be sufficient.

The heat generated by the reaction may be calculated:

Hourly throughput of iron = 10.478×10^6 g. (Section 3.3.5.1)

= 1.87×10^5 g. moles

Heat generated = $(1.87 \times 10^5) \times 20{,}300$ cals/hr.

= 3.81×10^9 cals/hr.

Total hourly reactor throughput = 78.883×10^6 g./hr. (Section 3.3.5.1)

This represents 48.5 cals/gm reactor throughput. The scrap iron is fed at ambient temperature and considerable evaporation of aqueous acid is likely to occur by evolution of hydrogen at the temperature of reaction, which is calculated in Section 6. Together these are expected to absorb a considerable proportion of the heat generated by reaction, and thus enable the temperature control system outlined above to be effective. A heat balance is included also in Section 6 which shows that additional heat exchange appears to be unnecessary, although if the temperature profile through the reactor deviates widely from 110°C, the reaction rate will vary and affect the reactor volume.

Under these circumstances it is possible to analyse the reaction system by analogue or digital computer using the mathematical model derived earlier and data provided herein, to discover the effect of initial acid temperature on final acid concentration, and/or reactor volume, under constant heat conditions. A differential equation may be set up relating rate of reaction with heat generated and heat capacities, which could be solved by analogue or digital simulation computation to either give the reactor effluent composition for a given reactor volume, or the reactor volume necessary for a specified reactor effluent composition. Alternatively this approach could be simplified by splitting the reactor into finite lengths and calculating heat balances etc., over each length. While development along these lines is likely to be interesting and worthwhile, in the context of providing a practical solution, it must be considered beyond the scope of this dissertation.

3.3.5.4 Pressure

Equations for the partial pressure of water and hydrogen chloride over hydrochloric acid are given by Perry (3-1) as:

$$\text{Water: } \log_{10} p.\ \text{mm} = 8.97877 - \frac{2334}{T}$$

$$\text{HCl: } \log_{10} p.\ \text{mm} = 10.3833 - \frac{3245}{T}$$

At 110°C, p for water = 767.0 mm

and p for HCl = 81.5 mm

This gives a total vapour pressure of 848.5 mm or 1.12 atm. As there is a large volume of hydrogen generated (Section 3.3.5.1) it is possible for the pressure to be maintained and controlled by a hydrogen blanket, at say 1.2 atm.

3.3.5.5 Reactor volume

For a residence time of 118.9 minutes, the volume of the reactor is made up of

$$\text{iron: } 1.397 \times 10^6\ \text{cm}^3 \times \frac{118.9}{60} = 2.768 \times 10^6\ \text{cm}^3$$

$$\text{acid: } 62.186 \times 10^6\ \text{cm}^3 \times \frac{118.9}{60} = 123.232 \times 10^6\ \text{cm}^3$$

hydrogen: this is produced continuously at the rate of 0.378×10^6 g./hr (Section 3.3.5.1) or 3566.0×10^6 cm^3/hr., and would be continuously removed. The hydrogen would however increase the volume of the fluid phase while the bubbles rise to the top of the reactor, and also collect in pockets. The speed of multiple gas bubbles rising through an aqueous medium is around 25 cm/sec. (3-11), which does not vary appreciably with different gases, aqueous phases or temperature etc. If the effective height of the reactor is 6 m, and assuming all the hydrogen is generated at the bottom of the reactor, then the time taken for hydrogen bubbles to travel the height of the reactor is 24 secs. As hydrogen is produced at the rate of 3566.0×10^6 cm^3) hr., the gas hold up is approximately 23.773×10^6 cm^3.

The total volume of the reactor is therefore 149.773×10^6 cm^3 or 149.773 m^3. If the overall shape is cylindrical with height equal to diameter, the dimensions are: height = dimater = 5.76 m. As the scrap iron feed may reach 1m. across, particularly for bales, this diameter appears reasonable to avoid "bridging."

The possible problem of the reactor volume being affected by temperature changes was discussed in Section 3.3.5.3.

3.3.5.6 Materials of Construction

The materials of construction of the reactor have to withstand highly corrosive materials as well as heavy physical wear and tear of large heavy lumps of iron falling through the reactor. While a range of materials are quoted as withstanding aqueous hydrochloric acid at 100°C, and aqueous ferric chloride (3-13), many are too expensive and/or difficult to fabricate on a large scale; for example platinum and tantalum. The essential requirements for the reactor are:

- a substantial outer support shell of steel or reinforced concrete,
- a corrosion resistant and gas-tight membrane of a rubber or a plastic e.g. butyl rubber, polypropylene or P.T.F.E.
- a shock and abrasion resistant inner lining of acid resistant brick.

Similar operating conditions are encountered in the metal pickling industry, and no difficulty is anticipated in constructing a suitable reactor.

3.3.5.7 Overall design and other features

By reference to the analysis of reactor functions in Table 3.5, the overall reactor design may be specified and is shown in Table 3.11and Figure 3.25. A number of features require amplification:

Hydrogen: Evolution of gas should effectively stir the reactor contents and remove some heat of reaction by evaporation of aqueous HCl, which may be recovered. The temperature of operation, 110°C, necessitates an operating pressure above atmospheric which may be controlled by hydrogen take off rates. This overpressure also helps prevent ingress of air. Disentrainment of aqueous solution and drying is also required prior to recycling to the reduction stage.

Ferrous chloride solution: The reactor product requires gas separation, and removal of insoluble impurities which may be carried over. Some of the clean solution is recyled to the hydraulic

TABLE 3.11

1.	Motion of water "in"	Pumped
2.	" " acid "	
3.	" " solid "	Mechanical feed
4.	Entry device for water	Inlet valve at reactor base
5.	" " " acid	
6.	" " " solid	Hydraulic seal using reactor effluent
7.	Distribution of water	Distribution device in reactor base, and evolution of gas
8.	" " acid	
9.	" " solid	Random/natural
10.	Energy transfer to liquid phase	Preheat
11.	Energy transfer to solid phase	None external
12.	Transport of acid through liquid bulk	Mixing effected by gas evolution
13.	Transport of acid through liquid laminar layer	
14.	Transport of acid through solid	--
15.	Transport of product through solid	--
16.	Transport of product through liquid laminar layer	Mixing effected by gas evolution
17.	Transport of product through liquid	
18.	Reaction equilibria	Goes to completion
19.	" kinetics	See previous sections
20.	" energy transfer to/ from solid	Heat of reaction absorbed by system
21.	Reaction energy transfer to/ from liquid	

22. Liquid separation from solid :) Impurities only;
) filtration after
23. Solid " " liquid :) reactor

24. Gas separation : After reactor

25. Liquid exit device : Weir

26. Solid " " : Impurities only; via liquid or reactor base

27. Liquid motion "out" : Gravity and/or pump

28. Solid " " : Impurities only, with liquid

29. Gas " " : Removed by compressor

Scrap iron dissolution reactor system

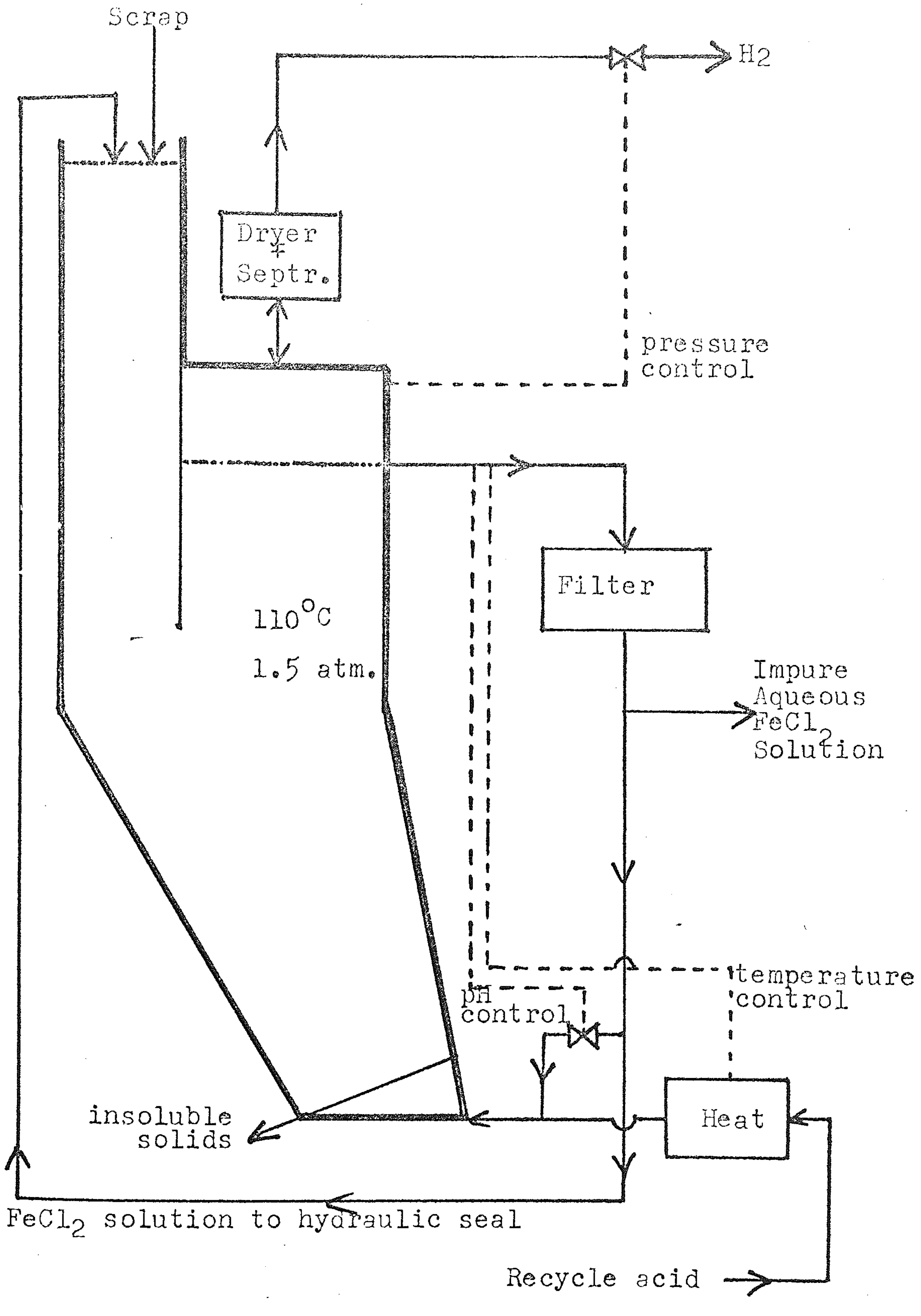


Figure 3.25

seal, and some may need to be recycled for pH control. The bulk of the solution goes to crystallisation/precipitation of $FeCl_2$, possibly via dissolved impurity recovery, for example copper by electrolysis.

Insoluble impurities: it is expected that insoluble impurities will tend to be carried out of the top of the reactor with the liquid effluent. Provision for removal from the base of the reactor is included.

Hydraulic seal: A simple "open" seal is shown in Figure 3.25 Experimentation is needed to find the best arrangement.

Controls: It is likely that temperature, pressure and pH controls will be necessary and these are included in Figure 3.25.

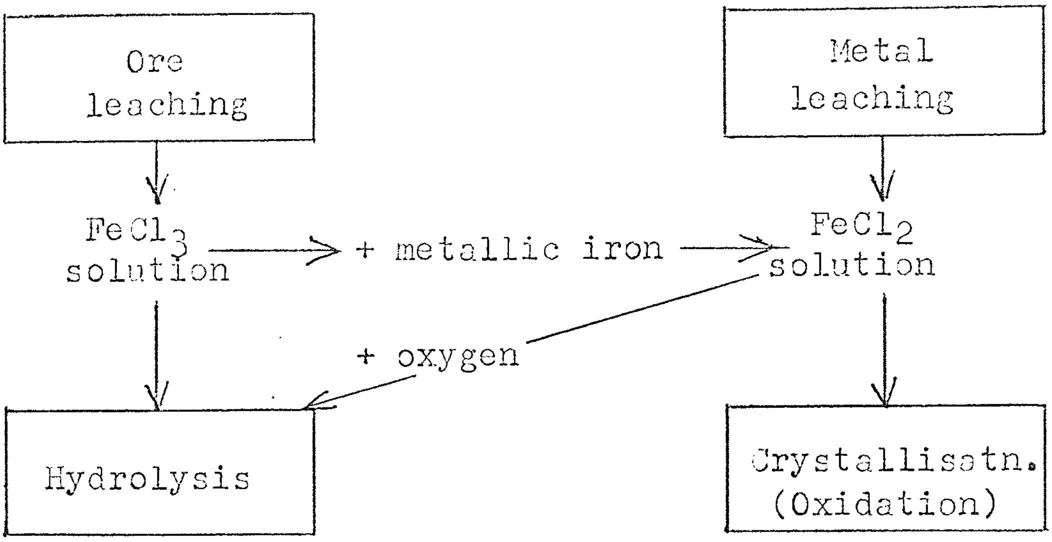
3.3.6 Conclusions

A reactor system has been designed in the previous sections to dissolve scrap iron with aqueous hydrochloric acid to produce 23781 Kg/hr. ferrous chloride in aqueous solution. The design is summarised in Figure 3.25 and the economics of the complete process calculated in Section 7.

It is clear that a substantial amount of work remains to be done. While the initial experimental results reported are valid, the effect of employing commercially available scrap iron in compressed bales, over wide size ranges, with a high proportion of impurities etc., requires determination. It is possible that a small bench scale model may provide further relevant information, and work is planned in this area together with reactor optimisation.

4. PURIFICATION

The processes proposed in Section 2.9 specify purification of ferric chloride solution from ore leaching by precipitative hydrolysis, and purification of ferrous chloride solution from scrap metal leaching by crystallisation. There is considerable flexibility between these processes which is shown below:



Ferric chloride solution may be reduced to ferrous chloride with scrap iron and crystallised; or the ferrous chloride solution hydrolysed with addition of oxygen. The former requires an additional reaction stage and the latter is likely to only require modifications to equipment. There is, therefore, considerable flexibility in the processes under investigation. Purification by hydrolysis is discussed in Section 4.1 with supporting experimentation, and crystallisation is discussed in Section 4.2. Further purification of the ferrous chloride produced by crystallisation is carried out by oxidation to ferric oxide and ferric chloride which is discussed in Section 4.4.

The impurities that are likely to occur in the leach liquors will need removing to prevent build-up in the recycle acid. This is discussed in Section 4.3.

4.1 Hydrolysis

A number of references have been found on precipitation of ferric oxide, basic nitrates and sulphates by heating aqueous solutions of nitrates or sulphates of iron to temperatures of 200°C or more under pressure, with or without the addition of oxygen (1-2). No references on parallel work on iron chlorides have been found however, although the gas phase oxidation and hydrolysis of iron chlorides has been completely surveyed by Topliss (2-1), and is discussed later in connection with one of the proposed processes. Superficially there appeared to be no valid reason why iron chlorides should not produce oxide under similar conditions.

4.1.1 Thermodynamics

Thermodynamic evidence supports the argument that hydrolysis will occur according to the reaction:

$$Fe_2O_3 + 6HCl \geqslant 2\,FeCl_3 + 3H_2O$$

The standard heat of reaction at 25°C, $\Delta H^o = -12{,}325$ cals/mole Fe product

The standard free energy of reaction at 25°C, $\Delta G^o = 1{,}026$ cals/mole Fe product

(Appendix II)

The free energy of reaction, ΔG is related to the equilibrium constant, K (3-6):

$\Delta G^o = - RT \ln K$

where ΔH^o = standard heat of reaction

ΔG^o = standard free energy of reaction

R = gas constant

T = temperature of reaction

K = equilibrium constant

and, $$K = \frac{(\text{concentration of } FeCl_3)^2}{(\text{concentration of } HCl)^6 \, (\text{concentration of } Fe_2O_3)}$$

More accurately, concentration is replaced by activity, but as there is no information on the activities of the solutions concerned, particularly at the high concentrations likely to be employed, this cannot be considered further.

The standard heat of reaction and free energy of reaction were calculated from data at 25°C (Appendix II), and could not be calculated at any other higher temperature due to lack of information, for example on heat of solution at different temperatures and varying heat capacities of solutions.

at 25°C $+ 1026 = - 1.98.298.\ln K$

and $\ln K = - 1.7389$

$= 2.2611$

and $K = 0.1757$

for the forward reaction shown above. The reverse reaction, hydrolysis of ferric chloride, has a negative free energy of reaction, and the reaction as shown above therefore goes to the left.

For the "ideal" reaction:

$$3H_2O + 2FeCl_{3(aq)} \rightarrow Fe_2O_{3(S)} + 6HCl_{(aq)}$$

$\Delta G = - 1026$ cals/mole $FeCl_3$ or $- 2052$ cals/Mole Fe_2O_3

$\ln K = 1.7389$ or 3.4778

and $K = 5.691$ or 32.39

which indicates that the reaction will take place as shown.

The equilibrium constant K is affected by temperature according to (3-6):

$$\frac{d\,(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

If ΔH is assumed constant and equal to ΔH^o (as it must be assumed in this case as there is insufficient data), this equation integrates to:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

For example at 200°C,

$$\ln\left(\frac{K_2}{32.39}\right) = -\frac{(+\,24,650)}{1.98}\left(\frac{1}{473} - \frac{1}{298}\right)$$

$$= 15.462$$

$$K_2 = 1.6791 \times 10^8$$

Although the result might be interpreted as showing the reaction goes to virtual completion at 200°C, no strong credence may be attached to the quantitative result as ΔH almost certainly will vary with temperature although the change cannot be calculated. However it can be shown that for an endothermic reaction, as in this case, the equilibrium conversion rises for an increase in temperature (3-6). For a variable ΔH, the above differential equation integrates to:

$$\ln \left(\frac{K_2}{K_1}\right) = \frac{1}{R}\int_{T_i}^{T_2} \frac{\Delta H}{T^2} \cdot dT$$

and H may often be expressed in the form:

$$\Delta H = \Delta H^o + \int_{T_o}^{T} \nabla Cp . dT.$$

Because of the complete absence of data, it was decided to undertake experiments, first to demonstrate the feasibility of the reaction and second to obtain some basic data for design.

4.1.2 Experimentation

The object of the experimental work was to demonstrate the feasibility of the hydrolysis reaction and obtain qualitative results and therefore sophisticated equipment was not considered necessary. Carius tubes were therefore employed. These are thickwalled borosilicate glass tubes, closed at one end, and with a constriction near the initially open end. The reaction tube is filled with reaction materials through the constriction to about two thirds of the volume then very carefully sealed. Such a tube will withstand considerable pressures and is regularly used at 200°C with water or ethanol as solvent bases when the internal pressure can reach 16 or 30 atmospheres respectively (4-1). Although special furnaces are designed for Carius tubes, in this case an ordinary laboratory furnace was used with a metal sheath put round the tube as an additional safety precaution and a safety screen round the furnace.

The reaction was investigated at three temperatures, 100°C, 150°C and 200°C, with four concentrations of ferric chloride, 25, 50, 100 and 200 g. per litre. Due to the heat capacity of the system, and the necessity of cooling the Carius tube before opening, which took several hours, it was not possible either to investigate the effect of different reaction times, or to analyse the reaction products immediately after reaction, which probably gave incorrect conversions due to the reverse reaction taking place at lower temperatures.

The precipitate formed by heating the tube to 100°C was yellow ochre in colour, and so finely divided that it settled only after prolonged standing; the precipitate at 150°C was purplish-brown and similarly finely divided; and at 200°C it was black (very dark brown when filtered and dried) and settled readily. Concentration of the initial ferric chloride solution did not affect the colour or apparent particle size. Filtration of the precipitates on a normal laboratory Buchner filter was not successful due to the small particle size, except for those at 200°C. This made subsequent analysis very difficult. A colour plate of the three types of precipitate is included, Plate 4.1, which also shows the sealing of the Carius tubes.

10 mls. of ferric chloride solution were titrated before and after each experiment using the standard iodine-thiosulphate titration. Ferric ions reduce iodide ions from potassium iodide solution to elemental iodine which forms a compled with further potassium iodide:

$$2Fe^{+++} + 3I^{-} \rightarrow 2Fe^{++} + \underset{(KI^{-}.I_2)}{I_3^{-}}$$

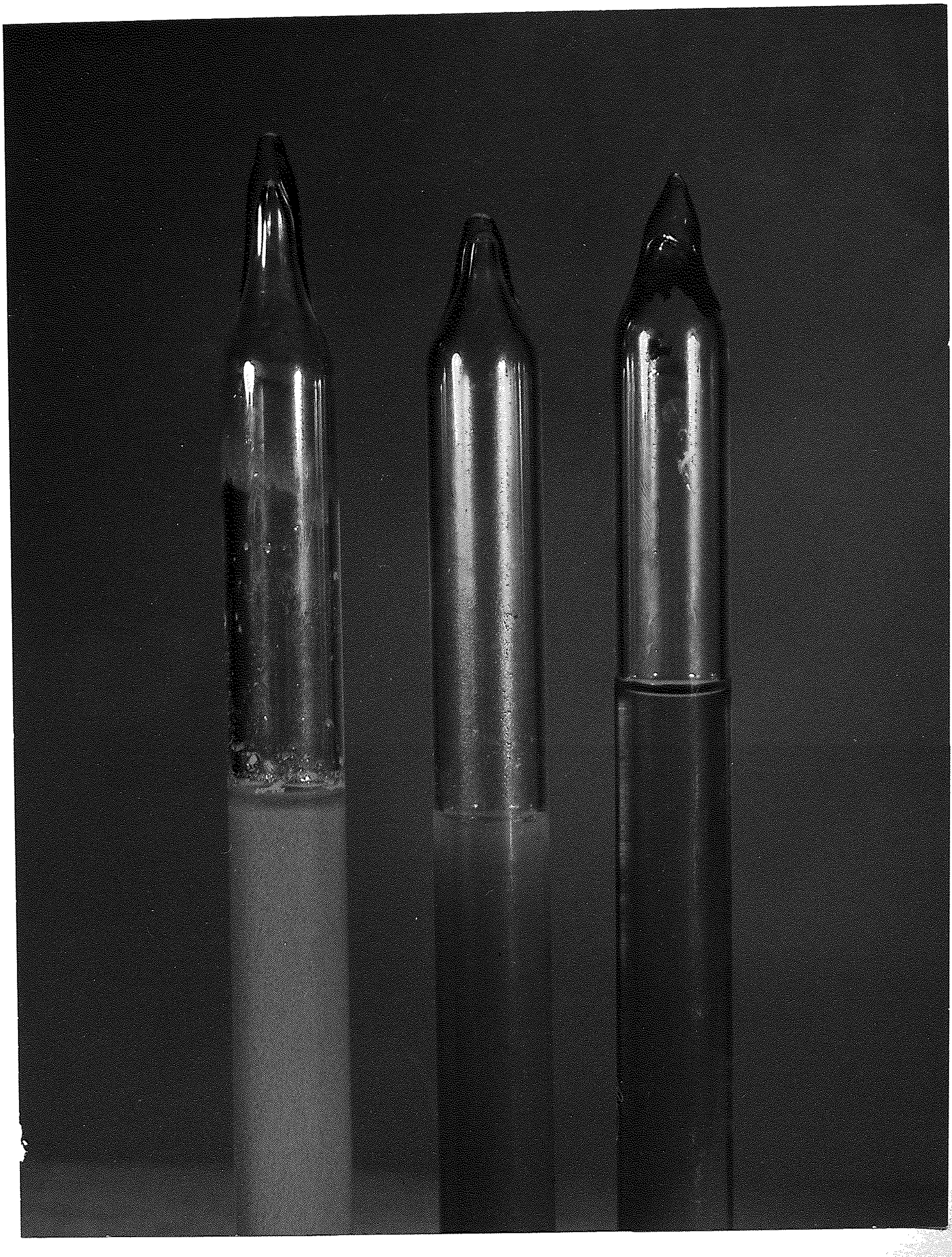
The iodine reacts with thiosulphate:

$$I_3^{-} + 2\ S_2O_3^{--} \rightarrow 3I^{-} + S_4O_6^{--}$$

The pH of the solutions before and after each experiment was also measured.

The quantitative results are given in Table 4.1 and presented graphically in Figures 4.1 and 4.2.

The solutions used at 200°C showed a substantially different Fe^{+++} ion concentration by titration from those



Hydrolysis of Ferric
Chloride in Carius
tubes @100,150,200°C
(200 g/l. $FeCl_3$)

Plate 4.1

Table 4.1

Hydrolysis of Aqueous Ferric Chloride

Analysis of Supernatant Liquid

Temp.	Nominal	Before Reaction			After Reaction			Convn.
°C	Concn. FeCl$_3$ g/l	Thio. titn.+ mls	Fe^{+++} concn. g/l	pH	Thio. titn.+ mls	Fe^{+++} concn. g/l	pH	%
100	25	1.5	8.38	1.7	1.2	6.70	1.0	20.0
100	50	2.9	16.19	1.5	2.6	14.52	0.9	10.3
100	100	5.95	31.83	1.3	5.7	31.27	0.7	4.2
100	200	11.9	66.45	0.9	11.3	63.10	0.6	5.0
150	25	1.5	8.38	1.7	0.5	2.79	1.0	66.7
150	50	2.9	16.19	1.5	1.8	10.05	0.8	37.9
150	100	5.95	31.83	1.3	3.7	20.66	0.7	37.8
150	200	11.9	66.45	0.9	8.7	48.58	0.4	26.9
200	25	1.5	8.38	-	0.2	1.12	0.7	86.7
200	50	2.7	15.08	-	1.2	6.70	0.6	55.6*
200	100	5.1	28.48	-	3.5	19.55	0.4	31.4*
200	200	9.6	53.6	-	8.8	49.15	0.2	8.3*

Notes: + mls of 1.0008 N sodium thiosulphate required for 10 mls ferric chloride solution (see text).

* corrected values are 58.5, 41.2, and 26.0, reading down. See text for explanation.

Hydrolysis
of
Ferric Chloride

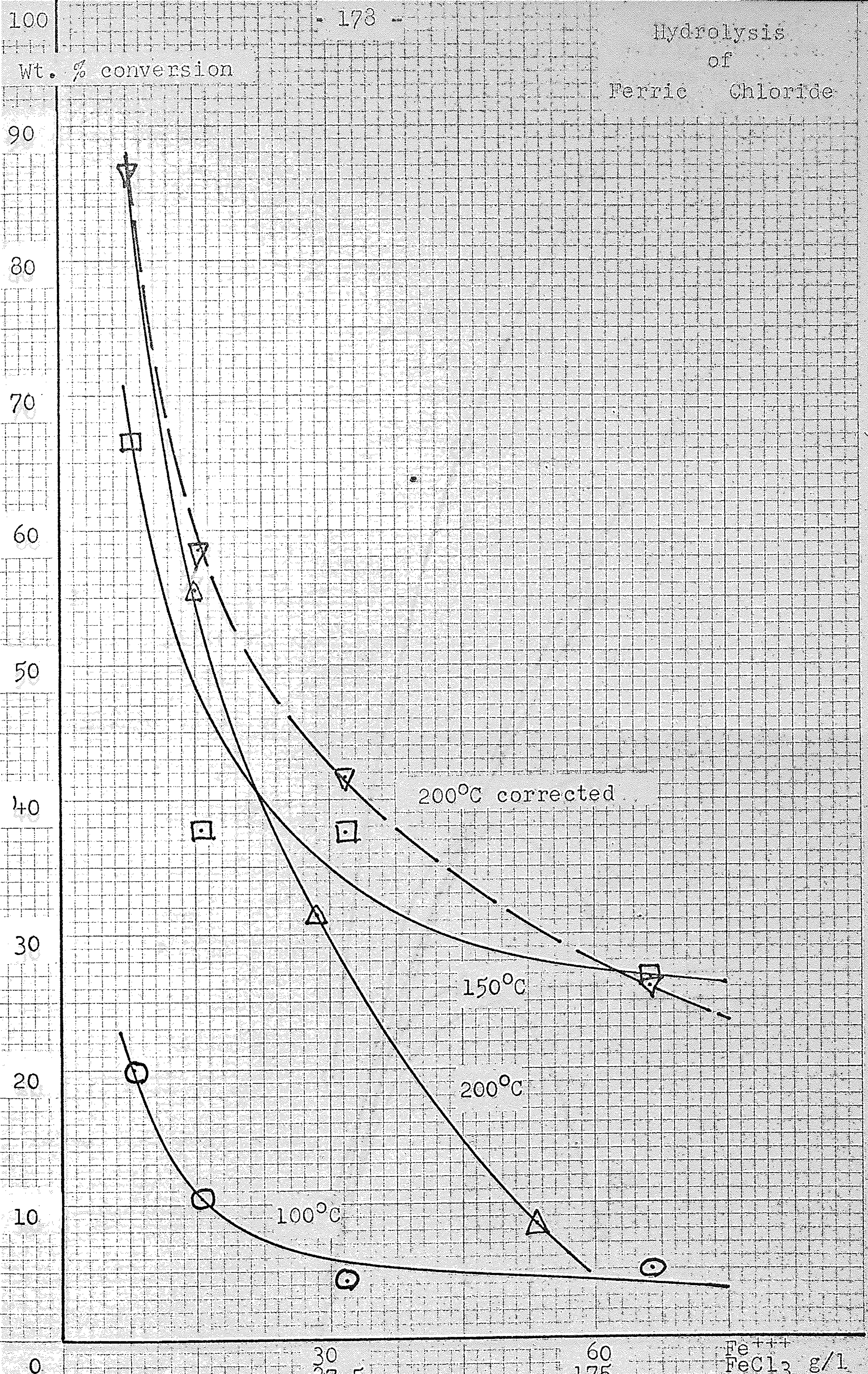


Figure 4.1

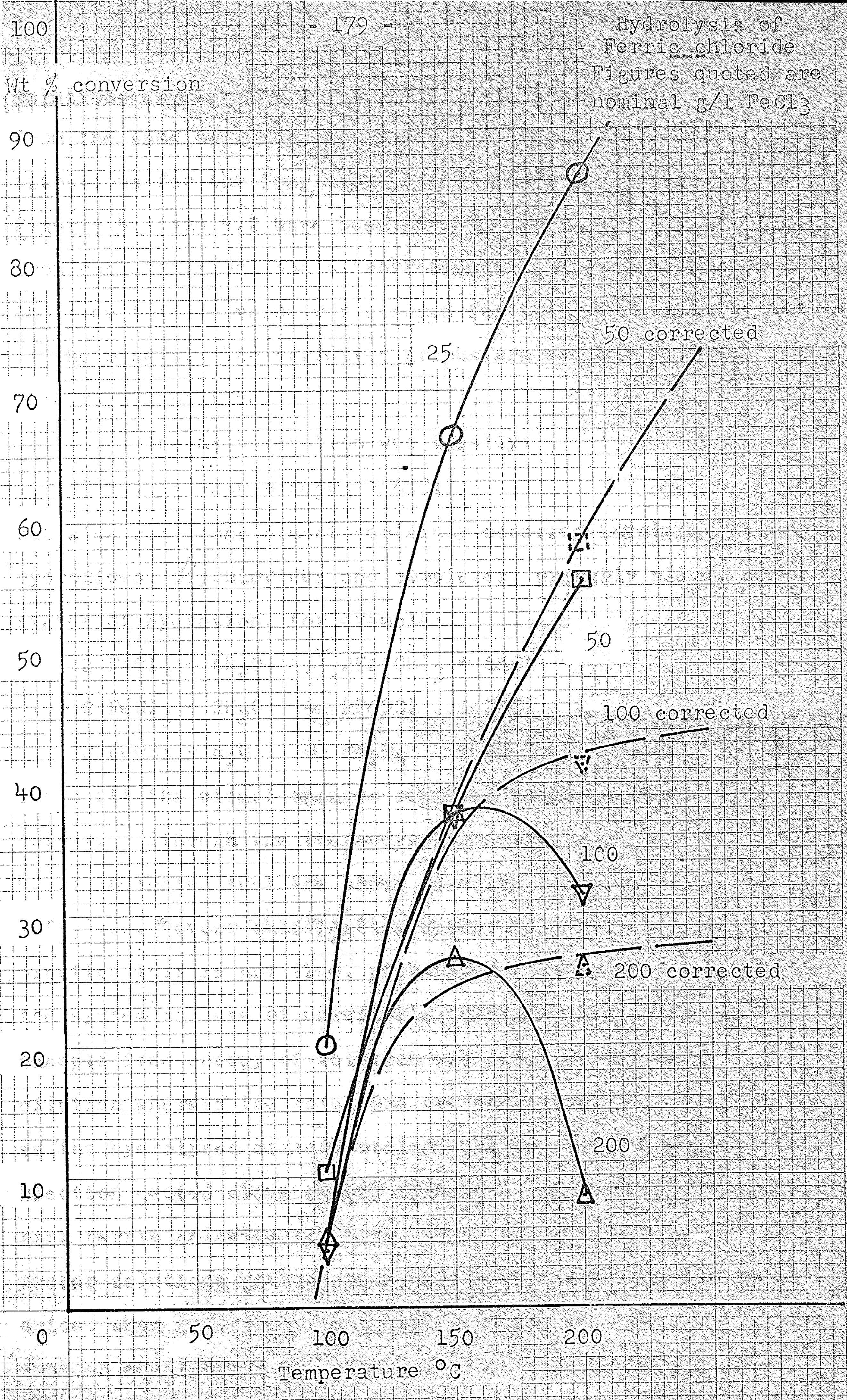

Hydrolysis of Ferric chloride
Figures quoted are nominal g/l $FeCl_3$
Wt % conversion
100
90
80
70
60
50
40
30
20
10
0
50
100
150
200
Temperature °C
25
50 corrected
50
100 corrected
100
200 corrected
200

Figure 4.2

solutions used at 150°C and 100°C. As each batch was taken from the same bulk supply, it was suspected that the titrations for the four experiments at 200°C were erroneous. Figures 4.1 and 4.2 have been plotted using both the measured iron concentration, and a "corrected"iron concentration when the same initial value was assumed for the 200°C experiments as the others. The corrected graphs are considered to be more representative.

The main reaction was ideally:

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl$$

but side reactions almost certainly occurred involving oxides, hydroxides, oxychlorides and complexes, probably all in various states of hydration, for example:

$$2\,FeCl_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 6HCl$$

$$2\,FeCl_3 + 2H_2O \rightarrow 2FeOCl + 2HCl$$

$$2\,FeOCl + H_2O \rightarrow Fe_2O_3 + 2HCl$$

These fit the visual changes reported above, particularly colour. Although the thermodynamic analysis in Section 4.1.1 indicated that the above reaction tends to go to the left, i.e. favour chloridation rather than hydrolysis, in practice this is not true, probably due to non-ideality of the system and use of unreliable thermodynamic data, for example free energy of solution was taken at infinite dilution whereas the solutions are concentrated. Consequently as the hydrolysed mixture cooled down for several hours, the reaction quoted above almost certainly was reversed to give back ferric chloride solution. This is supported by the weaker solutions giving apparently much higher conversion to oxide, when relatively less acid is produced. This suggested that an equilibrium was established at the pH quoted. There is also the formation of iron chloride complexes such as

$FeCl_4^-$, which was discussed in Section 3 and (1-2), and these are also dependant on acid and ferric chloride concentrations. The hydrocloric acid concentration after reaction was calculated from pH measurement and from conversion of ferric chloride (Table 4.1) but no meaningful results were obtained.

Schafer (4-9) has carried out an exhaustive investigation of the iron oxide/chloride systems both theoretically and practically, including a review of previous work. The gas phase hydrolysis of ferric chloride is included but no mention is made of the analogous aqueous phase reaction, which is surprising in view of his apparent thoroughness. The closest he comes to aqueous solutions is a study of the various hydrates of ferric chloride and their thermochemistry.

4.1.3 Conclusions and design

The composition of the precipitate formed by hydrolysis at 200°C was thought to be mainly ferric oxide formed by:

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl$$

The oxide may be hydrated or form complexes with other components present. At 150°C the following main reaction was thought to occur:

$$FeCl_3 + H_2O \rightarrow FeOCl + 2HCl$$

The precipitate had the characteristic purple-brown colour of ferric oxychloride (4-5). The bright yellow precipitate obtained by treatment at 100°C could not be identified, but was thought to be a complex hydrated oxide/hydroxide/oxychloride.

Even without heat treatment, hydrolysis of aqueous ferric chloride occurs, as shown by the low pH value of the solutions prior to heating (Table 4.1). Apparently very high conversions are possible, but only with dilute solutions when using the technique described earlier. By "freezing" the reaction, or removing one of the products before the reverse reaction can take place, it is thought that conversions of 90-95% may readily be obtained with high concentrations of ferric chloride, and perhaps using higher temperatures. This could probably be achieved in several ways and two tentative proposals are made which require demonstration:

A) After reaction, allow some acid to flash off, and quickly cool, filter and wash the precipitate.

B) Hydrolyse the solution in a relatively large unstirred vessel when the ferric oxide will settle out. Smaller particles will settle more slowly than larger particles and some control of particle size may be possible. The resultant slurry at the bottom of the holding tank may be pumped out under pressure, water added to reduce acid concentration and temperature, then filtered, washed, and dried. The "mother liquor" would be recycled to the leaching reactor. To avoid bypassing, several vessels in series may be required.

Corrosion problems are probably more severe than in the leaching reactor due to higher temperatures and pressures, but it is likely that a similar method of construction would be satisfactory, with more careful selection of materials.

Although not much information is yet available on the hydrolysis reaction, a tentative mass balance has been drawn up based on 85% conversion of ferric chloride to ferric oxide at 200°C. This efficiency has already been shown possible in experimental work, and is thought feasible in a commercial development. From Section 3.2.6.2, 135,172 kg/hr $FeCl_3$ are to be hydrolysed. This requires 159,026 kg/hr $FeCl_3$, leaving 23,854 kg/hr unreacted which would be recycled with the regenerated acid to the leaching stage via impurity removal. Due to lack of specification of the latter part of the process complete solution compositions cannot be predicted, but on the above basis the recycle stream is likely to contain:

$FeCl_3$	23,854 kg/hr.
HCl	119,650 kg/hr.
H_2O	478,600 (assuming water balance maintained) kg/hr.

plus impurities

These figures assume that all chloride combined with the aluminium, calcium and magnesium is recovered. This is unreasonable, but unavoidable without a considerable amount of extra design work specifying impurity removal processes. (see Section 4.3). Assuming that all impurities are removed prior to leaching, the leach liquor and hydrolysis feed solution will contain:

$FeCl_3$ = 159,026 kg/hr

$FeCl_2$ = 415 kg/hr

$AlCl_3$ = 19,140 kg/hr

$CaCl_2$ = 7,996 kg/hr

$MgCl_2$ = 1,290 kg/hr

H_2S = 116 kg/hr
H_3PO_4 = 2,260 kg/hr
H_2O = 522,942 kg/hr
HCl = 6,191 kg/hr
Total = 719,376 kg/hr

66,546 kg/hr ferric oxide are formed.

As with leaching, the water balance is important and it may be possible to remove some water by flash distilling the regenerated acid after hydrolysis. The precipitated iron oxide will require thorough washing, and the sensitivity analysis carried out for ore residue washing in Section 3.2.6.2, Table 3.3, is applicable here, except that 66,546 kg/hr ferric oxide are to be washed, and 66,546 kg/hr water and multiples thereof would be used. The losses of total chloride as HCl would then be the same as in Table 3.3.

The hydrolytic precipitation method proposed has been proved feasible and apparently highly efficient under the right conditions. There is still a considerable amount of work to be done, particularly into the following areas:

1) Identification of products
2) Effect of impurities
3) Effect of temperature
4) Effect of holding time
5) Effect of concentration
6) Control of particle size
7) Prevention of reverse reaction
8) Purity of product

For further laboratory experimentation a high pressure metering pump feeding ferric chloride solution to a directly heated titanium tube is proposed. The products of hydrolysis could either be flashed off as described above, or condensed in cold water for analysis.

4.2 Crystallisation

The leach liquor from scrap iron dissolution contains ferrous chloride which is purified by crystallisation. Precipitation of ferrous chloride dihydrate by adding hydrogen chloride has been practised for a long time and was specified in a number of chemical iron extraction processes including R.C.A. and S.M.W. (1-1, 1-2).

Two sets of data have been found and are presented in Table 4.2 and Figure 4.3. As there is some discrepancy between the different sets of data, the figures from reference 4-2 were chosen as probable more reliable and also as they would tend to overdesign the crystalliser.

In view of the technical feasibility of this process step, an outline material and equipment specification only is given.

The data for 60°C at the high acid concentration end of the graph was used to fix the composition of the liquor from the crystalliser:

HCl	:	27.0 g./100g.	saturated	solution	
$FeCl_2$	:	10.0 "	"	"	"
H_2O	:	63.0 "	"	"	"

From residence time calculations for the leaching reactor in section 3.3.5.2, the acid concentration in the solution from the leaching reactor to the crystalliser must be

Table 4.2

System : $FeCl_2$ - HCl - H_2O

Temp.	gms per 100 gms sat. soln.				Solid phase
	Ref.(4-1)		Ref.(4-2)		Ref.(4-1)
°C	HCl	$FeCl_2$	HCl	$FeCl_2$	
100	0	48.7	0	49.8	$FeCl_2.2H_2O$
"	1.3	46.4	5	41.0	"
"	5.3	39.9	8	33.0	"
"	11.05	31.05	12	28.6	"
"	13.0	28.4	16	18.0	"
75			0	46.0	
"			5	37.5	
"			8	32.6	
"			12	25.0	
"			16	15.0	
60	0	43.9			$FeCl_2.4H_2O$
"	5.2	36.65			"
"	13.85	25.7			"
"	15.2	23.9			$FeCl_2.4+2H_2O$
"	15.4	23.5			$FeCl_2.2H_2O$
"	15.5	23.3			"
"	15.7	22.7			"
"	16.3	21.8			"
"	20.7	16.4			"
"	26.5	10.35			"
"	27.3	9.3			"

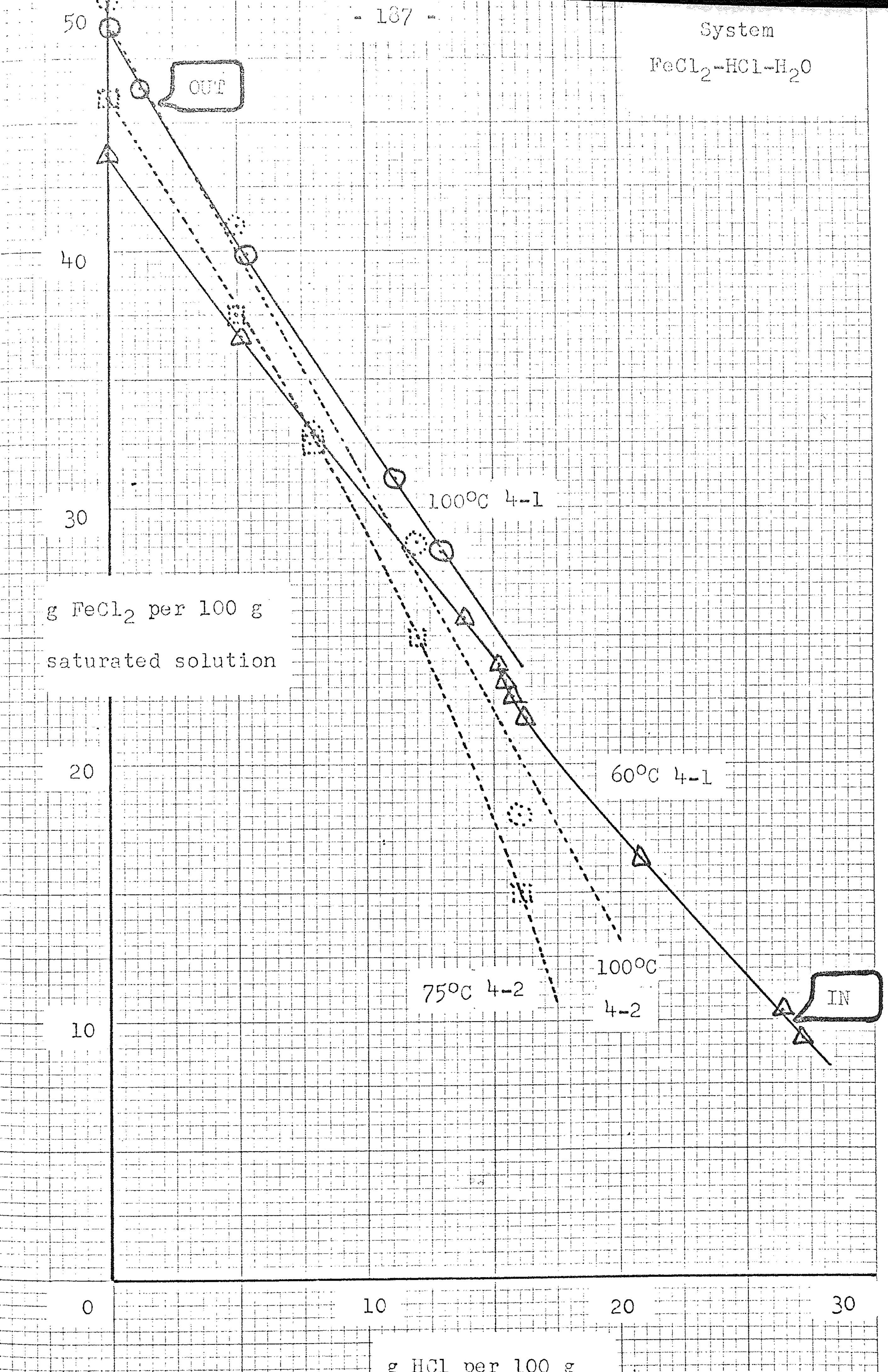

System
FeCl$_2$-HCl-H$_2$O
OUT
IN
100°C 4-1
60°C 4-1
75°C 4-2
100°C
4-2
g FeCl$_2$ per 100 g
saturated solution
g HCl per 100 g
saturated solution
50
40
30
20
10
0
10
20
30

Figure 4.3

1.35 g/100 g solution, as the ratio of acid concentration, in : out was specified as 20. This assumes that the density of the solution in the leaching reactor does not change.

The iron throughput of the leaching reactor is 10478 kg/hr. which produces 23781 kg/hr. $FeCl_2$ and requires 13684 kg/hr. HCl. (section 3.3.5.2). This quantity of HCl is contained in 50682 kg/hr. recycle liquor of composition:

HCl : 27.0 % wt. = 13684 kg/hr.
$FeCl_2$: 10.0 % wt.= 5068 kg/hr.
H_2O : 63.0 % wt. = 31930 kg/hr.

If complete reaction takes place this would give 23781 kg/hr. $FeCl_2$ or 28849 kg/hr. total $FeCl_2$, plus 31930 kg/hr. H_2O. It is necessary for the leach liquor to contain 1.35 % wt. HCl as specified above, and therefore additional recycle liquor is required. If this is X kg/hr., of composition :

0.27 X kg/hr. HCl
0.10 X kg/hr. $FeCl_2$
0.63 X kg/hr. H_2O

then X is found by specifying the leach liquor as containing 1.35 % wt. HCl:

$$\frac{0.27\ X}{28849 + 31930 + X} = \frac{1.35}{100}$$

hence $X = 3199$

The recycled acid from the crystalliser to the leaching reactor is therefore:

HCl	: 27.0 % wt.	= 14545	kg/hr.
$FeCl_2$	: 10.0 % wt.	= 5388	kg/hr.
H_2O	: 63.0 % wt.	= 33945	kg/hr.
		53878	

and the leach liquor from the reactor is:

HCl	:	1.35% wt.	= 864	kg/hr.
$FeCl_2$	:	45.6	= 29169	kg/hr.
H_2O	:	53.05	= 33945	kg/hr.
			63978	

This composition is just below the 100°C equilibrium line in Figure 4.3.

These specifications require minimum recycle and give maximum precipitation of $FeCl_2$. If difficulties should arise due to inaccurate data on the $FeCl_2$ - HCl - H_2O system, less $FeCl_2$ precipitation and greater recycle can be specified by moving the crystalliser mother liquor composition up the equilibrium line.

The ferrous chloride is precipitated as dihydrate, $FeCl_2.2H_2O$. While this will remove additional water from the crystalliser circuit, it may easily be replaced when the dihydrate is dried. This is shown in Figure 4.4: hot HCl and H_2 gases from the reduction stage and used first to dry the dihydrate, and then to precipitate ferrous chloride; the hydrogen is dried prior to recycling to the reduction stage, thus theoretically, no water is lost from the leaching/crystallisation system. Use of H_2/HCl mixture from reduction is specified for drying the ferrous chloride hydrate as air will oxidise the ferrous chloride, nitrogen might cause hydrolysis, and it is thought that a reducing gas with HCl, which is the product of oxidation or hydrolysis, will inhibit either of these reactions. Experimental verification is required however.

The heat of solution of HCl is 17787 cals/mole (Appendix II) which is given up when the gas dissolves, and

Scrap metal based iron extraction process

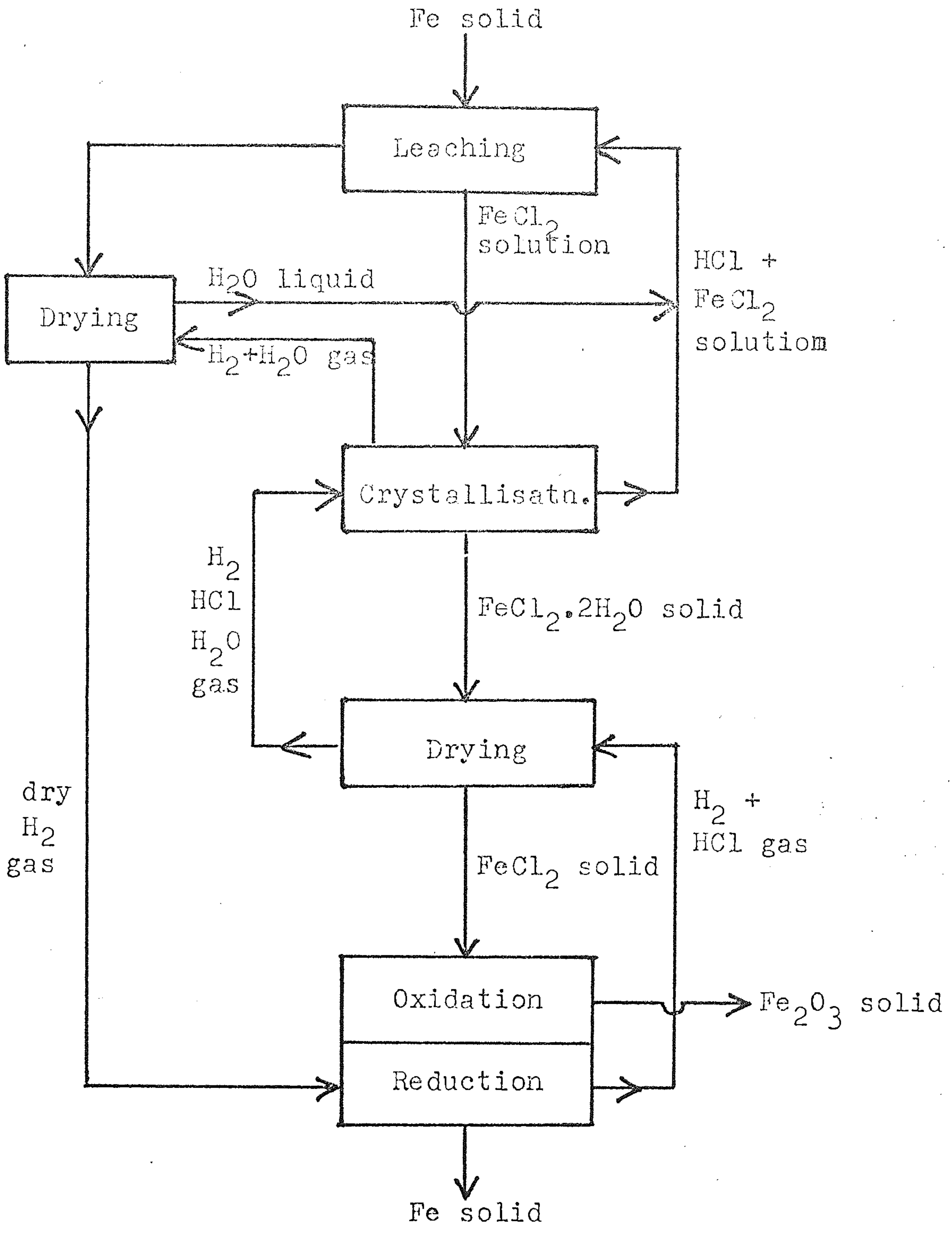
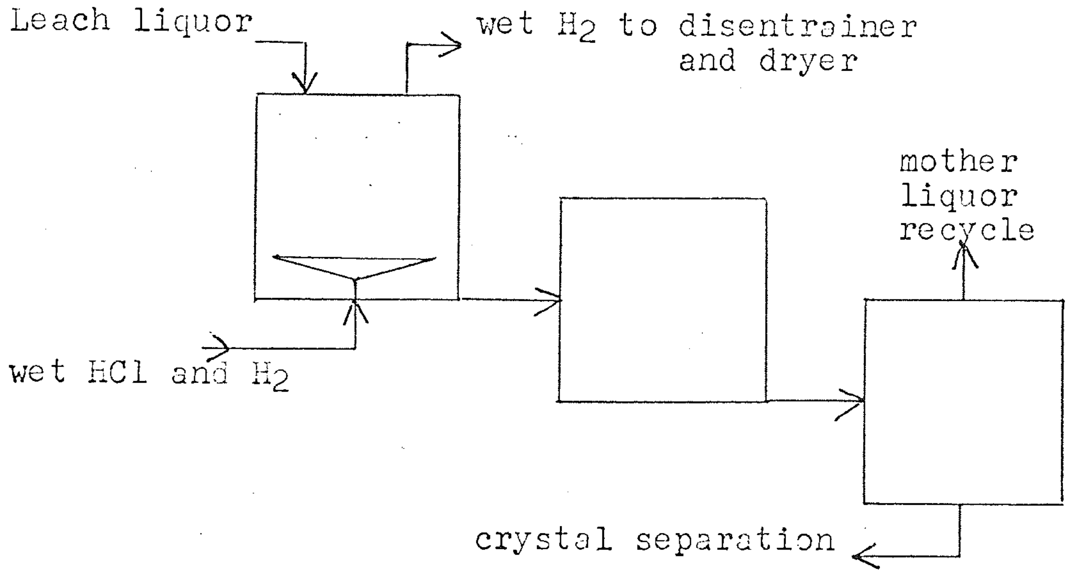


Figure 4.4

the heat of solution of $FeCl_2$ is 18100 cals/mole which is absorbed on crystallisation. As there are two moles of acid circulating for each mole of ferrous chloride, 17474 cals/mole $FeCl_2$ must be removed in addition to the sensible heat in the recycled gases and crystalliser feed stream. Cooling will therefore be necessary, either of the leach liquor prior to crystallisation, or during crystallisation. While the former is preferable to minimise crystalliser complexity, there is a possible problem of premature crystallisation by the cooling effect.

While further work is necessary to determine crystal size and growth rate characteristics, seeding requirements and supersaturation; an outline specification is provided. An initial countercurrent gas-liquid contacting vessel will absorb hydrogen chloride and cool the solution if necessary, and thorough mixing will be effected by the hydrogen. This will result in either supersaturation or immediate precipitation of dihydrate, or most probably both. Holding tanks will be required for crystal growth and to prevent any bypassing of solution without precipitation. At least two such tanks are suggested:



Successful separation of the resultant crystals was achieved by centrifugation in the R.C.A. process (1-1), but until more information is available, it is not considered possible to suggest alternatives. Similar materials of construction to those specified for the leaching reactor are suggested, although an acid resistant brick lining is probably unnecessary.

4.3 Impurity removal

The solutions from either ore or scrap leaching will contain impurities, and their removal is necessary, and in certain cases probably economically viable. The likely impurities from ore leaching are:

aluminium chloride calcium " magnesium "	in solution
phosphates	either in solution or precipitated
possible traces of titanium " " " vanadium	(form unknown)
silica	colloidal

and from scrap leaching they are:

copper chloride	in solution
zinc " aluminium " nickel "	probably in solution

4.3.1 Ore extraction

Perhaps the most interesting and important impurity is aluminium. As oxide, this can exceed 20% of the iron oxide content of the ore, and in terms of a 350,000 tons p.y. iron powder plant alumina can therefore be produced at up to 100,000 tons p.y. A considerable amount of work has gone into acid extraction of alumina for production of aluminium, which is discussed in Section 2, and while the technical feasibility is beyond dispute, the economics do not appear to have been sufficiently favourable. By adding a small number of stages to the basic iron extraction process described herein, it may be possible to produce significant quantities of pure alumina at a favourable price. This becomes more attractive with the commissioning of several new aluminium smelters in the U.K. in the near future.

The selection of a suitable process for alumina recovery may be effectively carried out by morphological analysis (see appended paper), but this is of comparable magnitude to the present problem and therefore beyond the scope of this dissertation. One of the better known methods is selective precipitative crystallisation of aluminium chloride from mixed chloride solution. For example, Dybina (4-4) investigated the system HCl-$FeCl_3$-H_2O at various $HCl:FeCl_3$ concentrations, with regard to complex chloroferrates formation. This, he claimed, was basic to purification of aluminium by precipitation of $AlCl_3.6H_2O$ from mixed solutions (see also Section 2.5.2). Gregory (4-3) reported that this separation has been successfully carried out, and reduction grade alumina produced according to tests by British Aluminium Co. Ltd. The process included precipitative crystallisation of $AlCl_3.6H_2O$ followed by hydrolysis to alumina with recovery of chloride. Standard solubility references (e.g. 4-2) include information on a wide variety of systems containing $FeCl_3$ and $AlCl_3$, but not specifically on the system: $FeCl_3-AlCl_3-HCl-H_2O$.

Other processes such as FLOX and R.C.A. (1-1) have claimed effective removal of colloidal silica and phosphorus, and recovery of chlorine from waste chlorides, and no difficulty is anticipated in treatment of these impurities. If vanadium and titanium occur to an appreciable extent, the possibility of recovery would require consideration.

4.3.2 Scrap dissolution

While a range of impurities can be tolerated in commercial scrap recycled to steelworks, copper is one of the non-ferrous metals that cannot be tolerated. There is a grade of scrap known as destructor scrap (see Section 2.2.2) which is cheaper but contains up to 2% wt. copper. Use of this material as feed to the proposed process could produce up to 1650 tons p.y. copper which, at £500 per ton, would be worth about £800,000. (As a comparison, 50,000 tons p.y. iron powder at £50 per ton would be worth £2,500,000). Copper is relatively easy to precipitate from aqueous solution in metallic form. Again a morphological analysis is beyond the scope of this dissertation but electrolysis or hydrogen pressure precipitation appears attractive and further work is necessary in this area, particularly the effect of dissolved copper chlorides on crystallisation of ferrous chloride. The copper removal stage may have to be virtually 100% efficient and be situated before the crystallisation stage.

Other possible impurities include (Section 2.2.2): Chromium, manganese, nickel, phosphorus, lead, sulphur, silicon, tin and zinc: up to 1.5% wt., and "other" (paper, plastics, and non-metallics): up to 3%. These are not considered further at this stage.

4.4 Oxidation

The scrap based process (Section 2.9) specified that the ferrous chloride dihydrate produced in the crystallisation stage is dried with HCl (to prevent hydrolysis) to the anhydrous state.

The inter-relationships of the ore and scrap based aqueous extraction processes have been discussed at the beginning of Section 4. Another process has been devised elsewhere (4-5) in parallel with the present work, but utilising gas phase reactions, and analogous to the scrap based process designed herein. This gas phase process reacts scrap iron with hydrogen chloride to give anhydrous ferrous chloride, which is oxidised to ferric oxide and ferric chloride. The volatilised ferric chloride is reduced to iron with hydrogen formed by the initial gas phase leaching reaction with hydrogen chloride. The process effectively forms a closed system as shown in Figure 4.5.

Gas phase iron extraction process

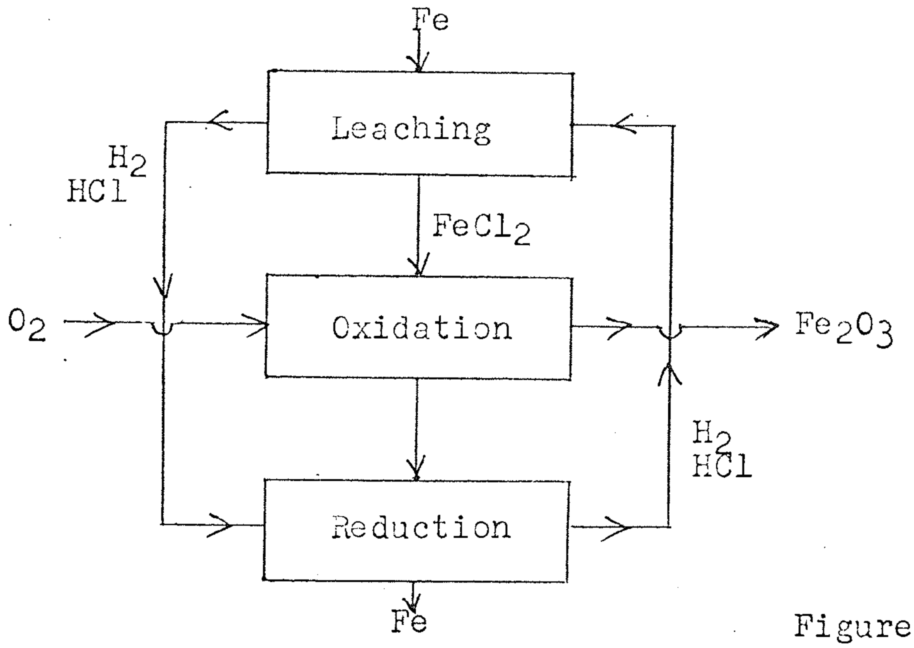


Figure 4.5

The equilibrium reaction:

$$Fe + 2HCl \rightleftharpoons FeCl_2 + H_2$$

is moved to give either leaching (forward reaction) or reduction (reverse reaction) by temperature and concentration adjustment.

The scrap based hydrometallurgical process produces anhydrous ferrous chloride which may be fed to the middle stage of the gas phase process outlined above.

It may be helpful to depict the total system of iron extraction by chloride formation before discussing the design further, and this is shown in Figure 4.6. Other possible interactions are also indicated by dotted lines.

Each main stage of the gaseous process has been *investigated qualitatively in the laboratory* and shown to be feasible.

4.4.1 Reactions and theory of oxidation of iron chlorides

The overall reaction is represented (4-6) by:

$$12FeCl_{2(s)} + 3O_2 = 8FeCl_{3(g)} + 2Fe_2O_{3(s)}$$

which is thought to proceed via the following reactions (4-7, 4-8)

$$4FeCl_{2(s)} + 3O_2 = 2Fe_2O_{3(s)} + 4Cl_2$$

$$8FeCl_{2(s)} + 4Cl_2 = 8FeCl_{3(g)}$$

There is also the possibility of other reactions involving ferric oxychloride (4-8, 4-9)

$$2FeCl_{2(s)} + O_2 = 2FeOCl_{(s)} + Cl_2$$

$$4FeCl_{2(s)} + O_2 = 2FeOCl_{(s)} + 2FeCl_{3(g)}$$

$$3FeCCl_{(s)} = Fe_2O_{3(g)} + FeCl_{3(g)}$$

All these reactions are reversible to a greater or lesser extent

Chloride based iron extraction system

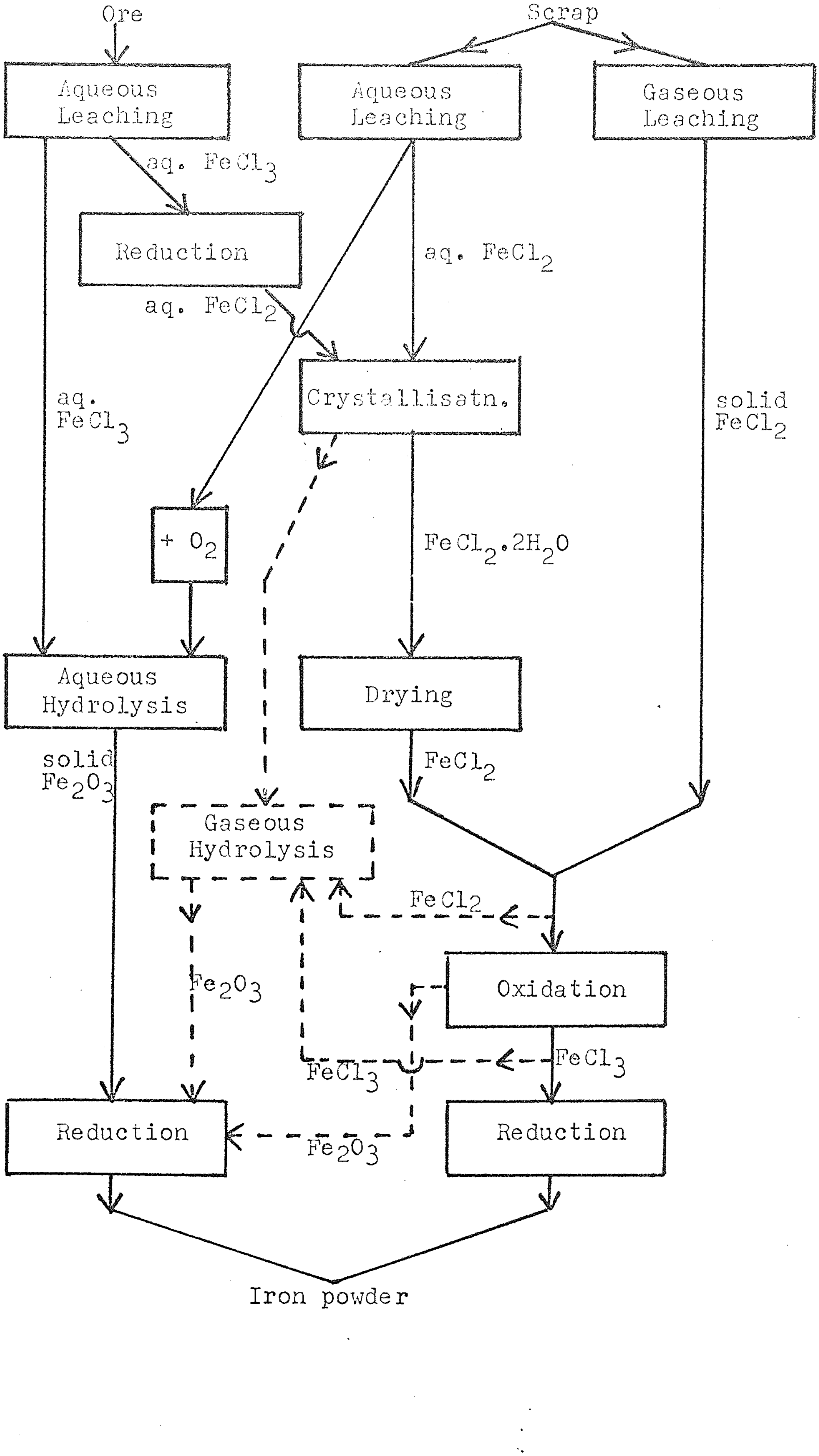


Figure 4.6

Apart from the desired products $Fe_2O_{3(s)}$ and $FeCl_{3(g)}$ there is also the possibility of forming $FeOCl_{(s)}$, and Cl_2, of which the latter would go forward with the gaseous $FeCl_3$, together with excess oxygen, which is clearly undesirable. FeOCl formation can be prevented by operating above 528°C, which is the temperature limit of existence of FeOCl (4-8, 4-9). Chlorine production can be controlled by operating with an oxygen supply restricted to the stoichiometric requirement which would also effectively prevent oxygen from passing on to the reduction stage. It is likely that any excess oxygen would tend to oxidise the ferric chloride. Other known reactions that may take place are:

$$4FeCl_3 + 3O_2 = 2Fe_2O_3 + 6Cl_2 \quad (4\text{-}10)$$

$$2FeCl_3 = 2FeCl_2 + Cl_2 \quad (4\text{-}9)$$

$$2FeCl_3 = Fe_2Cl_6 \quad (4\text{-}9)$$

See Section 4.4.3

Schäfer et al. (4-9) have given equations for calculating either equilibrium constants or partial pressures for some of the above equations:

$$6FeOCl = 2Fe_2O_3 + Fe_2Cl_{6(g)}$$

$$\text{Log } P_{(Fe_2Cl_6)} = 11.07 - \frac{26000}{4.57T}$$

$$Fe_2Cl_6 = 2FeCl_{2(s)} + Cl_2$$

$$\text{Log } Kp = 4.682 - \frac{2147}{T}$$

Willska (4-7) reported that the reaction:

$$12FeCl_{2(s)} + 3O_2 = 2Fe_2O_{3(s)} + 8FeCl_{3(g)}$$

occurred at 500°C, and was very slow at 200°C. Hill (4-6) specified 350-500°C in his patent for best results for the same reaction, and Wescott (4-10) patented a process for burning ferric chloride vapour in air to produce ferric oxide and chlorine according to the reaction:

$$4FeCl_{3(g)} + 3O_2 = 2Fe_2O_{3(s)} + 6Cl_2$$

which was subsequently developed. There is an extensive literature on these and related reactions which is not pertinent to the present work (2-1). Relevant experimental work is reported below.

4.4.2 Experimental work

The feasibility of the various steps in the gaseous route to iron powder has been demonstrated in the laboratory. In the context of the present problem, quantitative experimentation was not attempted.

Apparatus shown in Figure 4.7 was set up to first produce anhydrous ferrous chloride, then oxidise it "in situ" with oxygen to volatilise ferric chloride which condensed in the condenser.

Anhydrous ferrous chloride was formed near the outlet of the second pass of the tubular furnace by passing gaseous hydrogen chloride over steel turnings in both tubes at around 600°C. The reaction was found to be very slow (see later) and some of the impurities in the steel formed volatile compounds which caused slight discolourations. After about two hours of reaction, the system was thoroughly flushed with nitrogen, and oxygen to 10% volume added to the nitrogen. The oxidation reaction was rapid and exothermic at about 500°C. Dark red crystals typical of ferric chloride appeared in the condenser. Samples were collected and passed both qualitative and quantitative tests for ferric chloride.

Subsequent experimentation showed that transportation of volatilised ferric chloride in heated tubes was not difficult. One of the biggest problems was introducing

APPARATUS FOR ANHYDROUS FERROUS CHLORIDE PRODUCTION AND OXIDATION

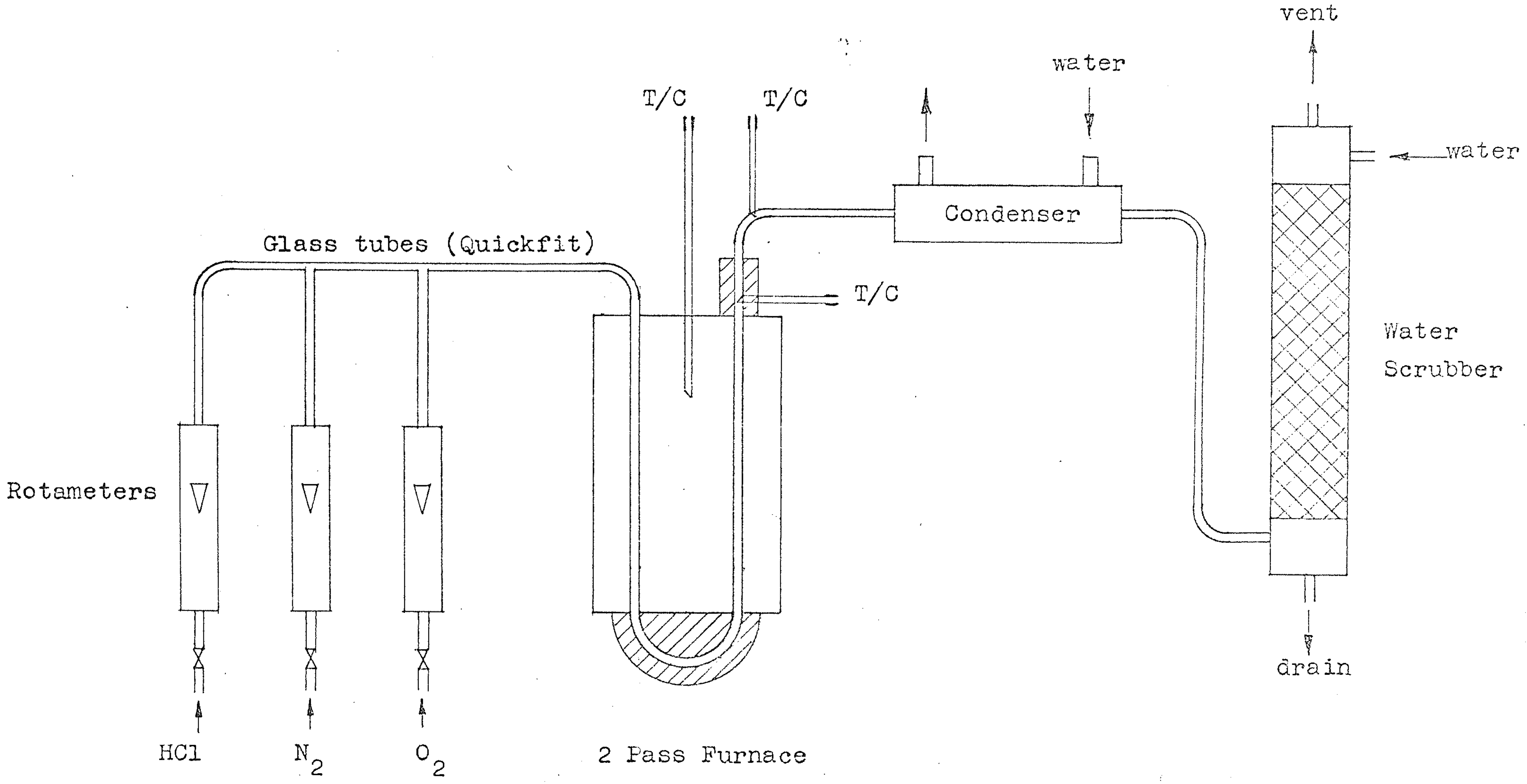


Figure 4.7 .

anhydrous ferric chloride solid into the system as it is very hygroscopic. In a continuous process the problem would not arise.

Although the feasibility of oxidation of anhydrous ferrous chloride to gaseous ferric chloride, and reduction of the latter, has only been demonstrated, some quantitative experiments were carried out on the gas leaching step prior to the oxidation experiments. This is not strictly relevant to the present problem, but it was considered worthwhile including a summary of the results of these experiments for completeness:

Reaction : $Fe + 2HCl_{(g)} = FeCl_{2(s)} + H_2$
Order of reaction : zero (with considerable excess HCl)
Activation energy : 8000-9000 cals/g mole
Rate controlling step : diffusion (boudary layer) up to Reynolds numbers of around 30 above which chemical reaction may take over
Rate of reaction : Figure 4.8 shows weight loss per unit surface area versus time

4.4.3 Association and pyrolysis of ferric chloride

During research on the oxidation of ferric chloride the question of association and pyrolysis of ferric chloride arose. Schäfer (4-9) has reviewed and investigated both phenomena in a comprehensive series of papers, and it was considered worthwhile including a summary of his findings although not entirely relevant at this stage of design.

Ferric chloride vapour associates thus:

$$2FeCl_3 = Fe_2Cl_6 \qquad \text{Heat of reaction} = -32550 \text{ cals.}$$

As a result of his work Schäfer proposed the following expression to predict the equilibrium constant:

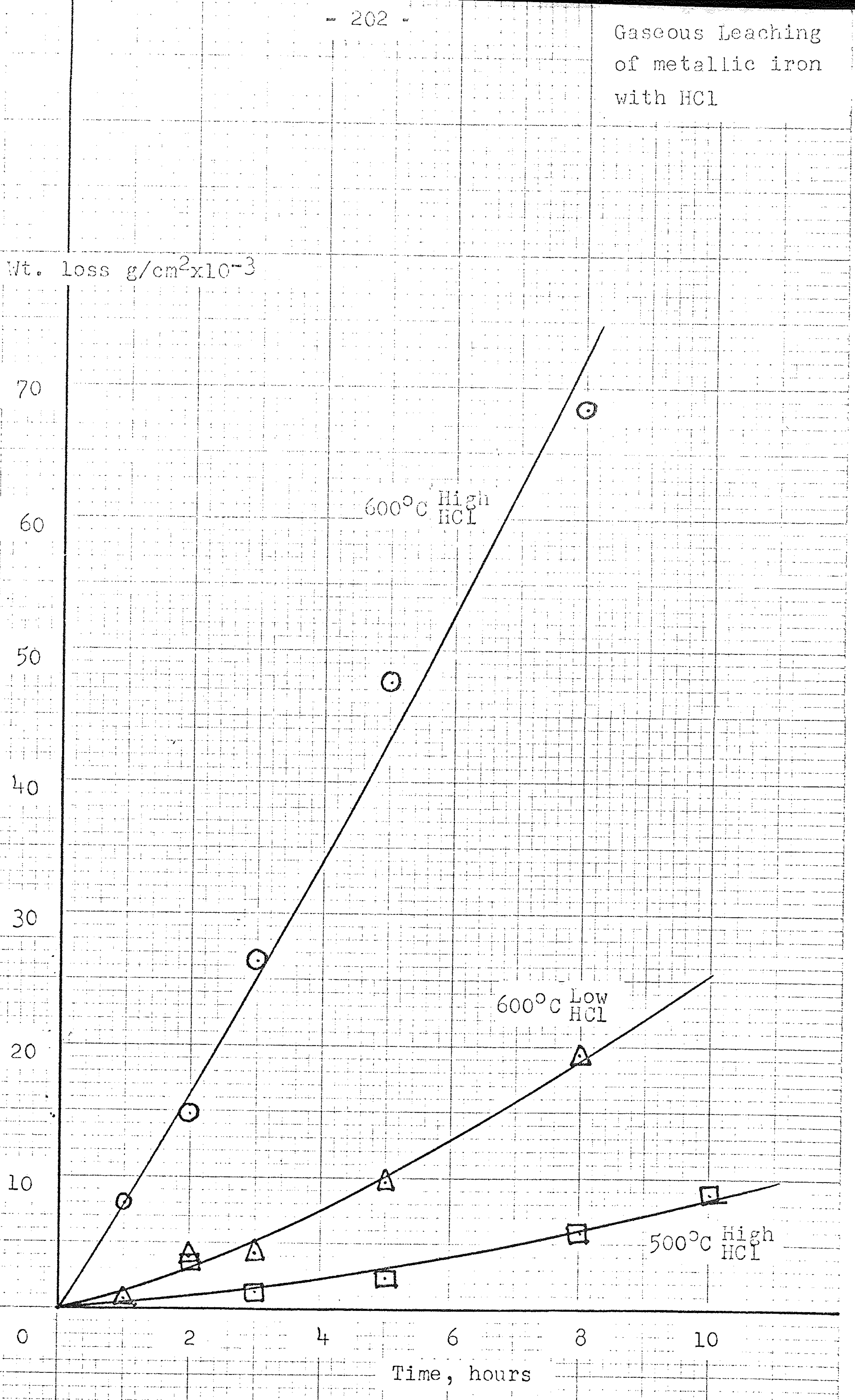

Gaseous Leaching of metallic iron with HCl
Wt. loss g/cm^{2}x10^{-3}
70
60
50
40
30
20
10
0
2
4
6
8
10
Time, hours
600°C High HCl
600°C Low HCl
500°C High HCl

Figure 4.8

$$\log K_{ass.} = -9.800 + \frac{32550}{4.57T}$$

where $K_{ass.}$ = equilibrium constant = $\dfrac{pp\ Fe_2Cl_6}{pp^2\ FeCl_3}$

pp = partial pressure, mm mercury

T = temperature, °A

The equation indicates that the existence of the monomer below about 400°C is negligible, and the presence of dimer above 800°C is likewise negligible. An expression for the mole fraction of ferric chloride monomer, a', was derived by Schäfer:

$$K_{ass.} = \frac{\text{partial pressure } Fe_2Cl_6}{\text{partial pressure } FeCl_3}$$

$$= \frac{\text{Total pressure} - \text{partial pressure } FeCl_3}{\text{partial pressure } FeCl_3}$$

Replacing $K_{ass.}$ by K,

Total pressure by P, and

partial pressure $FeCl_3$ by p,

then p is given by:

$$p^2.K = P - p$$

$$p^2K + p - P = 0$$

$$p = \frac{-1 \pm \sqrt{1 + 4KP}}{2K}$$

The mole fraction of monomer ($FeCl_3$), a', is given by:

$$a' = \frac{p}{P}$$

$$= \frac{-1 \pm \sqrt{1 + 4KP}}{2KP}$$

$$= \frac{\sqrt{1 + 4KP} - 1}{2KP}$$

An expression was developed from conventional equilibrium theory to predict the mole fraction of dissociated ferric chloride:

$$2FeCl_3 = Fe_2Cl_6$$

$$2(1-a) = a$$

where a = mole fraction dimer

$$K = \frac{\dfrac{a\ \ P}{(2-a)}}{\dfrac{(2-2a)^2.P^2}{(2-a)^2}}$$

$$KP = \frac{a(2-a)}{(2-2a)^2}$$

$$= \frac{2a - a^2}{4+4a^2-8a}$$

$$4KP+4KPa^2-8aKP = 2a - a^2$$

$$0 = a^2(1+4KP)-a(8KP+2)+4KP$$

$$a = \frac{(8KP+2)\pm\sqrt{(8KP+2)^2-4(4KP)(1+4KP)}}{2(1+4KP)}$$

$$= \frac{2(4KP+1)\pm2(4KP+1)\sqrt{1-\dfrac{4KP}{(4KP+1)}}}{2(4KP+1)}$$

$$= 1 \pm \sqrt{1 - \frac{4KP}{(4KP+1)}}$$

$$= 1 - \sqrt{\frac{1}{(4KP+1)}} \quad \text{(mole fraction dimer)}$$

and $$a' = \sqrt{\frac{1}{(4KP+1)}} \quad \text{(mole fraction monomer)}$$

It was found however that Schäfer's expression gave better agreement with his data. For example, at 700°C and 100 mm:

a' = 0.793 by Schäfer's equation

and 0.657 by conventional equation

The value obtained by using Schäfer's equation agrees with the experimental values reported by Schäfer. The theories differ apparently in that Schäfer's method considers the total pressure as made up of the sum of the partial pressures of the monomer and dimer, whereas the conventional method does not impose this limitation. Further investigation of the disparity was not undertaken.

Ferric chloride also pyrolyses thus (4-9):

$$2FeCl_{3(g)} = 2FeCl_{2(s)} + Cl_2$$

$$\Delta Hr = -46800 \text{ cals } (4\text{-}9)$$

$$Fe_2Cl_{6(g)} = 2FeCl_{2(s)} + Cl_2$$

$$\Delta Hr = -13600 \text{ cals } (4\text{-}9)$$

where ΔHr = heat of reaction

The equilibrium constant, Kp, was given by Schäfer (4-9) from Kangro and Petersen (4-11) as:

$$Kp = \frac{\text{partial pressure } Fe_2Cl_6}{\text{partial pressure } Cl_2}$$

$$\log Kp = 4.682 - \frac{2147}{T\ {}^{\circ}K}$$

for T between 606 and 949°K

Schäfer (4-9) included a review of all known work on this and related systems as well as results from his own experimentation. Appendix II contains further data.

4.4.4 Application to design

While the feasibility of the oxidation stage appears to be beyond doubt, there is insufficient information so far for any design specification. Possible problems include temperature control of the oxidation reaction with pure oxygen which may prove very difficult, in which case dilution with an inert gas may be necessary. If the ferric chloride produced from this oxidation stage is not pure enough, an additional condensation/resublimation stage may be necessary, when the inert gas might also be vented off. Transportation of vapourised ferric chloride is not expected to present any problems, but gas migration (oxygen and hydrogen) are likely to need careful consideration. Materials of construction are not likely to prove difficult when moisture is absent and no problems are expected in this area.

5. REDUCTION

The final major process step in both the processes considered is reduction of a purified iron compound - ferric oxide - from the ore based process, and ferric chloride vapour from the scrap based process.

5.1 Oxide reduction

As explained in Section 2.6, so much work has been carried out into reduction of iron oxides that it was considered no further useful contribution could be made in this field. For reduction of the ferric oxide produced from low grade ore by leaching and hydrolysis, the H-Iron process is proposed, and for the present design purposes might be bought in as a complete package. A brief technical and economic description of the process is included but a critical appraisal of alternatives is not considered worthwhile in this thesis.

The H-Iron process

The H-Iron process was originally designed toproduce relatively pure iron powder from upgraded high grade ore, as feed material to electric furnaces. Many flow sheets and descriptions are available in the literature from which some of the more informative are quoted: (5-1 to 5-4). An outline flow sheet is given in Figure 5.1, which excludes hydrogen production. In its original form, hydrogen was produced from coke oven gas by a relatively lengthy process, but for the present purpose, a more conventional hydrogen plant based on steam reforming or partial oxidation of natural gas or naphtha would be specified.

The oxide is reduced on a semi-continuous basis in three fluidized beds arranged vertically. The fluidized beds

H - IRON FLOW SHEET

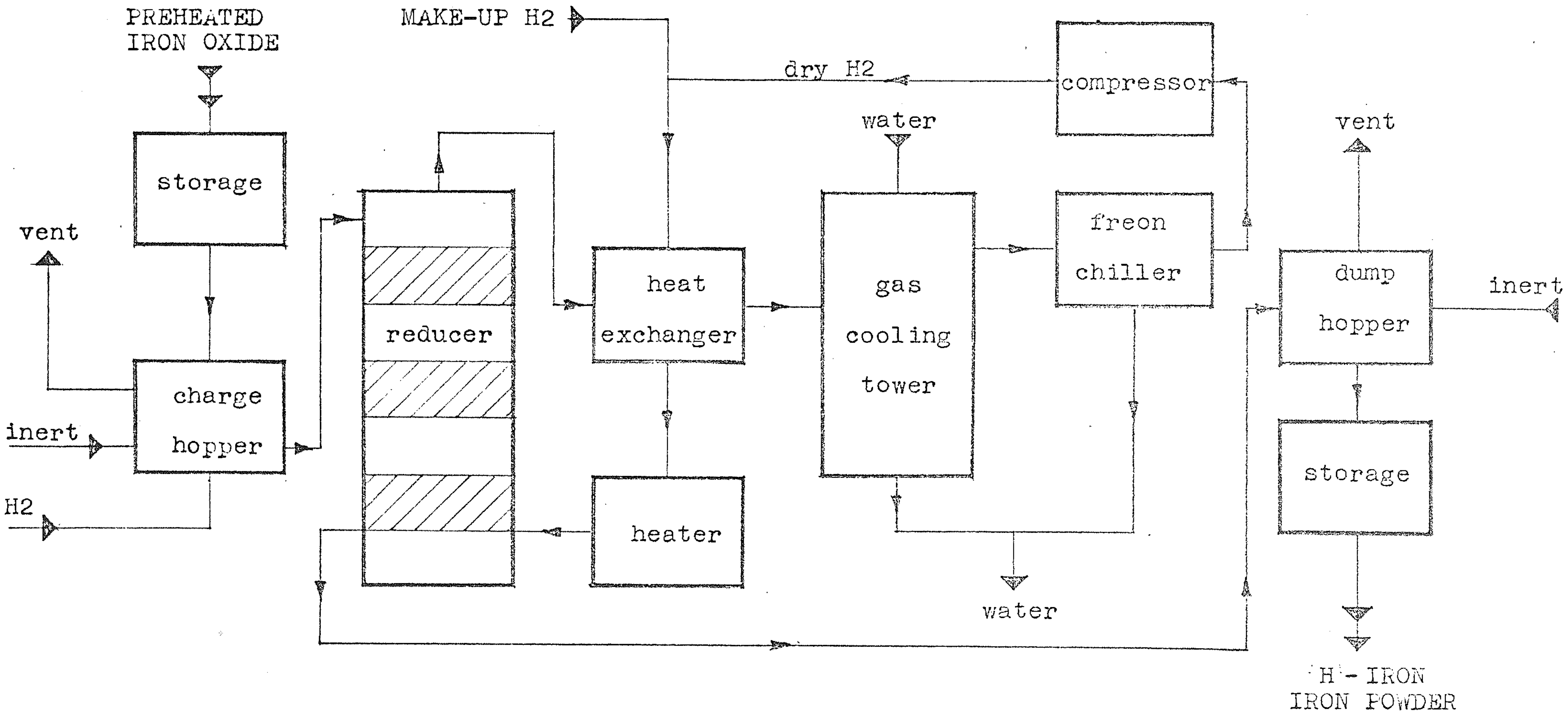


Figure 5.1

operate at 400 psi (500 in some references) and 550°C. The high pressure reduces the temperature necessary for reduction, and the relatively low temperature prevents sintering of the reduced iron particles. The size of the resultant iron powder is about the same as the feed material, and tends to be pyrophoric. All solids are transported pneumatically. About 23,000 s.c.f. hydrogen are required to reduce one long ton of ferric oxide. Hydrogen conversion is approximately 10% per pass, and the residence time of the iron oxide when employing ore feedstock is about 10-12 hours. The effect of using ferric oxide produced from the hydrolysis reaction is not known. This process is particularly attractive due to use of a pure reductant which cannot contaminate the pure ferric oxide, production of iron powder directly without briquetting and/or comminution, relatively good economics (see later), and well proven techniques.

Economics of the H-Iron process have been summarised:

Capital cost:

capacity, long tons/yr.	cost, $	year	reference
14,730	3,800,000	1960	5-1
648,200	24,000,000	1957	5-4 *
"	23,000,000	"	" *
160,700	8,700,000	1963	5-2
147,300	8,230,000	"	5-5

Operating costs:

op. cost, $ long ton	plant capacity	year	reference
14.92	648,200	1957	5-4 *
6.87	"	"	" *

10.58	160,700	1963	5-2
11.69	147,300	1963	5-5

Costs for the processes marked * are for the same processes on the east coast of U.S.A. and Texas respectively, and the differences in costs are almost entirely due to energy/fuel costs. The capital cost of the 147,300 ton p.y. plant was broken down by Dyck (5-5):

ore preparation and reduction:	\$ 4,900,000
hydrogen manufacture (S.R.nat.gas):	\$ 2,550,000
Offsites:	\$ 780,000

He also provided a detailed breakdown of service requirements and costs for each stage. The capital costs have been converted and updated in Section 7 for total process capital cost estimation. See also section 6.3.

5.2 Chloride reduction

The ferric chloride vapour produced by oxidation of ferrous chloride is to be reduced with hydrogen to give pure iron powder. This was reviewed and discussed in Section 2.6.2 which found that very little is known about reduction of ferric chloride except that it probably proceeds via ferrous chloride. The first stage is then:

$$FeCl_3 + \tfrac{1}{2}H_2 \rightarrow FeCl_2 + HCl$$

and this proceeds very quickly and goes to completion. Far more work has been carried out on reduction of ferrous chloride, both solid and gaseous, which was also discussed in Section 2.6.2. As this step is likely to be more important, and more data is available, the reaction is studied further.

5.2.1 Equilibrium of system $FeCl_2 - H_2 - HCl - Fe$

The proposed data is taken from a paper by Rigg (5-6) which reported progress in the design of a ferrous chloride reducer for the R.C.A. process. He summarised the results of five workers (5-7 to 5-11) to obtain the equation:

$$\log Kp = \frac{-7302}{T} + 6.29$$

where Kp = equilibrium constant

and T = temperature, °K

for the reaction:

$$FeCl_{2(s)} + H_2 = Fe + 2HCl_{(g)}$$

which fits the existing data as well as possible up to about 750°C. The only data above this temperature is by Bagdasarian (5-7) which disagrees with the results obtained by using Rigg's equation. Kangro and Petersen (5-8) calculated values of log Kp which agree closely with Bagdasarian's results. It is suggested that Rigg's equation is more accurate up to 750°C as it represents the best of known previous work, and a set of values is given in Table 5.1 with equilibrium concentrations of H_2 and HCl. Above 750°C it is considered likely that the data of Bagdasarian and Kangro and Petersen is accurate as their values of Kp were based on experimentation, while Rigg's values are extrapolated by using his equation. All three sets of data are given in Table 5.2 for comparison, as well as equilibrium concentrations of H_2 and HCl calculated from average values of Kp from Bagdasarian and Kangro and Petersen. A graph of the equilibrium concentration of HCl versus temperature is given in Figure 5.2 from which it

Table 5.1

Values of Kp and Equilibrium Concentrations of HCl and H_2 according to Rigg (5-6)

T°C	T°A	Log Kp	Kp	Mol. % HCl	Mol% H_2
200	473	-9.15	7.08×10^{-10}	0.003	99.997
300	573	-6.45	3.55×10^{-7}	0.060	99.94
350	623	-5.43	3.72×10^{-6}	0.19	99.81
400	673	-4.56	2.75×10^{-5}	0.52	99.48
425	698	-4.17	6.76×10^{-5}	0.82	99.18
450	723	-3.81	1.55×10^{-4}	1.24	98.76
475	748	-3.47	3.39×10^{-4}	1.82	98.18
500	773	-3.16	6.92×10^{-4}	2.61	97.39
525	798	-2.86	1.38×10^{-3}	3.65	96.35
550	823	-2.58	2.63×10^{-3}	4.99	95.01
575	848	-2.32	4.79×10^{-3}	6.71	93.29
600	873	-2.07	8.51×10^{-3}	8.80	91.20
625	898	-1.84	1.45×10^{-2}	11.32	88.68
650	923	-1.62	2.40×10^{-2}	14.30	85.70
675	948	-1.41	3.89×10^{-2}	17.85	82.15
700	973	-1.21	6.17×10^{-2}	21.91	78.09
725	998	-1.03	9.33×10^{-2}	26.23	73.77
750	1023	-0.85	1.41×10^{-1}	31.22	68.78
775	1048	-0.68	2.09×10^{-1}	36.47	63.53
800	1073	-0.52	3.02×10^{-1}	41.90	58.10
850	1123	-0.21	6.17×10^{-1}	53.59	46.41
900	1173	+0.06	1.15	64.13	35.87
950	1223	+0.32	2.09	73.77	26.23
1000	1273	+0.55	3.55	81.31	18.69

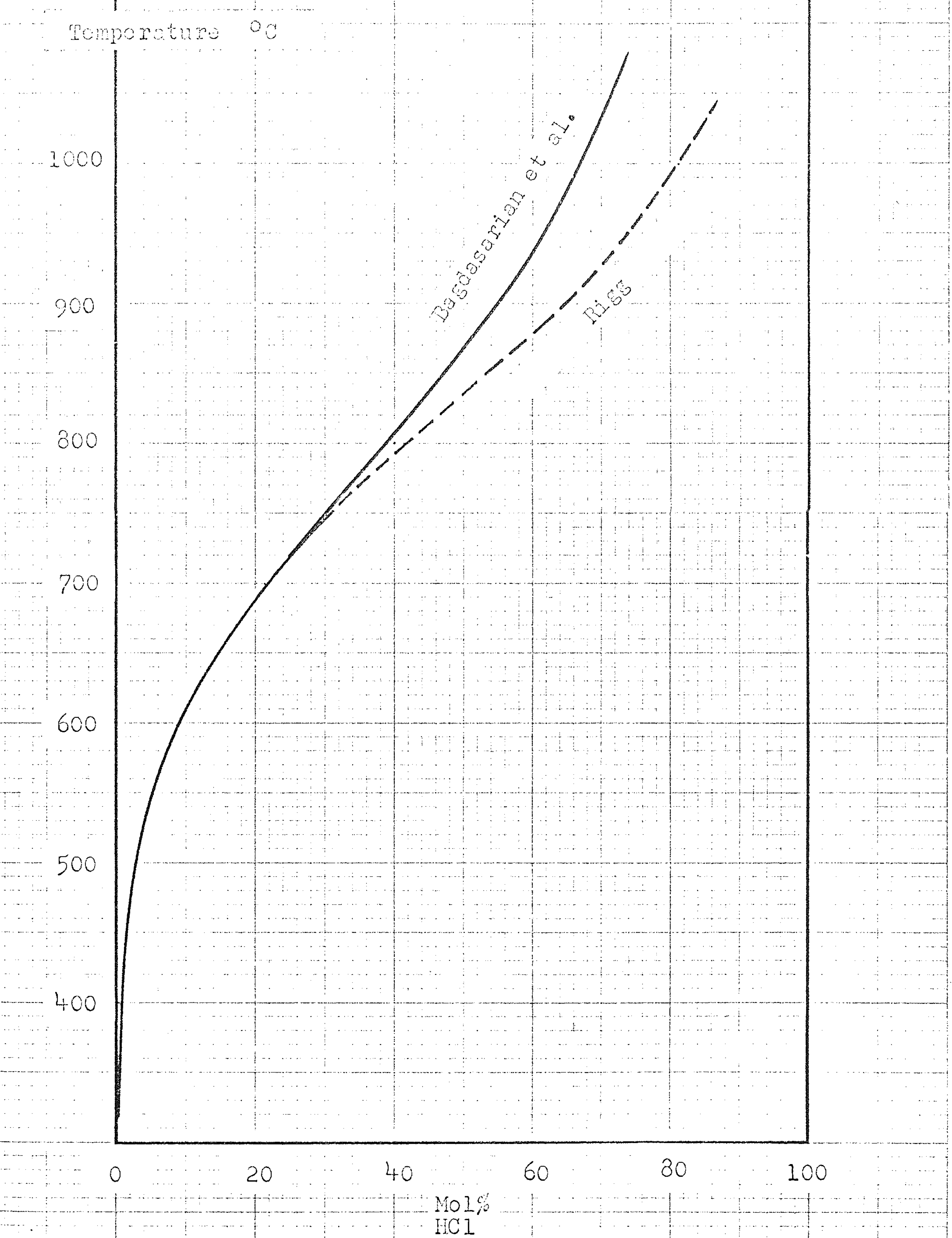
Table 5.2

Values of Kp and Equilibrium Concentrations of HCl and H_2 according to Bagdasarian, and Kangro and Petersen (5-7,8)

T°C	T°A	Log Kp			Kp	Mol % HCl		Mol%H_2
		B	K&P	R			R	
702	975	-1.19	-1.18	(-1.20)	6.53×10^{-2}	22.53	(22.25)	77.47
725	998	-0.96	-1.037	(-1.03)	1.00×10^{-1}	27.00	(26.23)	73.00
777	1050		-0.732	(-0.68)	1.85×10^{-1}	34.71	(36.90)	65.29
800	1073	-0.528	-0.620	(-0.52)	2.67×10^{-1}	40.00	(41.90)	60.00
857	1130		-0.356	(-0.18)	4.41×10^{-1}	48.02	(55.07)	51.98
897	1190		-0.184	(-0.05)	6.55×10^{-1}	54.65	(63.50)	45.35
925	1198	-0.116	-0.070	(+0.19)	8.07×10^{-1}	58.16	(68.95)	41.84
932	1205	-0.090	-0.048	(+0.22)	8.53×10^{-1}	59.15	(70.30)	40.85
1005	1278	+0.212	+0.210	(+0.57)	1.62	67.79	(82.06)	32.21

Notes: B : Bagdasarian (5-7)
K&P : Kangro and Petersen (5-8)
R : Rigg (5-6). Included for comparison. Values of mol % HCl in parentheses were calculated from Rigg's values of Kp

Where values of log Kp are given for both Bagdasarian and Kangro and Petersen, a mean was taken to calculate Kp and mol % HCl and H_2 .



Equilibrium concentrations of HCl in system $FeCl_2-H_2-Fe-HCl$.

Figure 5.2

may be seen that the higher the temperature the greater the conversion to hydrogen chloride and hence iron. The maximum temperature that can be used in practice is about 700°C to prevent sintering of the iron product.

The temperature dependency of the equilibrium is the basis of the gaseous process outlined in section 4.2. Gas "leaching" takes place at 600°C using an inlet mixture of 21.91 % mol HCl and 78.09 % mol H_2. Ferrous chloride is formed, and assuming equilibrium is reached, the exit gas has the composition 8.8 % mol HCl and 91.2 % mol H_2. This is heated to 700°C when it is used to reduce ferric chloride vapour formed by oxidation of ferrous chloride. The reducer exit gas is made up of 21.91 % mol HCl and 78.09 % mol H_2 (assuming equilibrium is attained) which is recycled back to the leaching stage.

The aqueous scrap leaching process designed in this dissertation would employ pure hydrogen for reduction at not more than 700°C, when the exit gas composition would be 21.91 % mol HCl and 78.09 % mol H_2 assuming equilibrium is reached. This represents about 22 % conversion of hydrogen per pass, or a gas flow through the reducer of approximately five times stoichiometric.

5.2.2 Kinetics of iron chloride reduction

Reduction of ferric chloride to ferrous chloride is taken to be very fast, and the rate controlling step of the overall reaction is then reduction of ferrous chloride. This agrees with empirical evidence.

Rigg (5-6) suggested that the rate of reduction of solid $FeCl_2$ with hydrogen is controlled by the vapourisation of ferrous chloride, and the diffusion of the vapour from the interface. As it is likely that the ferrous chloride formed by reduction of ferric chloride vapour is of submicron or even molecular proportions, although probably in the solid phase, it is unlikely that the extensive reduction time necessary for massive solid ferrous chloride will apply (5-12).

Of greater importance is the work of Yannopoulos and Themelis (5-13) who studied the kinetics of reduction of single particles of ferrous chloride circa one cm. in diameter. Their conclusions were that at Reynolds numbers above 17.5 the hydrogen gas velocity appeared to have no detectable effect on the rate of reduction. By comparing transfer coefficients, they found that at Reynolds numbers above 30 the influence of boundary layer diffusion was negligible under their range of conditions: 450 - 635°C and 0.7 - 2.0 cm. particle diameter.

In the proposed process gas mixing is likely to be the rate limiting step, and relative Reynolds numbers of 30 are unlikely to be achieved. Difficulties were experienced by Yannopoulos and Themelis at temperatures above 640°C due to ferrous chloride vapourising and diffusing to the particle surface, where on reduction a solid film of iron was formed hindering further reduction. This is unlikely to be encountered in the proposed gaseous process due to the extremely small particle size and probable high speed of reaction. The reaction rate was found to be inversely proportional to the particle diameter within their range of conditions. At 575°C for example, a particle 1.28 cm. diameter took 44 minutes for 99% reduction. By admittedly extrapolating to an unreasonable degree, a particle one micron in diameter would require 0.206 seconds for 99% reduction at 575°C, or about 0.246 seconds for 99.9% reduction at 575°C.

Their experiments were carried out with an hydrogen chloride/hydrogen mixture, and the rate of reduction was found to be proportional to the difference between the equilibrium hydrogen chloride concentration and the concentration of hydrogen chloride gas around the particle. This was predicted theoretically and verified experimentally.

In conclusion, a rate equation was suggested, applicable to reduction of solid $FeCl_2$ in the case of negligible resistance to boundary layer diffusion:

$$\frac{(1 - (1 - Rx)^{1/3})}{\Theta} = \frac{(3.15 \times 10^5)}{(\quad dp \quad)} \; e^{\frac{-27,500}{RT}} \; \frac{(xe - x)}{(\ xe\ )}$$

This was stated to represent the experimental results over the range of conditions investigated.

N.B. Rx = Fractional reduction of particle

Θ = Time of reaction

dp = Diameter of particle (cm)

xe = Fractional equilibrium concentration of HCl

x = Fractional concentration of HCl

It is possible that in the proposed gaseous process, the rate limiting step will be gas mixing.

No reference has been found to reduction of iron chlorides under the conditions specified and while the above information is useful, experimentation was necessary to obtain data for design.

5.2.3 Experimentation

As no direct experimental evidence could be found in the literature of the feasibility of reducing ferric chloride vapour, it was proposed that initial experimentation should demonstrate that reduction to metallic iron takes place, and determine the form of the resultant product. (Although several patents specifications associated with the gaseous FLOX processes specify this particular reaction (2-16, 2-20 et al.)). Quantitative experiments would need to follow, but as sophisticated experimental and analytical equipment would almost certainly be required (4-9, 5-13), this was considered to be beyond the scope of this dissertation.

The first stage of the experimental programme was transportation of volatilised ferric chloride. As no apparent difficulties were encountered, a hydrogen reduction stage was added. Standard laboratory glassware was used throughout. A diagram of the apparatus is shown in Figure 5.3 and Plate 5.1. Nitrogen carrier gas was preheated to about 200°C to aid the sublimation of ferric chloride which was heated to about 320°C in a 500 ml glass flask in an isomantle. The hot vapour and nitrogen was transported to the reaction tube where it met hydrogen preheated to as high a temperature as possible - about 250°C. The mixed gases passed down a narrow annular space passed a radiant tube heater which was controlled to give a temperature on the containing tube outer wall of 600 - 650°C. It was thought that this would give a reaction temperature of about 700°C. Gas heating was by heating tapes wrapped round glass tubes and all heated equipment was lagged with asbestos rope. The entire rig was screened with wire

FERRIC CHLORIDE REDUCTION APPARATUS

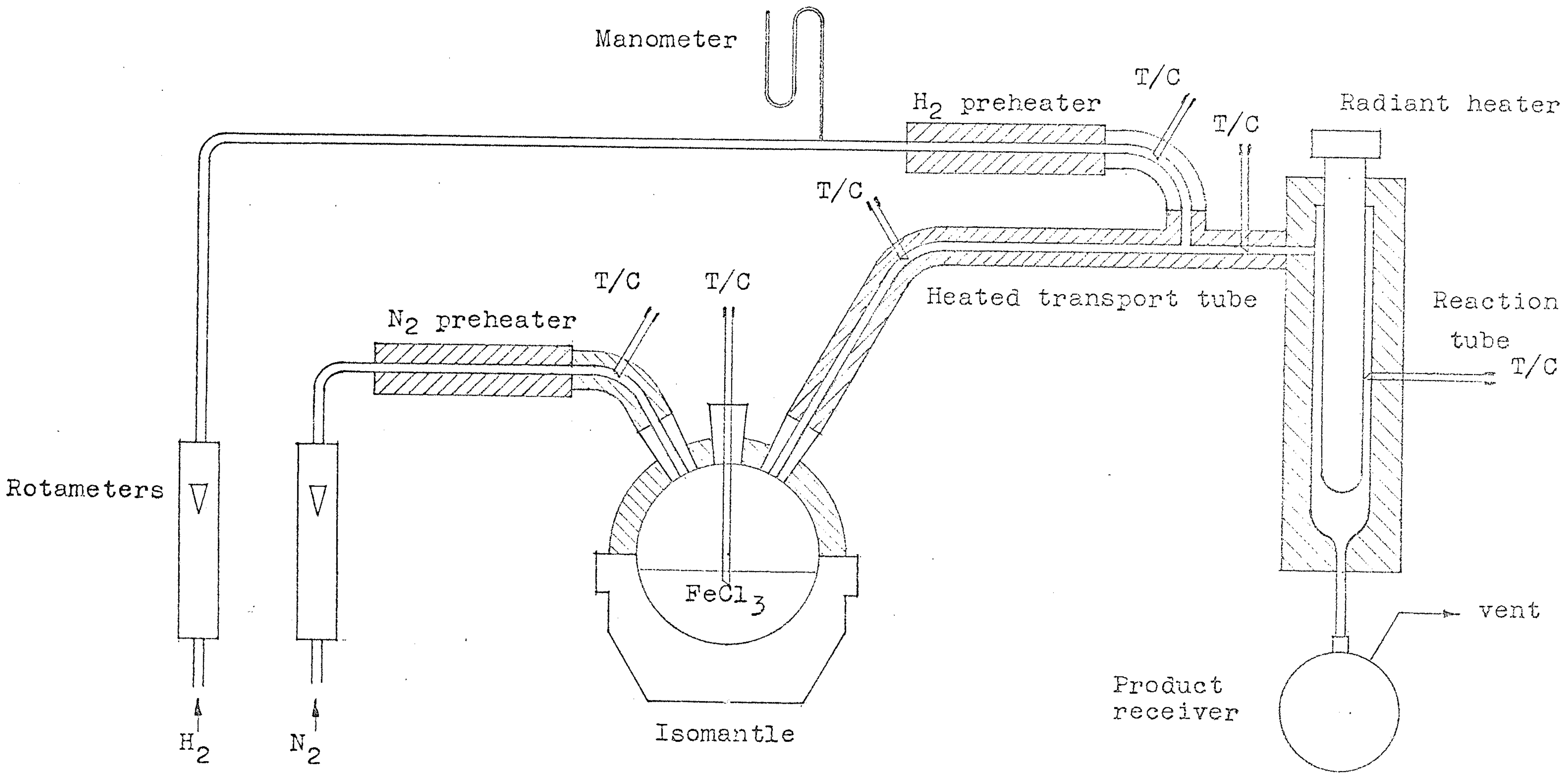
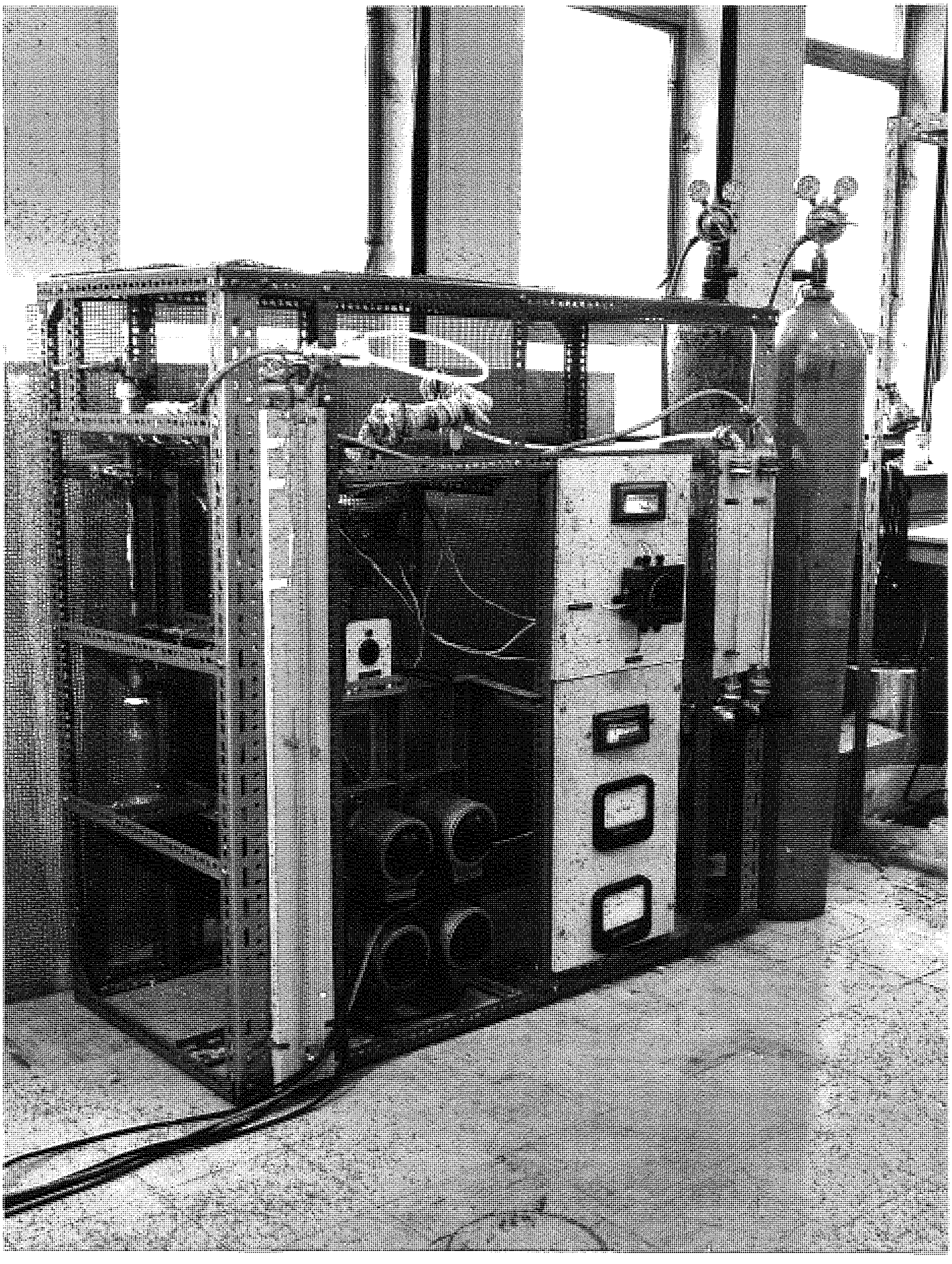


Figure 5.3



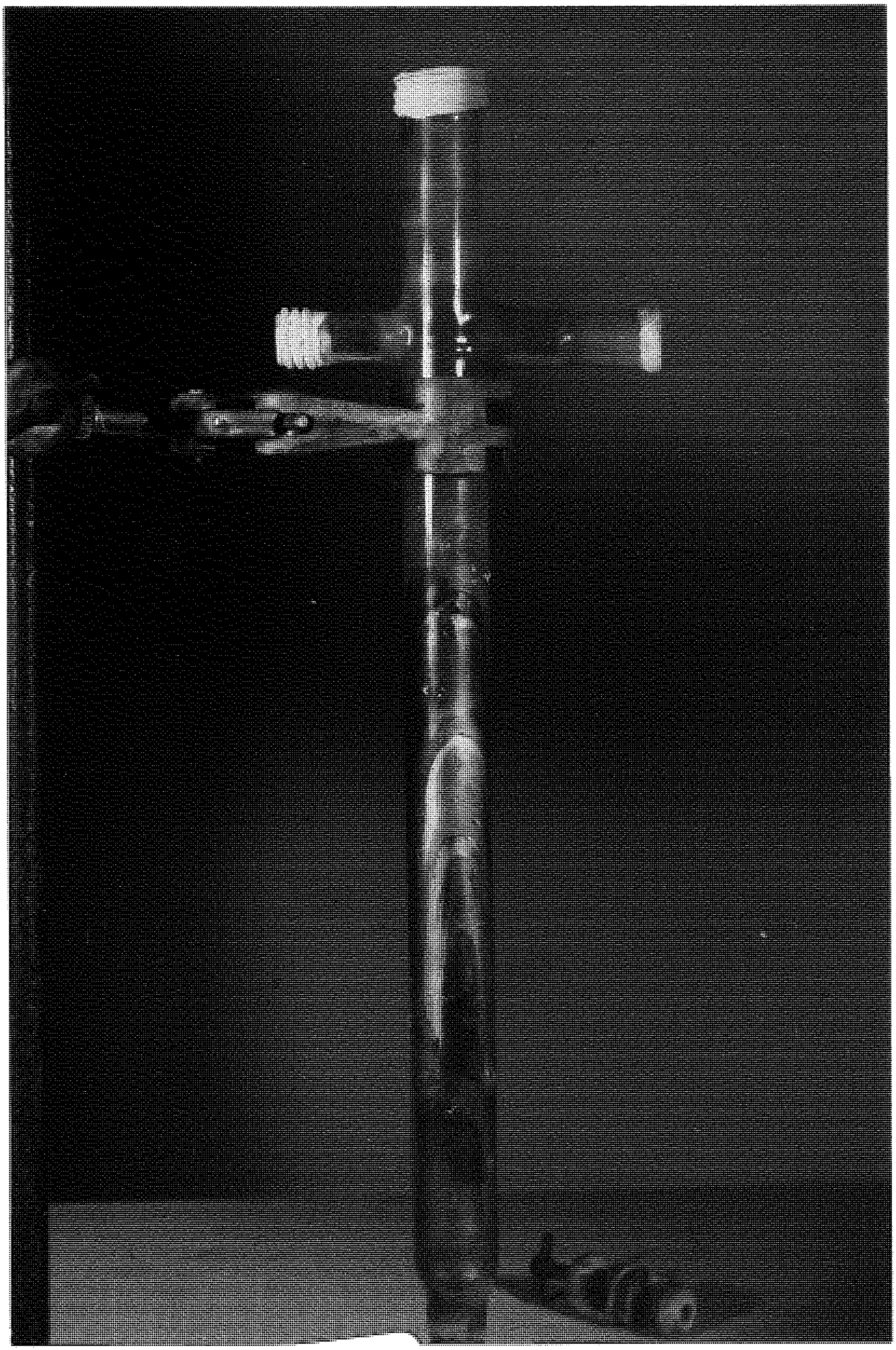
Experimental apparatus for hydrogen reduction of ferric chloride vapour

Plate 5.1

mesh for safety reasons.

As anhydrous ferric chloride is very hygroscopic it was loaded into the flask after the nitrogen and the flask had heated up to around 100°C. After sealing the flask, the equipment was flushed with nitrogen and the temperatures of the nitrogen preheater, flask, transport tube, hydrogen preheater and reactor were gradually raised to reaction temperatures. A number of runs were carried out lasting about four hours altogether, with two hours at reaction temperature, which was found to be the time required for a charge of about 100 g anhydrous ferric chloride to be volatilised during earlier experiments on vapour transport. The reactor was allowed to cool down under nitrogen, and then examined. Plate 5.2 shows the reaction tube after reduction.

Red deposits were found near the reactor inlet which were shown to be ferric chloride and ferric oxide formed by hydrolysis of ferric chloride with traces of moisture. Some red deposits of oxide and metallic iron 'mirror' were formed on the inside of the reactor alongside the radiant heating tube, and a black dusty deposit collected at the bottom of the reaction tube which was readily scraped off. This black powder was magnetic and would not dissolve in water or cold hydrochloric acid. On warming with acid a greenish solution formed which reacted with potassium ferricyanide - a test for ferrous ions. A gravimetric analysis was performed on a small sample of powder by dissolving an accurately weighed quantity in acid and titrating for ferrous iron. This showed that the powder was at least 90% Fe, and the other qualitative tests described above confirmed this conclusion. The formation of 'mirror' indicated possible



Reaction tube after
hydrogen reduction
of ferric chloride
at around 650°C

Plate 5.2

vapour phase transport of ferrous chloride, perhaps by a supersaturation effect.

There is clearly still a large amount of work to be carried out including the following:

Effect of varying temperature
" " " time of reaction
" " " pressure
" " " concentration of hydrogen
" " " " " inert gas
" " magnetic field
Control of particle size
Recirculation of iron particles
Purity of product
Control of heat input
Gas flow rates and Reynolds number
Technical and economic optimisation

Further experimentation with the existing equipment is recommended before establishment of the more sophisticated apparatus necessary for investigation of the areas of further work listed above.

5.2.4 Design

The reduction stage reduces vapourised ferric chloride from the oxidation step with hydrogen. It will have a capacity of 50,000 tons p.y. iron powder or 6.25 tons per hr. Hourly throughputs are:

$FeCl_3$	=	18.154 tons/hr.	=	18446 kg/hr.
H_2	=	0.339 tons/hr.	=	344 kg/hr.
HCl	=	12.243 tons/hr.	=	12440 kg/hr.
Fe	=	6.250 tons/hr.	=	6350 kg/hr.

At 700°C, which is taken as the maximum temperature employable, the exit gas composition is given by Table 5.1 as 21.9 % mol HCl and 78.1 % mol H_2 assuming equilibrium is reached. This means that the hydrogen throughput needs to be 2759 kg/hr. which gives the exit gas composition as:

HCl = 12440 kg/hr.
H_2 = 2415 kg/hr.

An outline design is suggested in Figure 5.4. It is possible that the reduction may behave as a gas phase crystalliser in which the iron powder particles are grown by recycling smaller ones. Some control of the final particle size and shape may therefore be possible. Movement of reagents through the reactor will be initially by gas pressure, then the resultant iron powder may fall by gravity assisted by gas flows, or possibly moved magnetically. Heat input to the system will be by hydrogen preheated to around 700°C, heating of recycled gas containing undersize iron powder, possibly induction heating of recirculating iron powder which may encourage reaction to take place at the particle surface, and heat in the ferric chloride vapour which would be at least at 530°C to suppress oxychloride formation. Because of the equilibrium prevailing, as long as the temperature of the exit gases is maintained above 700°C, mild steel may be employed as construction material other things being equal. Below 700°C the HCl will attack steel/iron to give ferrous chloride, and more resistant material is necessary.

Gas flows through the reactor are 1,482,262 g mols /hr. at the inlet ($FeCl_3$ and H_2) and 1,368,470 g mols/hr. at the outlet (HCl and H_2). Averaging these flows and

Ferric Chloride Reduction System

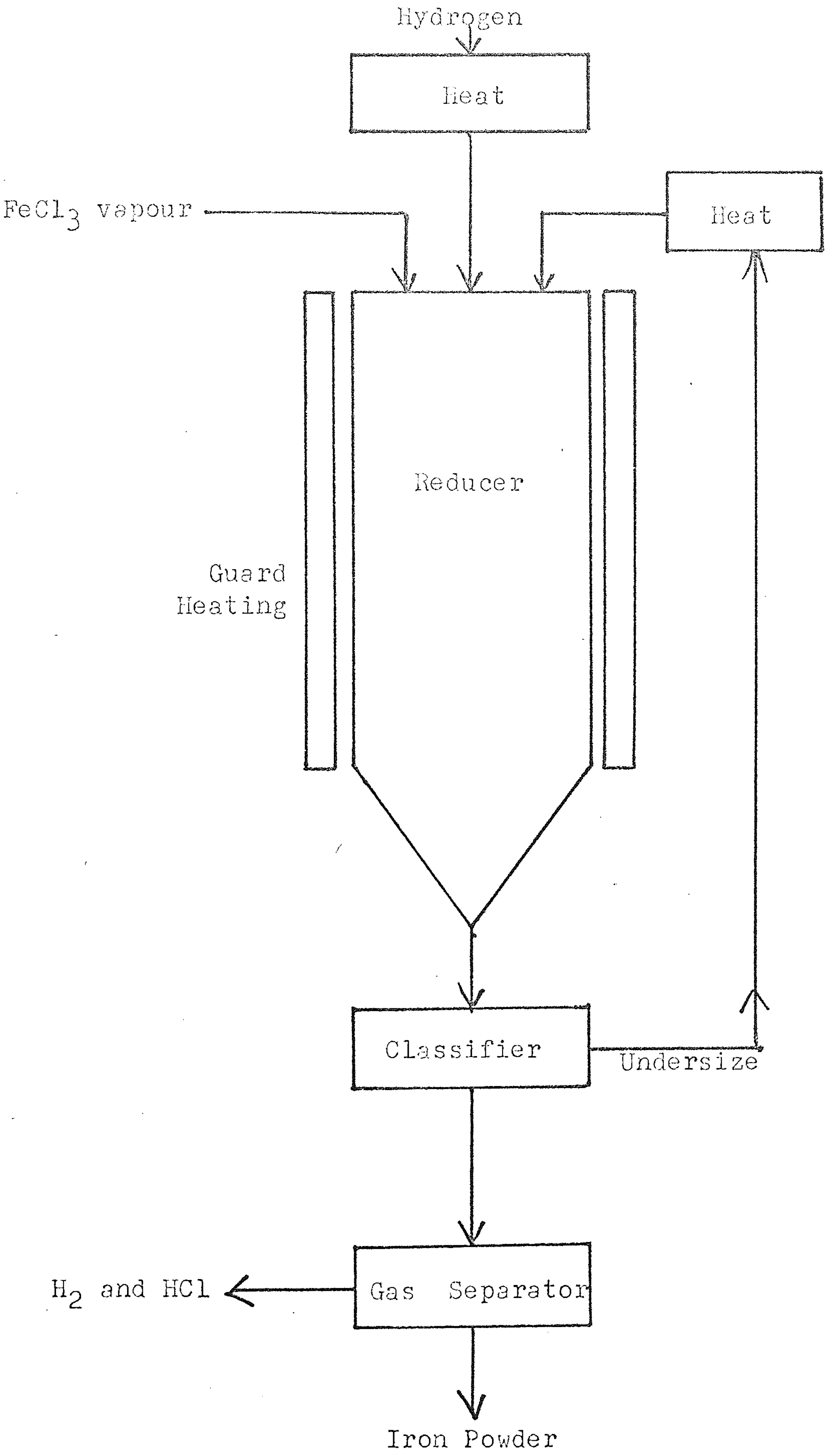


Figure 5.4

assuming the gases behave ideally in the absence of any other information, this represents 31,948 m^3/hr. at N.T.P., or 113,866 m^3/hr. at 700°C and 1 atm. pressure. If the reduction reaction arbitrarily takes 1 second, the volume of the reactor needs to be 31.63 m^3. The geometry of a suitable reaction vessel is not easily specified at this stage as not all the necessary data is available. The reactor might be tubular of 2 m diameter and 10.07 m long. In order to ensure good mixing of the gases, the Reynolds number, Re, needs to be above 3000 to give turbulent flow.

$$Re = \frac{d.\rho.v}{\mu}$$

where d = tube diameter, cm

ρ = fluid density, g/cm^3

v = fluid velocity, cm/sec.

μ = fluid viscosity, g/cm.sec.

$\rho = 3.86 \times 10^{-4}$ g/cm^3 at 700°C. This was taken as the proportional mean of the outlet gas composition assuming ideality.

d = 200 cm, specified above.

v = 1007 cm/sec, specified above.

$\mu = 2 \times 10^{-3}$ g/cm.sec for hydrogen at 700°C. No information was available on gas mixtures, so data for hydrogen as the predominant gas was used.

Hence Re = 38,900 which would probably be satisfactory.

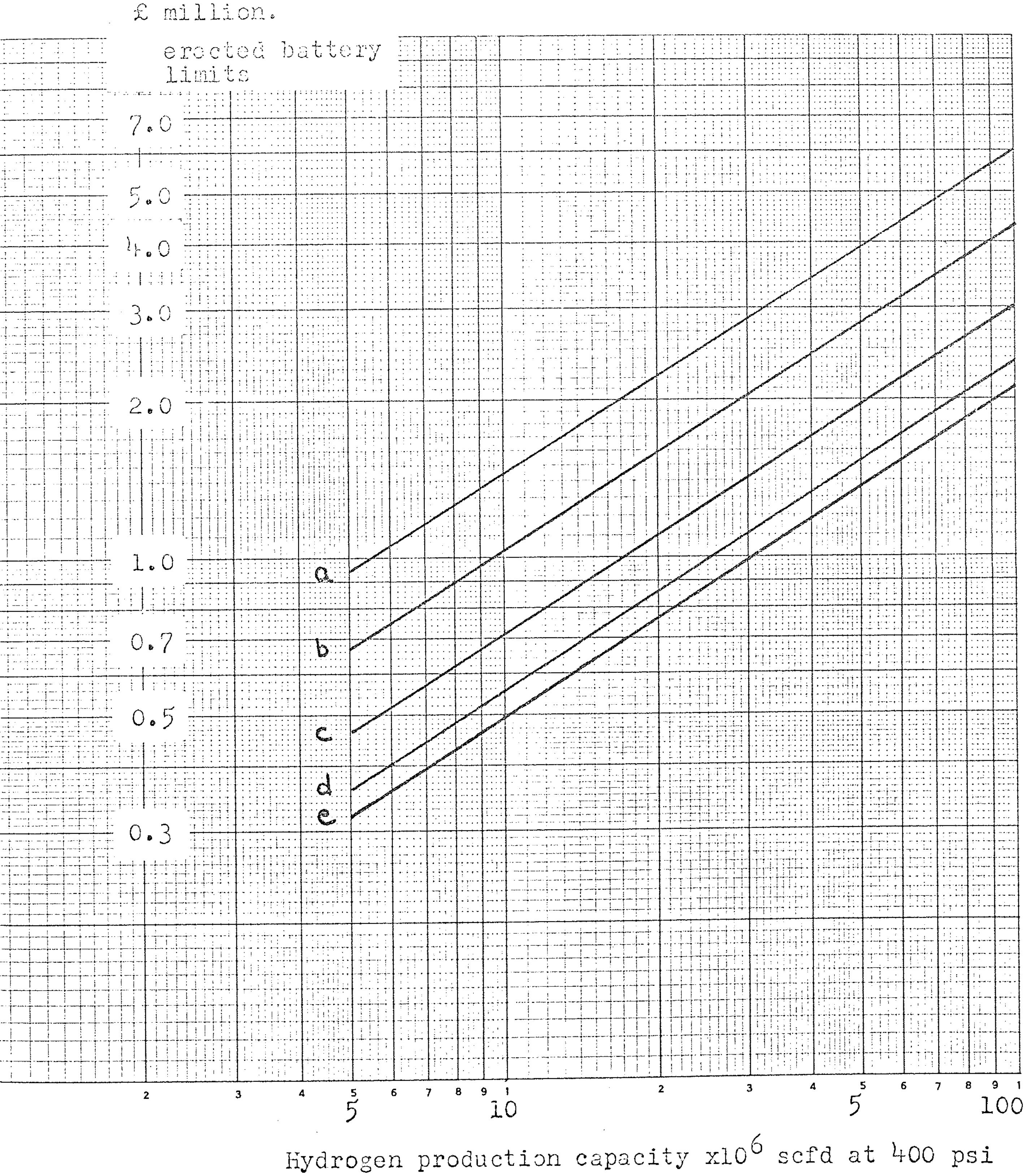
5.2.5 Conclusions

Reduction of ferric chloride to powder iron by hydrogen has been shown to be feasible. Preliminary design suggests that a simple reactor may be achieved. If subsequent experimentation is successful, there is a good indication that equipment for the process may be designed which will be suitable for fabrication and continuous operation on a large scale with satisfactory scale-up economy.

5.3 Hydrogen production

Information on capital and overall production costs for hydrogen are given in Figures 5.5 and 5.6 for a number of well known processes - steam reforming and partial oxidation. The information is given for 1966, but it is understood that the figures are substantially correct for 1970 (2-57).

Hydrogen Production - Capital Costs (Battery Limits) 1966



Hydrogen production capacity x10^6 scfd at 400 psi

a Partial oxidation (2000 psi incl. O_2 plant)
b Partial oxidation incl. O_2plant
c Steam reforming naphtha
d Steam reforming natural gas
e Partial oxidation excl. O_2 plant

Figure 5.5

Hydrogen Production
Total operating costs, including depreciation at 10 % p.a.

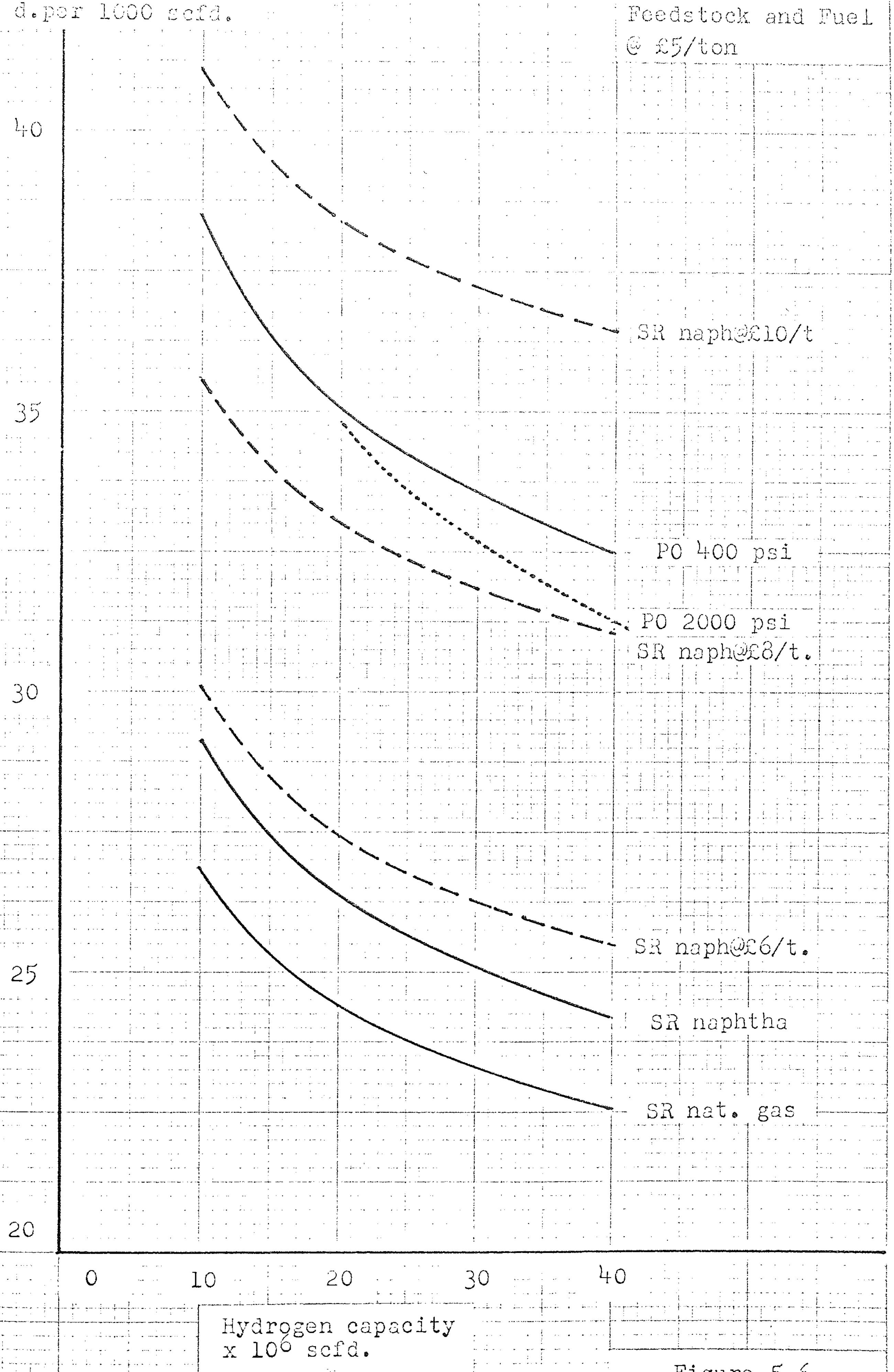


Figure 5.6

6. SUMMARY OF FLOW DIAGRAMS, MASS BALANCES, AND ENERGY REQUIREMENTS

Flow diagrams, outline mass balances and critical areas of energy balance are provided for the two processes specified in section 2.9, which formed the subject of investigations reported in sections 3, 4, and 5.

6.1 Ore based process

A simplified overall flow diagram of the process to manufacture iron powder from ore via oxide reduction is shown in Figure 6.1, and a more detailed flow diagram in Figure 6.2. Stage-wise mass balances follow based on previous calculations, except for the reduction process which is considered to be a self contained unit (see section 5). All quantities are expressed in kg/hr.

Flow Diagram of Process to Manufacture Iron Powder from Ore

(Outline)

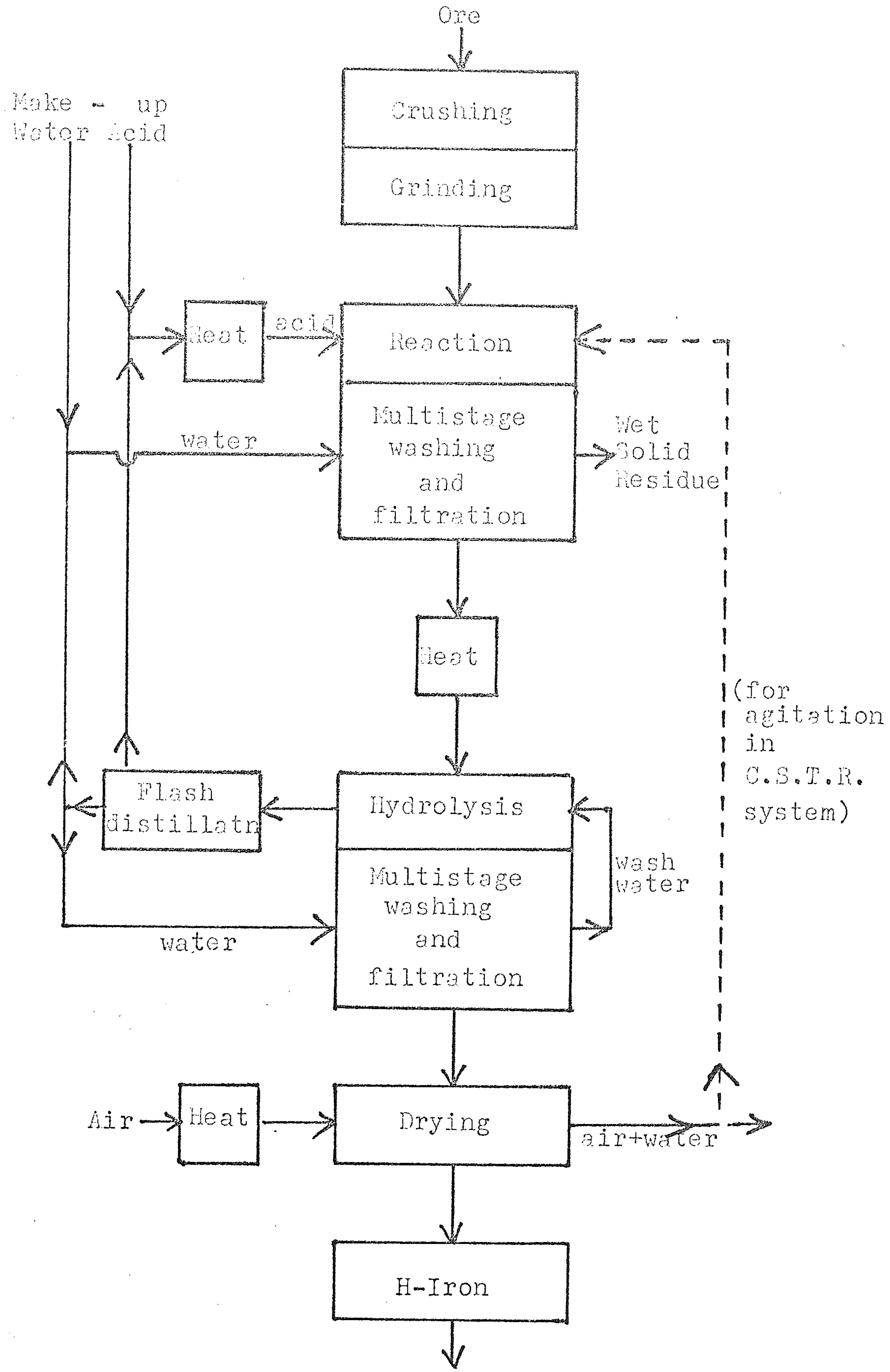


Figure 6.1

PRODUCTION OF IRON POWDER FROM ORE

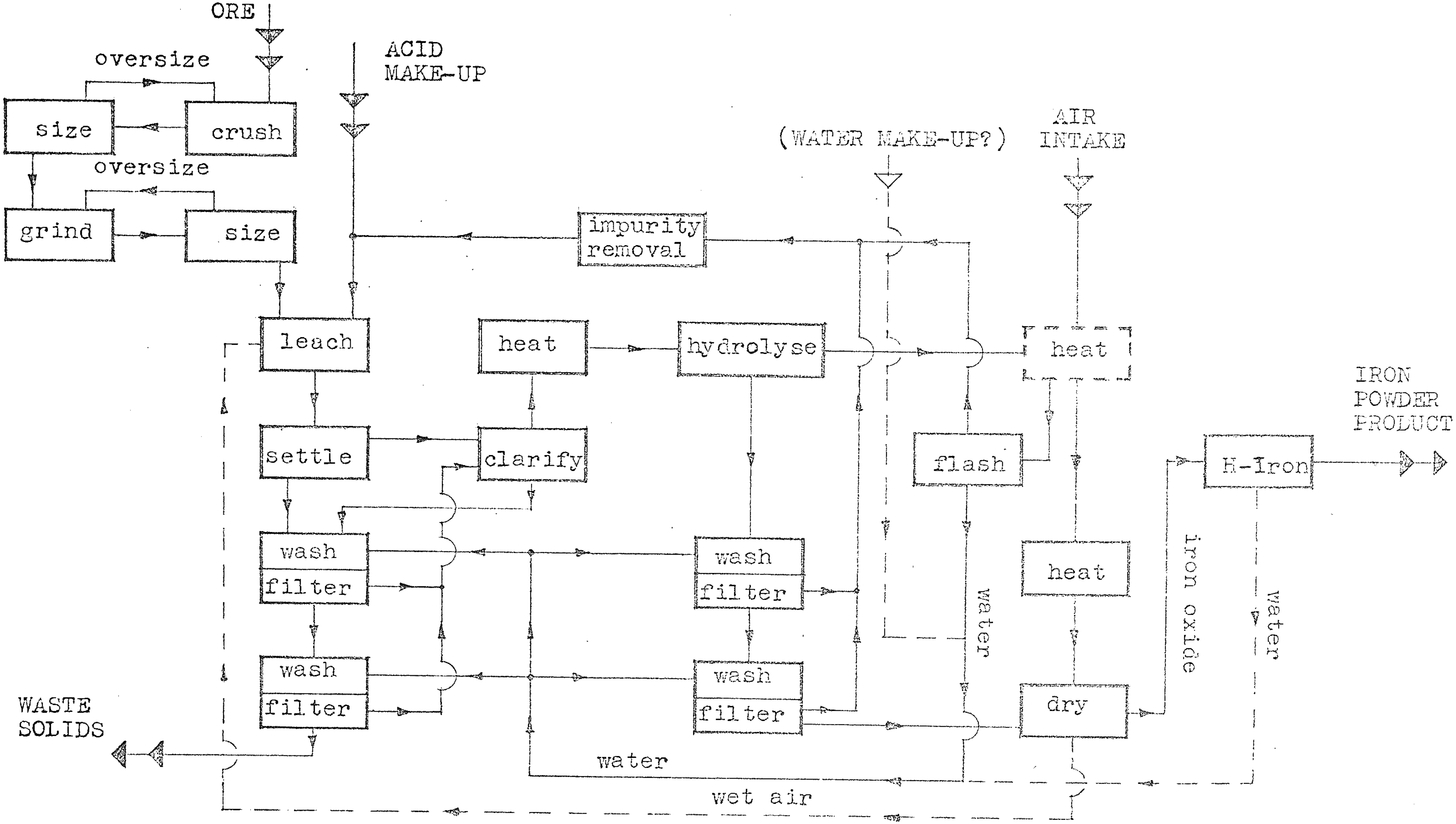


Figure 6.2

6.1.1 Leaching, reaction and washing

(All quantities are expressed in kg/hr.)

Ore

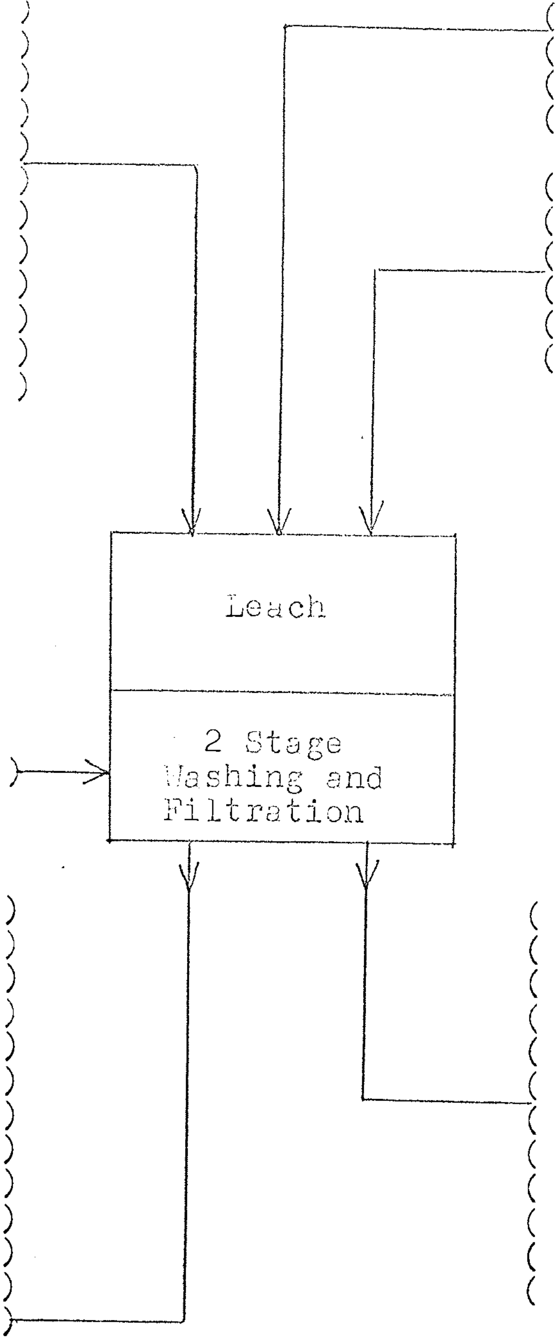
(Fe	49254)
Fe_2O_3	70048
FeO	348
Al_2O_3	7783
SiO_2	11617
CaO	4298
MgO	581
H_2O	4414
S	116
P_2O_5	1742
L.O.I.	15218
	116165

Make-up acid
(40 % wt.)

HCl	4230
H_2O	6345
	10575

Recycle acid

$FeCl_3$	23854
HCl	115420
H_2O	472255
	611529



Wash water

H_2O	37786

Residue
Solid

Fe_2O_3	3502
FeO	21
Al_2O_3	467
SiO_2	11617
CaO	258
MgO	35
H_2O	700
S	7
P_2O_5	105
L.O.I.	2181
	18893

Solution

$FeCl_3$	1045
$AlCl_3$	127
$CaCl_2$	52
$MgCl_2$	9
H_3PO_4	15
HCl	41
H_2O	17604
	18893

Leach liquor

$FeCl_3$	157981
$FeCl_2$	415
$AlCl_3$	19013
$CaCl_2$	7944
$MgCl_2$	1281
H_2S	116
H_3PO_4	2245
H_2O	543124
HCl	6150
	738269

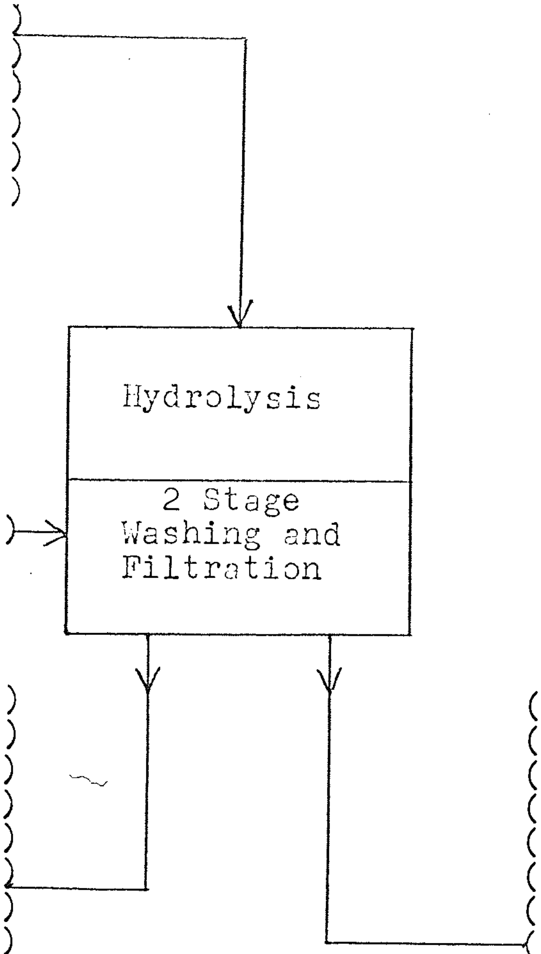
Impurities recycled with the regenerated acid from the hydrolysis stage were not included in the above mass balance because of lack of sufficient data. A two stage water wash of the unreacted ore is suggested which keeps chloride loss down to 0.68 % of reactor throughput. All information was derived from section 3.

6.1.2 Hydrolysis, reaction and washing

(All quantities are expressed in kg/hr.)

Leach liquor

$FeCl_3$	157981
$FeCl_2$	415
$AlCl_3$	19013
$CaCl_2$	7944
$MgCl_2$	1281
H_2S	116
H_3PO_4	2245
H_2O	543124
HCl	6150
	738269



Wash water

H_2O	131538

Hydrolysis liquor

$FeCl_3$	23854
$FeCl_2$	415
$AlCl_3$	18599
$CaCl_2$	7771
$MgCl_2$	1253
H_2S	116
H_3PO_4	2196
H_2O	589917
HCl	94148
	738269

Precipitate

Solid

Fe_2O_3	65769

Solution

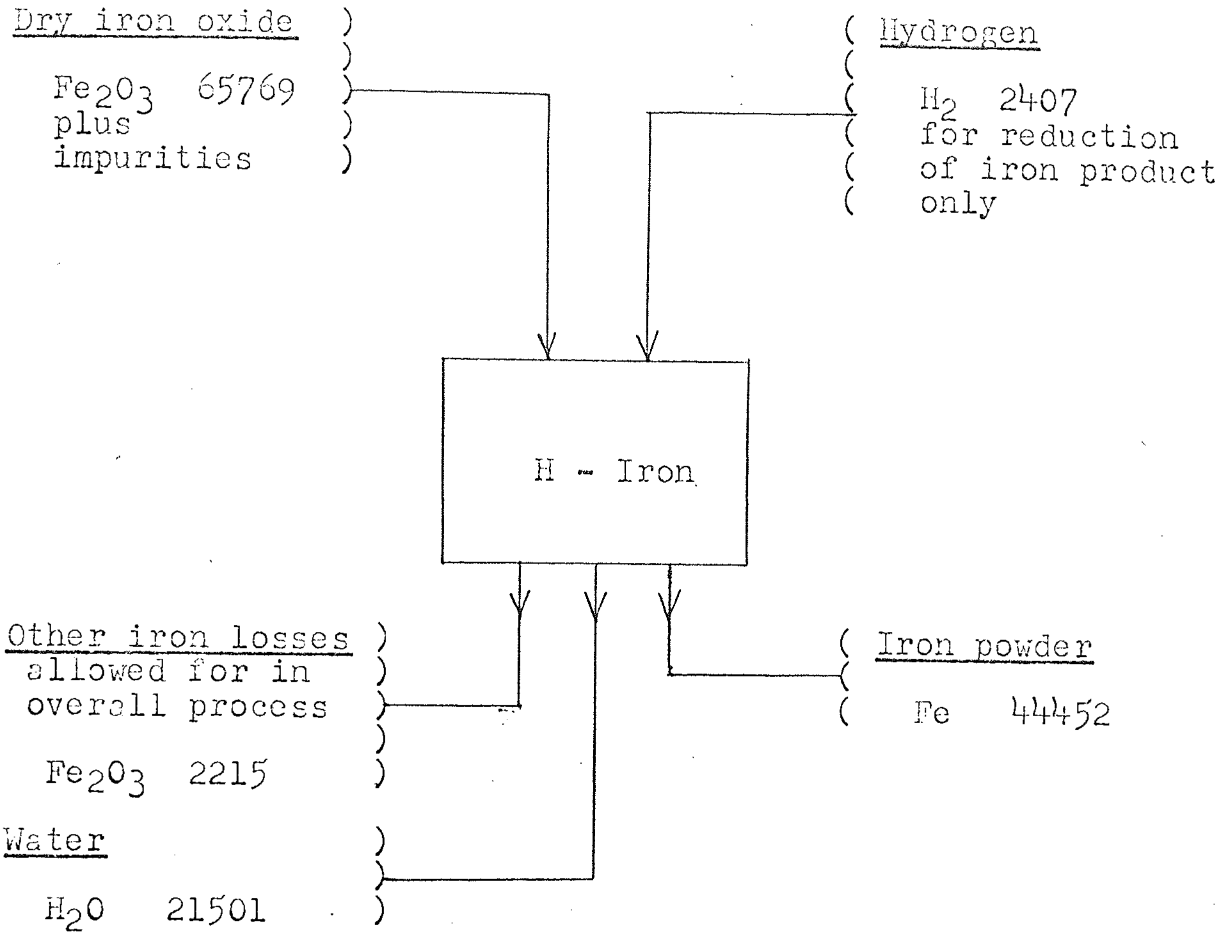
$FeCl_3$	531
$AlCl_3$	414
$CaCl_2$	173
$MgCl_2$	28
H_3PO_4	49
H_2O	62456
HCl	2118
	131538

The hydrolysis efficiency is 85.8 % by the above mass balance. The precipitated ferric oxide contains some impurities, of which the $FeCl_3$ is unimportant as it will be either hydrolysed in the drying stage, or reduced in the H-Iron process. HCl will either be removed in drying or react with some Fe_2O_3 to give $FeCl_3$ which is discussed above. This leaves aluminium, calcium, magnesium, and phosphate to contaminate the oxide and iron powder, and in the mass balance given above they constitute 1.0096 % wt. impurity in the oxide. The effect on the final iron powder is not known, although the presence of chloride ions in iron powder is known to reduce pyrophoricity. More efficient washing of the precipitated ferric oxide may be necessary and the levels to which these impurities may be reduced is shown below based on Table 3.4, and assuming a wet solid containing 50 % wt. solids:

131538 kg/hr. water total
  in 1 stage reduces impurity level in Fe_2O_3 to 1.35 % wt.
  in 2 stages " " " " " " 1.01 "
  in 3 stages " " " " " " 0.87 "
197307 kg/hr. water total
  in 1 stage " " " " " " 1.01 "
  in 2 stages " " " " " " 0.65 "
  in 3 stages " " " " " " 0.51 "
263076 kg/hr. water total
  in 1 stage " " " " " " 0.81 "
  in 2 stages " " " " " " 0.45 "
  in 3 stages " " " " " " 0.32 "

6.1.3 H-Iron

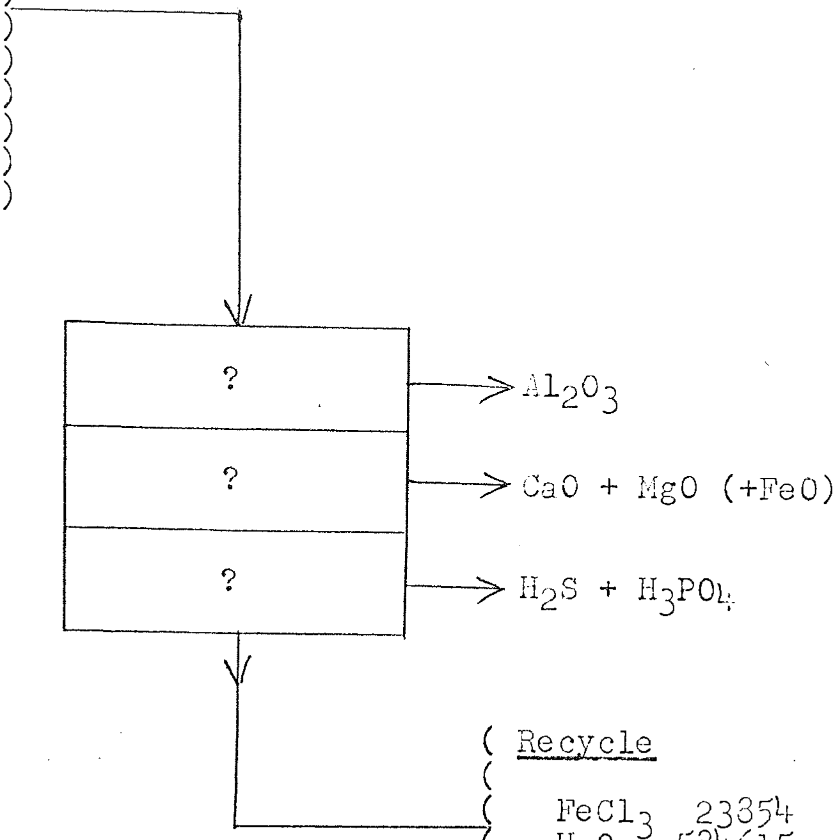
(All quantities are expressed in kg/hr.)



6.1.4 Impurity removal

The problems of impurity removal from recycle streams were discussed in section 4, without drawing any conclusions. It is not possible therefore to present a realistic mass balance, only a series of "black boxes" showing complete removal of each impurity and regeneration of acid. There will inevitably be some impurity recycling and acid loss, neither of which are included in the mass balance

Hydrolysis liquor	
$FeCl_3$	23854
$FeCl_2$	415
$AlCl_3$	18599
$CaCl_2$	7771
$MgCl_2$	1253
H_2S	116
H_3PO_4	2196
H_2O	589917
HCl	94148
	738269



Recycle	
$FeCl_3$	23854
H_2O	584615
HCl	115420
	723889

6.1.5 Acid balance

Acid and equivalent lost in ore residue	812 kg/hr.
Acid lost in ferric oxide after hydrolysis	2118 kg/hr.
Acid equivalent lost in ferric oxide after hydrolysis, approximately	700 kg/hr.
Estimated acid and equivalent lost in impurity removal, "pro rata", approximately	600 kg/hr.
	4230 kg/hr.

Of this 4230 kg/hr. , about half or 2118 kg/hr. may be recovered directly if the drying air is used for leaching agitation and heating. All the acid could be recovered theoretically, but at great expense, and optimisation would be necessary to specify minimum acid loss and minimum cost of washing, which is beyond the scope of this dissertation. Different washing techniques that do not rely on stage-wise contact and equilibrium may be used instead of the two stage washing specified, which may reduce chloride loss. The above figure of 4230 kg/hr. represents a 3.5% acid loss, or 0.095 kg acid / kg iron produced, which is probably too high.

6.1.6 Water balance over leaching and hydrolysis steps

(All quantities are expressed in kg/hr.)

	In	Out
Leaching		
Water in ore	19632	
Wash water	37786	
Water in leached residue		2881
Water associated with residue		17604
Water produced by reaction	R	
Hydrolysis		
Wash water	131538	
Water associated with oxide		62456
Water consumed by reaction (assumed to include all impurities also)		R
	188956	82941

Net water gain = 106015

Assuming the water balance is maintained over the impurity removal stages, this would result in the acid returned to leaching being 16.4 % wt. It is unlikely that concentration to 20.2 % wt. would prove difficult, and this may conveniently be carried out by flashing the hydrolysis liquor from around 250°C and 20 atm. to atmospheric temperature and pressure, with possible subsequent distillation. As an azeotrope forms at 20.2 % wt. HCl at

108.5°C, a weaker solution boils off water until this point is reached. The resulting water, 112360 kg/hr. would contribute the bulk of the water required for washing, and thus only 56964 kg/hr. would have to be provided from external sources. If the wet air from ferric oxide drying was used for leaching reactor agitation, and the product water from H-Iron reduction also used, it is likely that a surplus of water would result.

6.1.7 Heat and energy

Apart from the H-Iron reduction plant which is discussed in section 6.3, there are three areas where there appears to be a substantial heat load. These are leaching, hydrolysis, and drying, which operate at about 100°C, 250°C, and 150°C respectively. There is no reliable information on specific heats of solutions as used in this process, but in order to obtain an idea of the heat loads necessary, several simplifications have been introduced into the calculations, notably assuming that all solutions have the same thermal characteristics as water.

Leaching:

Heat required to raise all materials
in leaching system from
15°C to 100°C = $85x775x10^{6}$ cals/hr.
= 6.59×10^{7} kcals/hr.
Heat of reaction produces = $1,36 \times 10^{7}$ kcals/hr.
Net heat required = 5.23×10^{7} kcals/hr.

Hydrolysis

Heat required to raise all materials
in hydrolysis system from
100°C to 250°C (max) = $150x870x10^{6}$cals/hr.
= 13.05×10^{7}kcals/hr.

Heat of reaction requires = 1.36×10^7 kcals/hr.

Net heat required = 14.41×10^7 kcals/hr.

Drying

Heat required to evaporate water from wet ferric oxide (at say 200°C) assuming no sensible heat required = $500 \times 65.8 \times 10^6$ cals/hr.

= 3.29×10^7 kcals/hr.

The heat requirements may therefore be summarised as:

Leaching : 52.3×10^6 kcals/hr.

Hydrolysis : 144.1×10^6 kcals/hr.

Drying : 32.9×10^6 kcals/hr.

It is likely that all the heat necessary for leaching and acid concentration, and some of the preheat for drying air may be obtained from hydrolysis liquor at 250°C. The overall heating requirements are therefore thought to be about 160×10^6 kcals/hr. or 6350 therms/hr. which represents 145 therms per long ton iron. The reduction process is considered as a separate unit with no interchange of energy. (See section 8).

6.2 Scrap based process

An overall flow diagram of the process to manufacture iron powder from scrap iron via chloride reduction is shown in Figure 6.3. Stage - wise mass balances follow based on earlier calculations in sections 3, 4, and 5. Impurities are not considered. All quantities are expressed in kg/hr.

Flow Diagram of Process to Manufacture Iron Powder from Scrap

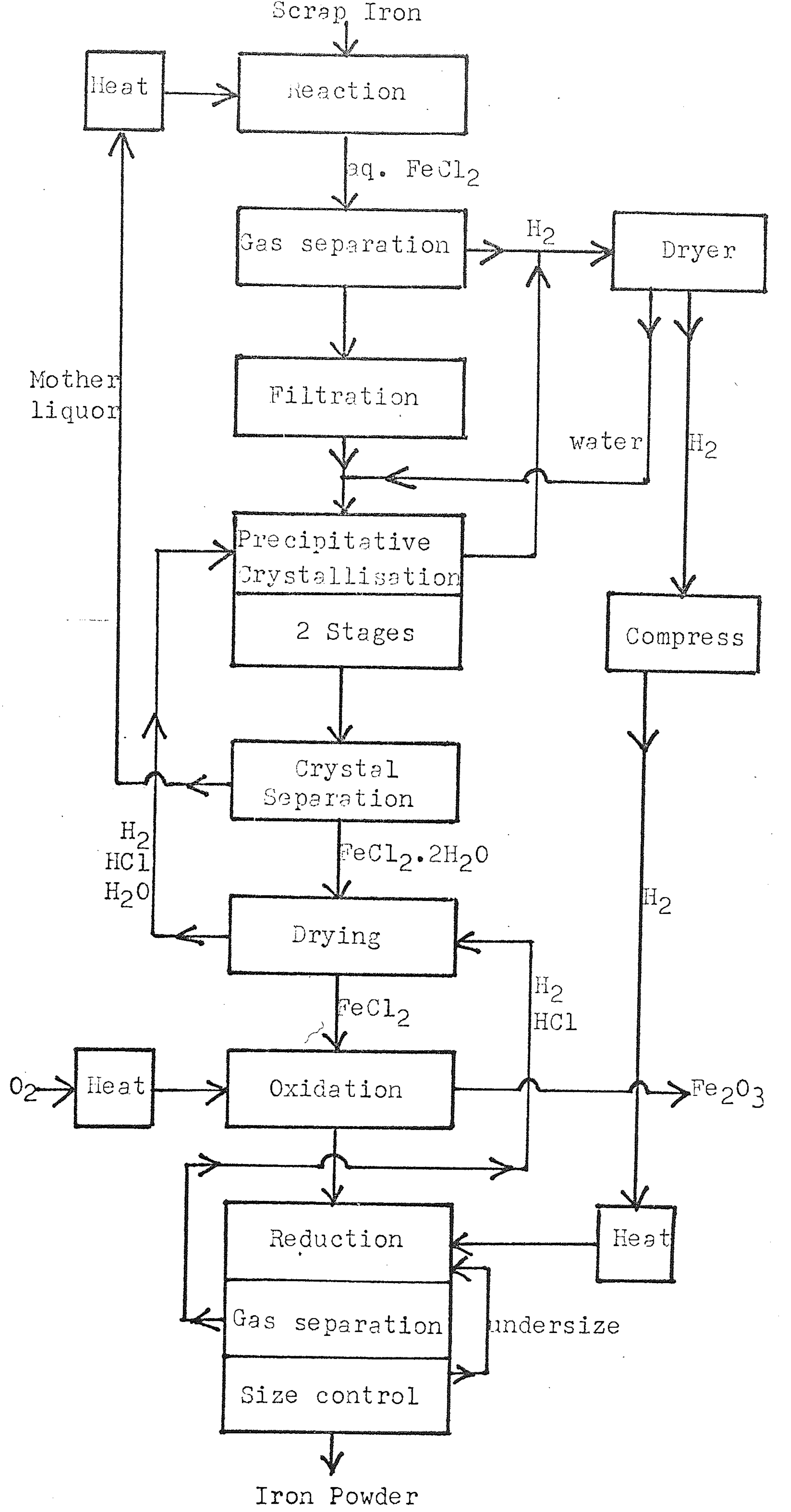
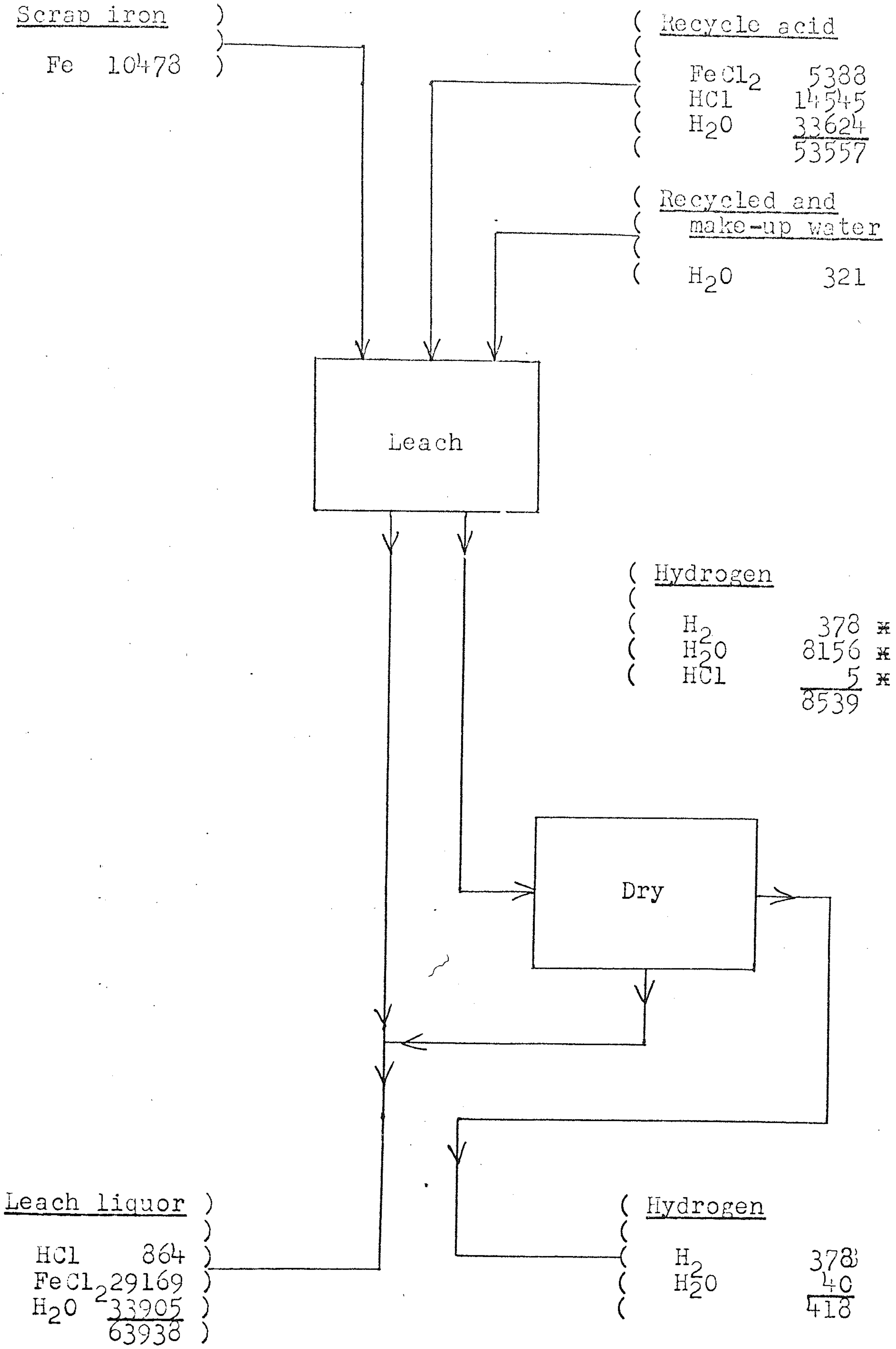


Figure 6.3

6.2.1 Leaching

(All quantities are expressed in kg/hr.)



Notes: ⁎ assuming total pressure of 2 atm (see text following)

If the hydrogen from the top of the reactor is assumed to be in equilibrium with the liquid at the top of the reactor, then for 1.35 % wt. HCl the partial pressure of HCl at 110°C is 0.20 mm mercury, and of H_2O at 110°C is 1074.6 mm. (Appendix II). The water and acid content of the hydrogen depend on the total pressure of the system, which is shown below as exit gas composition in kg/hr:

	Total Pressure		
	1½ atm.	2 atm.	3 atm.
H_2O	55673	8156	3012
HCl	24	5	1
H_2	378	378	378

As it is necessary to return all water, or as much as possible, to the leach liquor to prevent precipitation of ferrous chloride, the hydrogen needs to be cooled to condense the water. This is also necessary to prepare the hydrogen for reduction later, and may serve as temperature control. (see section 3.3 et seq.) The choice of total system pressure depends therefore on a heat balance of the system and the dissipation of heat of reaction. Ideally an optimisation should be carried out on the heat requirements of the reactor, and its relationship to equipment size and hence cost, but this is beyond the scope of this dissertation. If the hydrogen is cooled to 20°C, it will have the following composition (kg/hr.):

	Total Pressure		
	1½ atm.	2 atm.	3 atm.
H_2O	53	40	26
HCl	0	0	0
H_2	378	378	378

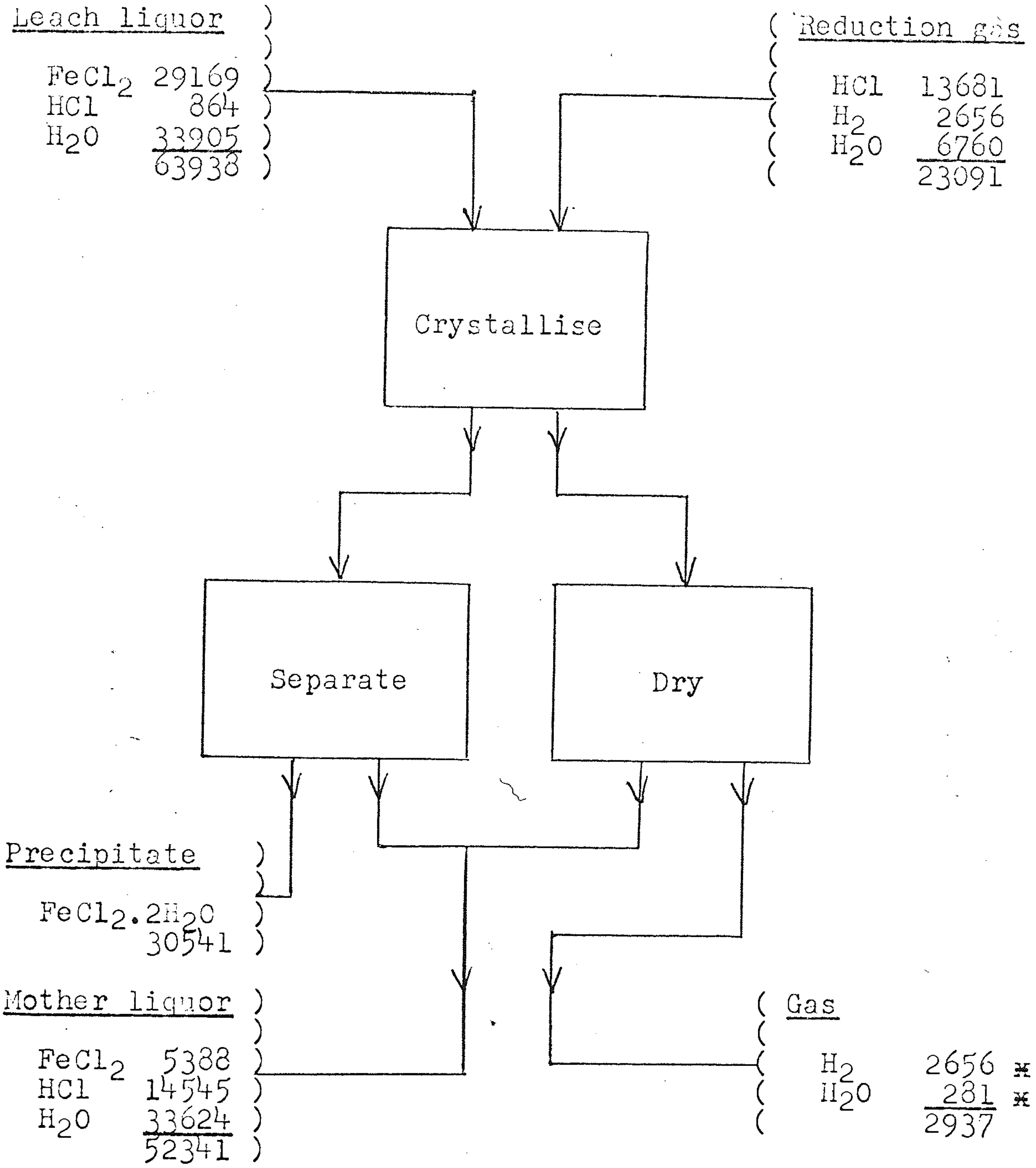
The condensed acid will then contain (kg/hr.):

	$1\frac{1}{2}$ atm.	2 atm.	3 atm.
H_2O	55620	8116	2986
HCl	24	5	1

which is returned to the leach liquor. Figures for operation at 2 atm. are included in the mass balance above.

6.2.2 Precipitative crystallisation

(All quantities are expressed in kg/hr.)



Leach liquor

$FeCl_2$	29169
HCl	864
H_2O	33905
	63938

Reduction gas

HCl	13681
H_2	2656
H_2O	6760
	23091

Precipitate

$FeCl_2.2H_2O$	30541

Mother liquor

$FeCl_2$	5388
HCl	14545
H_2O	33624
	52341

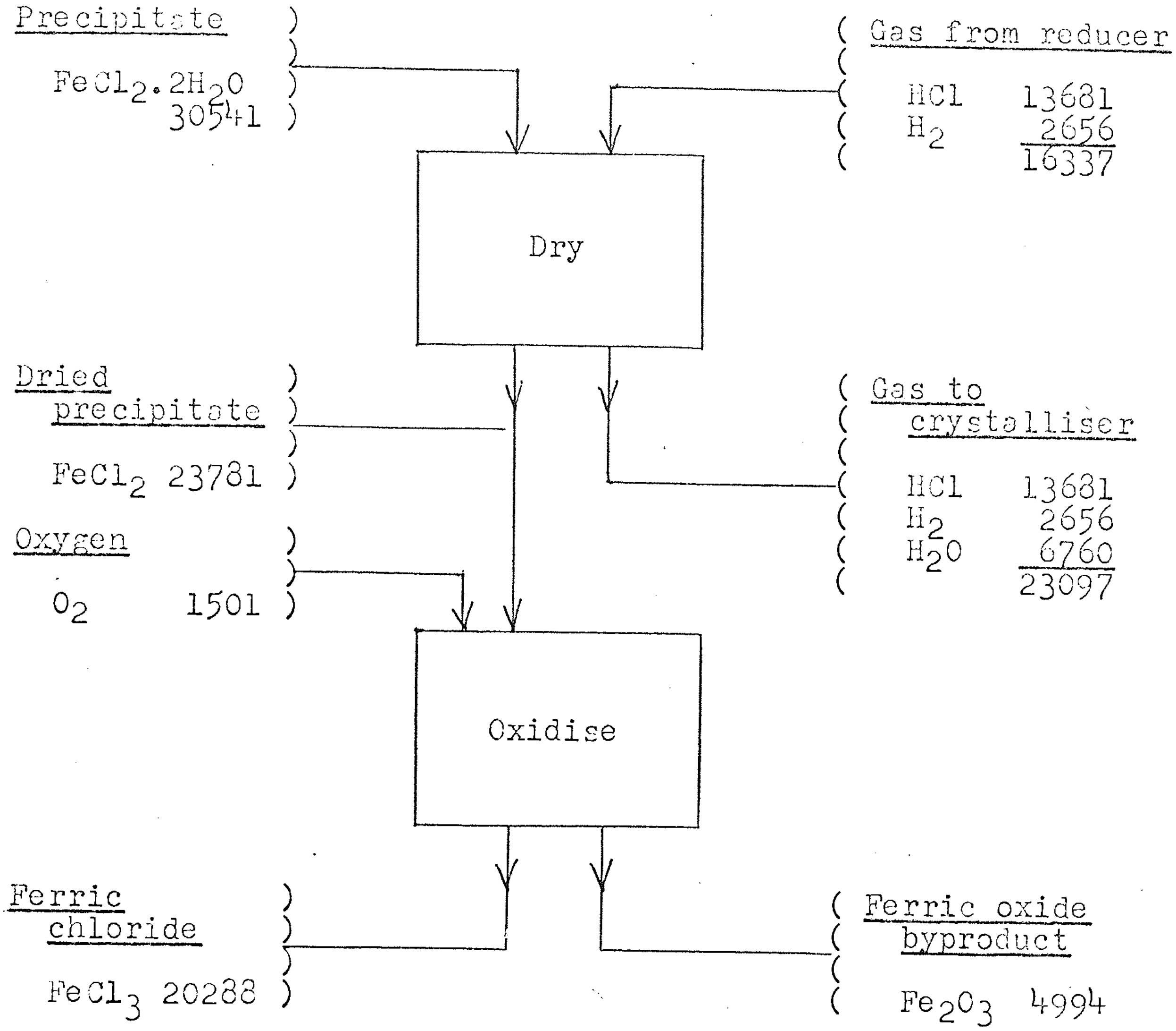
Gas

H_2	2656 *
H_2O	281 *
	2937

Notes: * drying assumed at 2 atm. pressure and 20°C, as discussed in previous section.

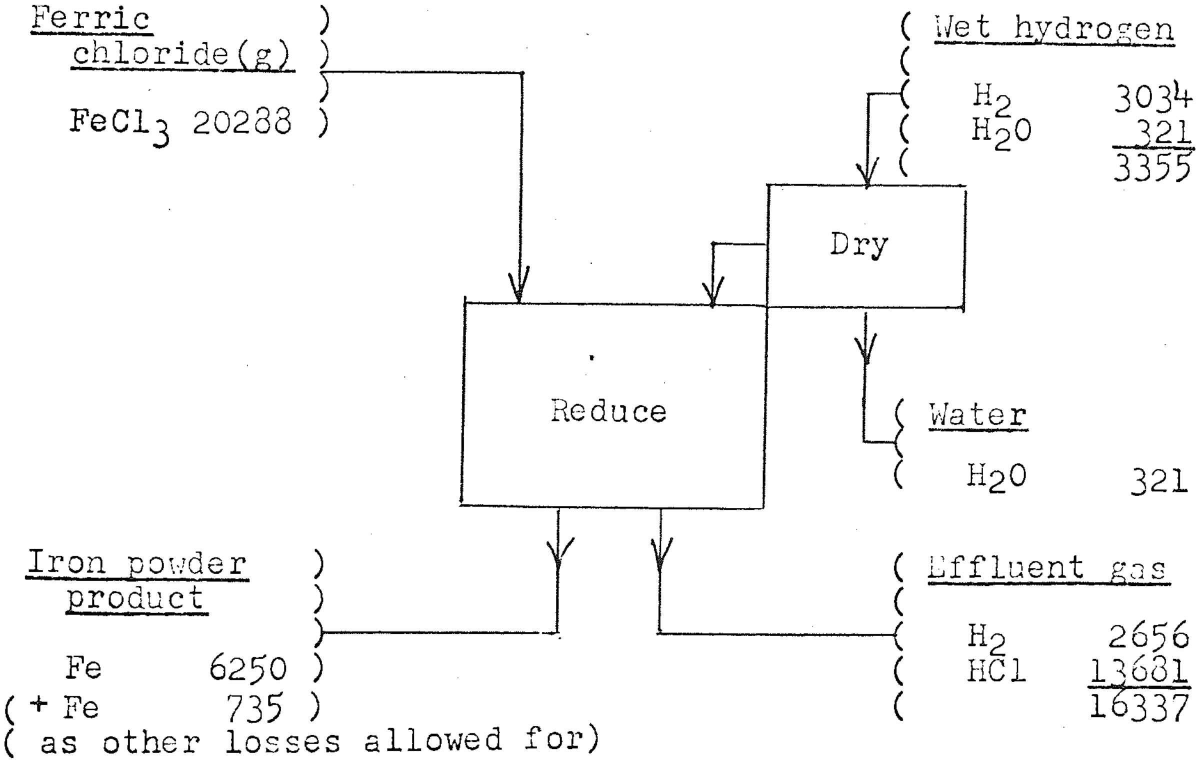
6.2.3 Drying and Oxidation

(All quantities are expressed in kg/hr.)



6.2.4 Reduction

(All quantities are expressed in kg/hr.)



6.2.5 Heat and Energy

Since the scrap based process starts with metallic iron, and produces metallic iron and ferric oxide in the ratio of 2:1, the theoretical total energy requirement is minus one third the heat of formation of ferric oxide; i.e. a surplus of 32,800 cals/g mole Fe_2O_3 which corresponds to 1.0257×10^6 kcals/hr. of heat produced.

Unfortunately this is not realistic, and approximate heat balances have been calculated for each stage of the process with similar underlying assumptions as section 6.1.7. A heat "flow diagram" with temperatures is shown in Figure 6.4. From this diagram it may be seen that there are five areas requiring a substantial heat load: leaching, crystallisation, drying, oxidation, and reduction.

Leaching:

Heat required to preheat recycle acid = assumed 0, except at start up, and losses.

Heat required to raise iron feed from 15°C to 110°C = $95 \times 6.27 \times 1.0478 \times 10^7$ cals/hr.

= 6.24×10^6 kcals/hr.

Heat generated by reaction = $20300 \times 1.8761 \times 10^5$ cals/hr.

= 3.81×10^6 kcals/hr.

Net heat required = 2.44×10^6 kcals/hr.

Heat required for evaporation of water is not included, as this both controls and is controlled by the temperature and pressure of the reactor. See section 3.3 et seq. and section 6.2.1

Temperature and Heat Requirements of Scrap based Process

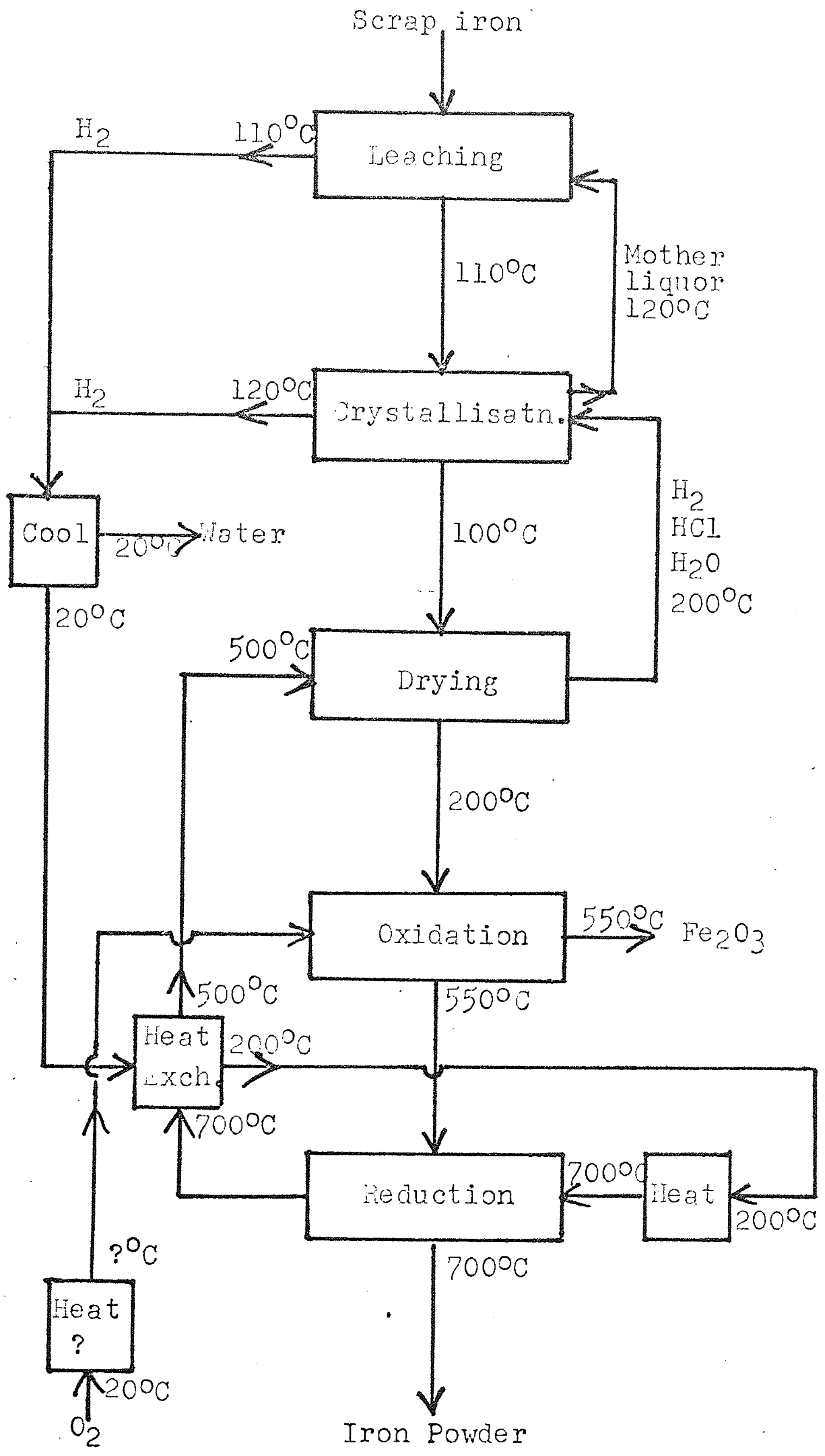


Figure 6.4

Crystallisation:

Heat generated by dissolution of HCl = $487.7 \times 1.3681 \times 10^7$ cals/hr.

= 6.67×10^6 kcals/hr.

Heat generated by condensation of water = $542.2 \times 6.76 \times 10^6$ cals/hr.

= 3.67×10^6 kcals/hr.

Sensible heat in gas stream above 100°C = $7 \times 50(?) \times 2.078 \times 10^6$ cals/hr.

= 0.73×10^6 kcals/hr.

Heat taken up by crystallisation of $FeCl_2.2H_2O$ = $142.79 \times 2.3781 \times 10^7$ cals/hr.

= 3.40×10^6 kcals/hr.

Net surplus heat = 7.67×10^6 kcals/hr.

Heat required for evaporation of water is not included, as this may be used for control purposes as above.

Drying:

Heat required to evaporate water (and dehydrate ?) = 3.67×10^6 kcals/hr. (from above)

Sensible heat in gas stream 'out' above 100 °C = 0.73×10^6 kcals/hr. (from above)

Heat required to heat dihydrate and contained in dried $FeCl_2$ = 0

Net heat required = 4.40×10^6 kcals/hr.

Heat contained in gas stream to drier (from reducer) = $7 \times 1.703 \times 10^3$ kcals/°C.hr.

= 11.92×10^3 kcals/°C.hr.

The reducer gas to the drier therefore needs to be 367°C above the drier outlet temperature to provide enough heat for drying, i.e. at about 500°C. As the reducer gas exit temperature is at 700°C it is unlikely that additional external heat would be required for this stage.

Oxidation:

Heat required to heat $FeCl_2$ from
100°C to 550°C = $20 \times 450 \times 187.61 \times 10^3$ cals/hr.
= 1.69×10^6 kcals/hr.

Heat required to heat oxygen to 550°C = $7 \times 530 \times 46.9 \times 10^3$ cals/hr.
= 0.17×10^6 kcals/hr.

Heat produced by reaction = $45840 \times 15.63 \times 10^3$ cals/hr.
= 0.72×10^6 kcals/hr.

Net heat required = $\underline{1.14 \times 10^6}$ kcals/hr.

Reduction:

Heat required to heat hydrogen
from 200°C to 700°C (preheated) = $7 \times 500 \times 1.328 \times 10^6$ cals/hr.
= 4.65×10^6 kcals/hr.

Heat required to heat $FeCl_3$ vapour
from 550°C to 700°C = $7 \times 150 \times 1.25 \times 10^5$ cals/hr.
= 0.13×10^6 kcals/hr.

Heat required by reaction varies between $13191 \times 1.12 \times 10^5$ cals/hr. and $-3109 \times 1.12 \times 10^5$ cals/hr. depending on extent of dimerisation of $FeCl_3$ and mode of reduction. The worst case gives the heat required = 1.48×10^6 kcals/hr.

Heat of association of $FeCl_3$ = 0, incorporated in heat of reaction above.

Net heat required = $\underline{6.26 \times 10^6}$ kcals/hr.

The heat requirements may be summarised:

Leaching : 2.44×10^6 kcals/hr.) Plus heat for water
Crystallisation : -7.67×10^6 kcals/hr.) evaporation by H_2) evolution
Drying : 0
Oxidation : 1.15×10^6 kcals/hr.
Reduction : 6.26×10^6 kcals/hr.

Based on these calculations, the overall heat requirements of this process are 9.35×10^6 kcals/hr. or 392 therms/hr. which represents 62.7 therms/long ton iron. The surplus heat in the crystallisation stage may be used to supply the heat requirements of the leaching stage when the overall heat requirement drops to 47 therms/ton iron, or it may be used for evaporation of water or preheating which have not been included. It must be emphasised that these figures are only intended to indicate the magnitude of the heat requirements. Rigg (2-46,2-55) suggested that heat losses of about 35% were obtained in the reduction end of the R.C.A. process, but this figure is not thought meaningful for the process considered here, and allowances for heat losses have not been included.

6.3 H-Iron process

The reduction plant is considered a self-contained unit. Relevant details have been extracted from Dyck et al. (5-5), and are given below for a 147,300 long tons p.y. plant:

	H_2 plant	Ore prepn.	Ore redn.	Offsites	Total
H_2, m scfd.			11.0		11.0
Fuel, therms/hr.	2260	470	603	478	3466
(credit, vent gas)			345		
Electricity, Kw	113	370	200	740	1788
650 psig steam, lb/hr			34100		34100

	H_2 plant	Ore prepn.	Ore redn.	Offsites	Total
Water circn., gpm	3700		7100		10800
Water make-up, gpm	80	200	66	557	903
Catalysts, chemicals etc. £/d	86.90	30.00		10.00	126.90
N_2, m scfd	1.2		0.3		1.5
Labour, man-hrs/day	96.0	192.0		24.0	312.0

The total heat (energy) requirement is 210 therms/long ton iron, or 184 therms/long ton iron excluding ore preparation.

6.4 Comparative energy requirements

Calculations have been made on the heat requirements for both processes considered in this dissertation, the "dry" chloride process described in section 4, and the R.C.A. process. The results are summarised in Table 6.1, and are merely a guide to the overall process heat requirements and should be treated with caution. The units of therms/long ton iron were chosen in order to compare these chemical routes with orthodox iron and steel manufacturing practice, which has been adequately covered in an appended paper. It is the first time that realistic heat requirement estimates have been obtained for the "wet" processes discussed herein, and it is likely therefore that the figures quoted in Table 6.1 are more accurate than those in the appended paper.

Table 6.1

Comparison of Heat Requirements

Therms per long ton Iron

Operation	Wet, Oxide Reduction		Wet, Chloride Reduction		Dry, Chloride Reduction		R.C.A. (10)	
	Ore feed	Scrap feed	Ore feed	Scrap feed	Ore feed	Scrap feed	Ore feed	Scrap feed
Preredn.(1)	-	-	80(2)	-	160	-	13.7	0
Leaching	0(6)	15.5	0(7)	15.5(8)	(3)	(3)	-	-
Evaporatn.	-	-	-	-	-	-	160	160
Hydrolysis	131	91(4)	-	-	-	-	-	-
Crystalln.	-	-	0(8,9)	0(8,9)	-	-	-	-
Drying	15	15	0	0	-	-	53	53
Oxidation	-	-	7.3	7.3	7.3	7.3	-	-
Subtotal	146	121.5	87.3	22.8	167.3	7.3	226.7	213
Reduction	190	95(?)	39.7(5)	39.7(5)	45(5)	45(5)	145	74
TOTAL	336	216.5	127	62.5	212	52	372	287

Notes:

(1) Reduction using the cheapest method available e.g. Stelco-Lurgi (coal reduction).

(2) Assuming partial metallization to ensure iron is in the ferrous form. The alternative is reduction of ferric chloride solution from ore leaching with scrap iron which would require much less heat.

(3) Surplus of 24 therms.

(4) Hydro-oxidation of $FeCl_2$ with O_2 and H_2O is exothermic, compared to the endothermic hydrolysis of $FeCl_3$.

(5) Excluding H_2 plant.

(6) Heat obtained from hydrolysis.

(7) Heat obtained from crystallisation.

(8) Excluding heat for water evaporation.

(9) Surplus of 48.7 therms.

(10) The R.C.A. process is "wet", with chloride [illegible] reduction.

7. CAPITAL COST ESTIMATION

A number of capital cost estimating techniques were discussed in Section 2.8.1, concluding that the functional unit approach appears to offer the most interesting development for a rapid capital cost estimate requiring minimal information.

7.1 Parameters

The overall capital cost of a process may be considered to be a function of:-

Number of functional units
Plant capacity, or preferably throughput
Temperature requirements
Pressure requirements
Cost Index
Materials of construction

It is particularly important that each parameter be defined as precisely as possible.

Functional unit: This is the key to the whole estimating technique, but is also probably the most difficult term to define. Functional units are significant pieces of plant that carry out physical or chemical operations on the main process stream or substantial recycle streams. These are usually represented by individual blocks in initial flow diagrams. Examples would include distillation columns and rotary vacuum filters, whereas items such as pumps, heat exchangers, reboilers, hoppers which are subsidiary to a unit operation or process are included in the functional unit. Similarly, the actual size or number of sub-units (as in a multi-effect evaporator) are neglected.

Storage tanks and hoppers are also ignored. Pieces of equipment that carry out mechanical separation only count as functional units if they constitute substantial systems in their own right, and cannot reasonably be built into a unit operation or unit process. Included would be crushers, centrifuges, and rotary vacuum filters, but not cyclones, or simple gravity settlers without mechanical gear. Mechanical items for feeding, discharging, heating or cooling (the latter two only for excessive heat loads) complete process systems count as a functional unit. It is sometimes difficult to determine if an item is a functional unit, and while this comes with practice it is sometimes helpful to think of halves of functional units. An example is given in Section 2.8.

The number of functional units in a process is represented by N.

Plant capacity or throughput: The cost of a plant may be expected to bear a relationship to the throughput rather than capacity particularly when large recycles are encountered. Gore, in his work on gas processes used a molar expression (i.e. volumetric) rather than mass, to take account of varying densities, but for liquid-solid systems a mass term is considered satisfactory. Since information is usually available on capacity, a term $\frac{Q}{S}$ is proposed where Q is stated plant capacity in long tons p.y., and S represents a "conversion" factor which will effectively account for recycle. More precisely, to take into account the work studied here when inert solvents are encountered, S is defined as:

$$\frac{\text{weight of desired reactor product}}{\text{weight of total reactor input (or output)}}$$

. Where more than one reactor (as a functional unit) is encountered, the lowest value of S is used. The ratio Q/S is raised to a power x to account for effect of scale, and x would be expected to be around 0.6 - 0.7, but requires determination.

Temperature requirements: Previous work by Gore (see Section 2.8.1) used essentially a ratio of maximum process temperature to ambient temperature. The ratio was raised to a power dependent on plant throughput, and this term had a significant effect on the capital cost which might be expected for gas based processes. In view of the apparent importance of process temperature, and in order to try and obtain a better correlation; an attempt was made to relate capital cost to the proportion of functional units operating at high temperature. The following term is proposed:

$$\left(T \times \frac{n}{N}\right)^{y}$$

where T = maximum process temperature ^{o}C

n = number of functional units of maximum temperature greater than T/2

N = Total number of functional units

y requires determination

An alternative is to consider the total number of functional unit-temperature units involved in the process which may be represented as $(T.n)^{y}$.

Pressure requirements: The effect of pressure was found to be less marked by Gore (see Section 2.8.1); with capital cost proportional to $P^{0.395}$ where P = maximum process pressure in atmospheres. Again, the size of a gas based process might be expected to be more influenced by pressure than a liquid based process. As very little data has been found on capital costs of hydrometallurgical processes, and as few of these operate at a pressure greater than atmospheric, it may not be possible to include a useful correlation. A similar term might be employed for pressure as temperature, i.e. $\left(P \times \frac{n'}{N}\right)^3$ where

P = maximum process pressure, atm

n' = number of functional units of maximum pressure greater than P/2

N = Number of functional units

3 requires determination

As for the temperature term, an alternative expression is $(P.n')^3$.

Both pressure and temperature terms are not expected to influence the capital cost of aqueous processes as much as gaseous processes.

Materials of Construction: Gore (Section 2.8.1) could not obtain a meaningful correlation for materials of construction effect on capital cost. Zevnik and Buchanan (2-63) employed a factor Fm ranging between 0 and 0.4. This, together with expressions for maximum temperature and pressure, was used in the following expression:

$2 \times 10^{(Fr + Fp + Fm)}$ which gives an effective range of 1.0 to 5.0. This was multiplied by throughput and functional unit number terms to obtain capital cost. Stallworthy (2-65) employed a directly proportional factor ranging between 1.0 and 2.0.

Clearly plants constructed of stainless steel for example are likely to cost more than plants constructed from mild steel, but it is difficult to put actual values to the materials of construction factor Fm. All the hydrometallurgical data presented in this section is based on acid processes, and can therefore be considered as being constructed of similar types of equipment using the same Fm. factor. For aqueous mineral acid processes therefore, Fm will be considered as 1.0: which would account for a plant built of stainless steel, or similar corrosion resistant material including lined vessels. Equipment for alkaline and neutral operation might then be expected to cost say 20-25% less, when mild steel equipment could be employed. In these circumstances Fm might be 0.80. A "mixed" process, such as aqueous oxidation of pyrite, when some acid might be produced could be given Fm of 0.90. Initially, the effect of materials of construction will be ignored for simplicity.

Cost Index: There are a number of cost indices for building and construction, which relate cost of construction or equipment to raw material and labour prices in a given year. Cost of construction is usually made up of cost of equipment plus cost of labour, and while these might be expected to bear a constant relationship, this is in fact not so. One of the more widely known cost construction indices is E.N.R. (Engineering News Record), of the U.S.A. This journal carries out a state by state survey every month and publishes detailed information weekly, quarterly and annually. In view of the general availability of this index and apparent accuracy, it has been chosen for incorporation in the equation below and is given in Table 7.1. Another well known index in the U.S.A. is Marshall and Stevens, and there are several others, all included in E.N.R. for comparison. In the U.K. the journal "Chemical Engineering" (7-1) publishes a cost index monthly but no details are given and it is only a relatively recent introduction.

Other terms: The capital cost derived from the proposed equation will apply to processes for the U.K. and North America. Factors will be necessary for conversion to other countries and the following information is available (2-64).

U.S.A. and U.K.	1.0
France, Holland, Belgium, Spain	1.0
Germany	0.97
Italy	0.92
Scandinavia	1.1
Japan	0.9
India	1.35
Zambia	approx. 2.5

When devaluation has occurred, it is usually more reliable to employ the pre-devaluation exchange rate until the relative economies of the countries concerned have stabilised.

The above discussion gives the following general equation:

$$\text{Capital cost £} = A.N. \left(\frac{Q}{S}\right)^{x} \cdot \left(\frac{T.n}{N}\right)^{y} \cdot \left(\frac{P.n'}{N}\right)^{3} \cdot Fm. \frac{ENR.}{1300}$$

which was used as a basis for development in the following section.

TABLE 7.1

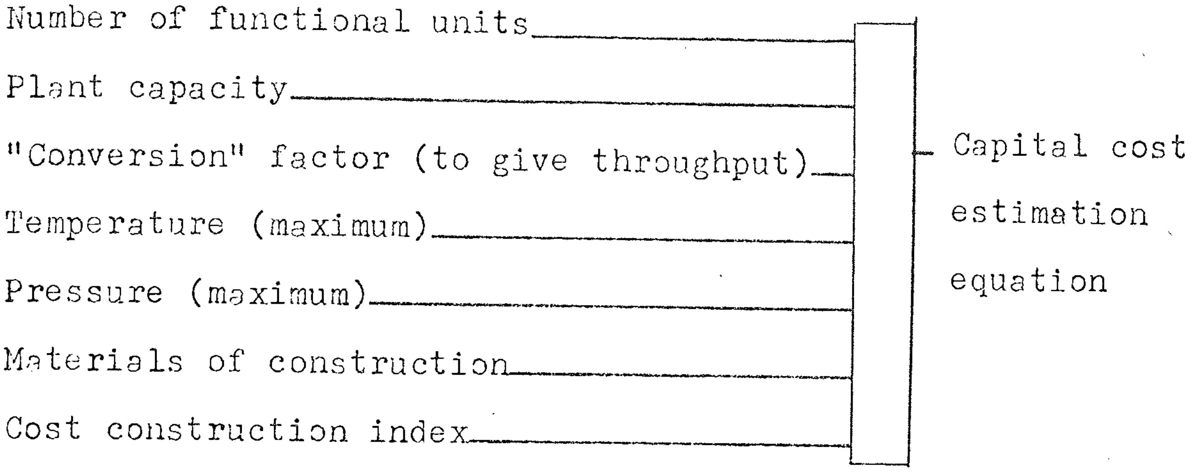
E.N.R. Cost Construction Index

1903	93.9	1948	460.72
1905	90.55	1949	477.02
1910	96.33	1950	509.62
1913	100.00 (Base)	1951	542.62
1915	92.58	1952	569.40
1920	251.28	1953	599.99
1925	206.68	1954	627.96
1930	202.85	1955	659.72
1931	181.35	1956	692.37
1932	156.97	1957	723.85
1933	170.18	1958	759.16
1934	198.10	1959	796.91
1935	196.44	1960	823.55
1936	206.42	1961	847.05
1937	234.71	1962	871.84
1938	235.83	1963	900.73
1939	235.51	1964	936.38
1940	241.96	1965	971.22
1941	257.84	1966	1019.08
1942	276.30	1967	1070.40
1943	289.95	1968	1154.04
1944	298.72	1969	1270.46
1945	307.75	1970	1340 *
1946	346.04	1971	1500 *
1947	413.16		

* estimated

7.2 Method

From the preceding section a general equation was obtained based on all the parameters that are considered to affect capital cost:



$$\text{Capital cost} = A.N.\left(\frac{Q}{S}\right)^{b}.\left(\frac{T.n}{N}\right)^{c}.\left(\frac{P.n'}{N}\right)^{d}.\ Fm.\frac{ENR}{1300} \quad \text{(Eqn.7.1)}$$

It must be emphasised that this equation is purely empirical in form and content, being based on earlier work by Gore, Stallworthy and Zevnik and Buchanan (see Section 2). The principle is that the average cost of a functional unit is dependant on the parameters outlined above. The notion of expressing the inter-relationships in the form given appeared to be the most reasonable point to start the development without including complex functions which could be incorporated when necessary.

Data on capital costs and operating details was obtained from the literature and industrial concerns, and the relevant information extracted and collated in Table 7.2. The most difficult parameter to assess was number of functional units, which was obtained usually from a flow diagram in the reference. The definitions in the preceding section were followed as closely as possible, particularly for functional

TABLE 7.2

No.	Process	Cap. Cost £	N F.U.N.	Q Cap. L.T.p.a.	S "Conversion"	T Max. Temp. °C	n No. of E U. temp. T/2	P Max. Press. Atm.	n' No. of F.U. press.P/2	Fm	Year	ENR Cost Index	Reference
1	R.C.A.	5,350,000	14	44,600	0.20	750	2	1	(14)	1.0	1968	1154	Appended
2		3,075,000	14	17,900	0.20	750	2	1	(14)	1.0	1968	1154	Appended
3		8,170,000	14	89,300	0.20	750	2	1	(14)	1.0	1968	1154	Appended
4	FLOX	17,300,000	13	350,000	0.21	700	3	1	(13)	1.0	1959	797	2-68
5		4,550,000	13	50,000	0.21	700	3	1	(13)	1.0	1959	797	2-68
6	Al_2O_3	28,629,000	21	312,480	0.19	1,100	3	1	(21)	1.0	(1962/3)	886	2-26
7	(Peters)	35,895,000	21	312,480	0.19	1,100	4	1	(21)	1.0	(1962/3)	886	2-26
8		44,574,000	26	312,480	0.19	1,100	4	1	(26)	1.0	(1962/3)	886	2-26
9		33,310,000	23	312,480	0.19	1,100	3	1	(23)	1.0	(1962/3)	886	2-26
10		34,892,000	21	312,480	0.19	1,100	4	1	(21)	1.0	(1962/3)	886	2-26
11		37,615,000	23	312,480	0.16	1,300	3	1	(23)	1.0	(1962/3)	886	2-27
12		33,072,000	22	312,480	0.17	1,300	3	1	(22)	1.0	(1962/3)	886	2-27
13		31,018,000	21	312,480	0.16	1,300	3	1	(21)	1.0	(1962/3)	886	2-27
14	Sponge Fe	6,288,000	13	109,375	0.31	980	3	10.2	1	1.0	1967	1070	2-70
15	(ex pyrite)	7,841,000	16	109,375	0.31	980	3	10.2	1	1.0	1967	1070	2-70
16		11,212,000	13	218,750	0.31	980	3	10.2	1	1.0	1967	1070	2-70
17		13,599,000	16	218.750	0.31	980	3	10.2	1	1.0	1967	1070	2-70
18		19,470,000	13	437,500	0.31	980	3	10.2	1	1.0	1967	1070	2-70
19		24,016,000	16	437,500	0.31	980	3	10.2	1	1.0	1967	1070	2-70
20	Ni	31,250,000	28	22,320	0.016	700	1	30	1	1.0	1971	1500	2-73
21	Fe powder	1,727,000	20	29,460	0.091	950	5	1	(20)	1.0	1941	253	2-12
22	NiS	26,786,000	31	62,430	0.015	550	8	7	5	1.0	1959	797	2-77
23	Ni	15,000,000	32	13,390	0.037	950	2	47.6	5	1.0	1971	1500	2-71
24	BeO	1,381,800	24	375	0.13	750(?)	2	1	(24)	1.0	1964/5	954	2-71
25		3,129,000	28	375	0.032	750(?)	2	1	(28)	1.0	1964/5	954	2-71
26		1,052,100	24	188	0.13	750(?)	2	1	(24)	1.0	1964/5	954	2-71
27		2,060,100	28	188	0.032	750(?)	2	1	(28)	1.0	1964/5	954	2-71

TABLE 7.2 Continued

No.	Process	Cap. Cost £	N F.U.N.	Q Cap. L.T.p.a.	S "Conversion"	T Max. Temp. °C.	n No. of F.U. temp. T/2	P Max. Press. Atm.	n' No. of F.U. press. P/2	Fm	Year	ENR Cost Index	Reference
28		1,913,100	21	375	0.068	1,250	1½	1	(21)	1.0	1964/5	954	2-71
29		3,908,000	26	375	0.013	1,250	1½	1	(26)	1.0	1964/5	954	2-71
30		1,506,750	21	188	0.068	1,250	1½	1	(21)	1.0	1964/5	954	2-71
31		2,554,650	26	188	0.013	1,250	1½	1	(26)	1.0	1964/5	954	2-71
32		1,684,200	23	375	0.067	1,500	1	1	(23)	1.0	1964/5	954	2-71
33		1,381,800	23	188	0.067	1,500	1	1	(23)	1.0	1964/5	954	2-71
34		1,663,200	20	375	0.026	1,500(?)	1	1	(20)	1.0	1964/5	954	2-71
35		1,317,750	20	188	0.026	1,500(?)	1	1	(20)	1.0	1964/5	954	2-71
36	Co	4,000,000	30	1071	0.017	680	3	40	1	1.0	1968	1,154	2-72
37	Zn(and Pb)	1,286,000	17	11000	0.21	450	4	54.4	1	1.0	1963	900	2-81

Notes to Table 7.2

Data number	
1 - 3	Process details have been widely published but not the offical capital cost. The figure quoted for 1 has not been denied by Woodall Duckham. 2 and 3 are derived by 1 by simply applying the usual two-thirds power law. This is discussed later.
4, 5	Confidential information. The capital cost of 5 is derived from 4 as described above. See later discussion.
6 - 13	Complete cost details have been published (see ref.) which prices each individual item of equipment. The order of accuracy may therefore be expected to be high.
14 - 19	A single product - sponge iron is considered. Virtually identical data is obtained if the other major product of the process - sulphur - is considered instead. The information in the reference, while not as detailed as 6-13, has been broken down into sections, and it is probable that these costs are not just simple estimates.
20	The cost quoted is the official investment figure for an extraction process now being built, and due to be commissioned in 1971.
21	This process is discussed in more detail in Section 2 and is the oldest process for which cost data is available. Comprehensive costs are given in the reference.

22 The data is based on the quoted investment cost of a process similar to 20 for the extraction of nickel concentrates. Information for the whole process producing nickel metal has not been included due to difficulties of isolating unnecessary ancillary equipment in the reference.

23 Similar to 20.

24 - 35 It is not clear in the reference how the capital cost figures are derived - only a depreciation figure over five years is given. The costs do not include land and apply only to the U.K.

36 The capital cost quoted is the official cost of the plant when built, and while this is probably correct, it is frequently not known what such figures include.

37 The process treats a complex sulphide ore recovering a wide range of products from zinc to silver and gold. The data is based on zinc recovery only, with no functional unit allowance for minor impurity (e.g. silver and gold) recovery.

unit, and it became clear as analysis of the results progressed that all functional units must be considered, even for treating byproducts; but only the primary product is considered for plant capacity and conversion. It was sometimes necessary to supplement published information on functional units with additional items, such as gas cleaning or feed material handling, to put each process on the same basis. The capital cost is for constructing a new process on a green-field (or grass roots) site in the U.K. or U.S.A. including all necessary costs prior to commissioning. Working capital, "learning" factors, development allowances and similar costs are not included.

A regression analysis of the data was performed using the least mean squares technique. Details of the computer programme and techniques, and the significant results are reproduced in Appendix III.

7.3 Results

Preliminary examination of all the data available, and reference to Gore's work (q.v.) indicated that data for small processes (24-37 inclusive) was not likely to fit into the type of equation proposed. This assumption was verified in the development of a suitable correlation and is discussed later. The suggested correlation -

$$\text{Cap. cost} = \text{A.N.} \left(\frac{Q}{S}\right)^{b} \left(\frac{T.n}{N}\right)^{c} \left(\frac{P.n'}{N}\right)^{d} \text{Fm.} \frac{\text{ENR}}{1300} \qquad \text{(Eqn.7.1)}$$

was fitted to the first 23 sets of data ("large" plants) which gave the following values:

$A = 25.24$

$b = 0.67$

$c = 0.304$

$$d = \quad -0.019 \qquad \text{(Eqn. 7.2)}$$

The deviation of estimated capital cost from quoted cost was measured as:

Estimated/Actual x 100%. For equation 7.2 the estimates ranged from 70% to 240% which was too wide a range to be useful. Correlations were also derived for the first thirteen and last ten sets of data which by comparison indicated that pressure, and to a lesser extent temperature, appeared to have less effect on capital cost than plant capacity and conversion. A solution to the following equation was found by a small manipulation of the basic computer programme:

$$\text{Cap. cost} = A.N. \, (Q)^{b} \cdot \left(\frac{T.n}{N}\right)^{c} \cdot (S)^{e} \cdot \; Fm. \frac{ENR}{1300} \qquad \text{(Eqn.7.3)}$$

Slightly different results were obtained from using various combinations of data, but generally 'e' was about half the value of 'b' and negative. This gave a relationship for plant throughput as $\left(\frac{Q}{S^{0.5}}\right)$ which was incorporated into the original equation.

It became apparent that some of the data was inconsistent and therefore a complete cross check was carried out which revealed a number of serious errors; for example the R.C.A. process data 2 and 3 and FLOX data 5 had been derived by simple application of the two thirds power law, and was therefore invalid.

The corrected data 1, 4 and 6 to 23 was fitted to the modified equation:

$$\text{Cap. cost} = A.N. \left(\frac{Q}{S^{0.5}}\right)^{b} \cdot \left(\frac{T.n}{N}\right)^{c} \cdot \left(\frac{P.n'}{N}\right)^{d} \cdot \; Fm. \frac{ENR}{1300} \qquad \text{(Eqn. 7.4)}$$

which gave $A = 50.26$
$b = 0.85$
$c = -0.17$
$d = 0.14$ (Eqn.7.5)

This gave results within the range 80% to 116% which was considered to be reasonable under the circumstances of limited data of sometimes doubtful reliability. These are reproduced in the Appendix.

Similarly acceptable correlations were also obtained for the low capacity processes 24-36 using both equation 7.1, which gave

$A = 2634.4$
$b = 0.34$
$c = 0.18$
$d = (1.0)$ (Eqn.7.6)

and equation 7.4, which gave

$A = 967.8$
$b = 0.54$
$c = 0.19$
$d = -2.29$ (Eqn.7.7)

Not much credence may be attached to either of these results however, as twelve of the thirteen processes originated from one source of perhaps doubtful reliability, and only one operated at elevated pressure. The equation for the large processes (Eqn. 7.5) was also tried out on these thirteen which gave estimates from 12% to 30%.

An attempt was then made to incorporate all the data available into one satisfactory correlation. Use of equation 7.4 gave the following values:

$A = 7150.0$

$b = 0.48$

$c = -0.21$

$d = -0.36$

and estimates ranged from 64% to 176%. While pressure and temperature effects are not insignificant, it was considered that the effect of throughput was more marked than equation 7.4 could allow for, which was particularly noticeable when using equation 7.5 for the small processes. There are many conjectural possibilities for expressing the throughput function, but within the scope of this dissertation only a few could be attempted. These included additional functions of Q such as: A^{Q^f}, $(\ln Q)^g$, and $\frac{Q}{S}$ or $\frac{Q}{S^{0.5}}$ in place of Q. Of these, incorporation of $(\ln Q)^g$ proved the most successful, but only improved the correlation to a range 72% to 147%. This work was brought to a fortuitous conclusion by a breakdown in the computer and was not resumed. This decision was considered justified due to the meagre data available providing an acceptable correlation, which could not be reasonably improved.

7.4 Discussion and Conclusions

A correlation for capital cost has been derived for plants of greater than 10,000 tons per year capacity, which is:

$$\text{£Capital cost} = 50.26.\ N.\ \left(\frac{Q}{S^{0.5}}\right)^{0.85}.\left(\frac{T.n}{N}\right)^{-0.17}.\ \left(\frac{P.n'}{N}\right)^{0.14}.Fm.\frac{ENR}{1300}$$

There are no apparent limitations imposed on number of functional units, N; "conversion," S; maximum temperature, T^oC: maximum pressure, P atm.: or cost of construction index, ENR. The equation was derived from data on 20 processes by a least mean squares regression analysis, and in view of the lack of comprehensive data must be treated with caution. It is suggested that for small processes of up to 1000 tons p.a. capacity the proportionality constant, A, is around 400, and for processes from 1000 to 10,000 tons p.a. the constant is around 140. The "conversion" factor, S, is square rooted, which has a smoothing effect, and it is thought that this effectively averages out the reactor throughput over the whole process. There appears to be a direct relationship also between S and grade of ore (as fraction of metal), but due to lack of data it was not possible to explore this notion.

The reason for the negative exponent for the temperature factor may be explained by reactions occurring so much faster at elevated temperature that the cost saving in equipment size outweighs the extra expense of operating at elevated temperature. The pressure exponent is positive as may be expected since pressure plant costs more, and no volume reduction would occur as liquids and solids are relatively incompressible. In view of this it is however perhaps a little surprising that the value is so small compared to that found by Gore..

The materials of construction factor, Fm, was set at 1.0 for all processes. It is interesting to note however, that the average percentage agreement figure for the first seven processes in the 20 large scale plants (see Appendix), is around 12% lower than for the other 13. This difference was noticed in practically all the correlations obtained, and may be related to the first seven processes all being chloride based, and the remainder sulphuric acid based. It does not seem unreasonable to suggest, therefore, that chloride processes might cost more than other acid processes due to increased corrosivity, and this extra cost might be 5% or even 10%.

Without substantially more data being available from which to derive a more accurate equation, it is not possible to draw any other useful conclusions that are not already included in the above correlation and discussion. Further suggestions are however included in the following section.

It was appreciated throughout this development that the choice of expressions for each parameter although arbitrary, can be given some intuitive justification as noted, with a wide range of alternatives being available. With the primary objective of obtaining a useful correlation with the sparse data available, the simplest expression was chosen when possible. It is clear from the work carried out so far that a great deal of development may still be carried out in this field, and several possibilities are explored in the following section.

7.5 Application to Proposed Processes

The capital cost estimating equation derived above has been used to estimate the capital cost of the two processes described in Section 2.9 which form the subject of this dissertation. The necessary data and results are conveniently presented in tabular form.

	Process A (Scrap feed, chloride reduction)	Process B (Ore feed, oxide reduction)
Functional Units, N:	Scrap handling	Ore handling
	Leaching	Size reduction

Hydrogen drying

Hydrogen blower

Crystallisation

Centrifugation

Crystal washing and drying

Oxidation

Reduction

HCl blower

Purification step

Product handling

Leaching

Hydrolysis

Solid separation

Impurity removal

(Drying)
( )
( )
(Reduction)
( )
(Product handling)
( )
(Hydrogen production)

N.B. Items in brackets were estimated separately as an H-Iron plant.

Total:	12	6
Capacity Q:	50,000 long tons p.y.	350,000 long tons p.y.
S:	0.30	0.22
Max. temperature T:	700°C	300°C
n:	3	3
Max. pressure P:	1 atm	17 atm
n':	- (12)	1
Fm:	1.0	1.0
Cost construction index: (1970 base)	1300	1300
Capital cost:	£4,115,000	£14,600,000 plus H-Iron

Process B: Hydrogen plant - steam reforming natural gas for 350,000 tons per year iron powder allowing operation for 330 days per year and adding 10% for losses = 25 x 10^6 s.c.f.d. In 1967 capital cost was £970,000 and in 1970 this would be £1,180,000.

H-Iron plant producing 350,000 tons per year iron powder, including hydrogen production by partial oxidation, feed drying and handling, and offsites, costs about £6,800,000 of which around £2,100,000 is for hydrogen generation by partial oxidation. If steam reforming natural gas were substituted the H-Iron plant cost would be reduced to £5,900,000 (1970 price) (See also Section 5).

The total capital cost of Process B is therefore £20,500,000 based on the above figures. A specially designed reduction system might reduce this.

These capital costs are employed in the economic analysis in Section 6: process A - £4,100,000 and process B - £20,500,000.

As well as estimating the capital costs of the processes investigated in this dissertation, it was considered important to include costs of related hydrometallurgical processes for comparison. These processes are outlined in Figure 7.1 from which certain parts of the processes are seen to be common. The capital cost of these common parts have been estimated using equation 7.5, and presented in Table 7.3 together with relevant information on H-Iron and hydrogen costs from Section 5. These constituent costs have been added together to give overall capital costs of all the related processes, Tables 7.4 and 7.5, including the all-gas phase ("dry") process discussed in Section 2.9. Gore's equation (see discussion earlier in Section 7) was also employed to calculate the cost of the "dry" process as the gas phase is used extensively, and Gore developed his correlation on this basis. The results are included in Table 7.3 and vary considerably from those obtained using the correlation derived

Summary of Related Hydrometallurgical Processes

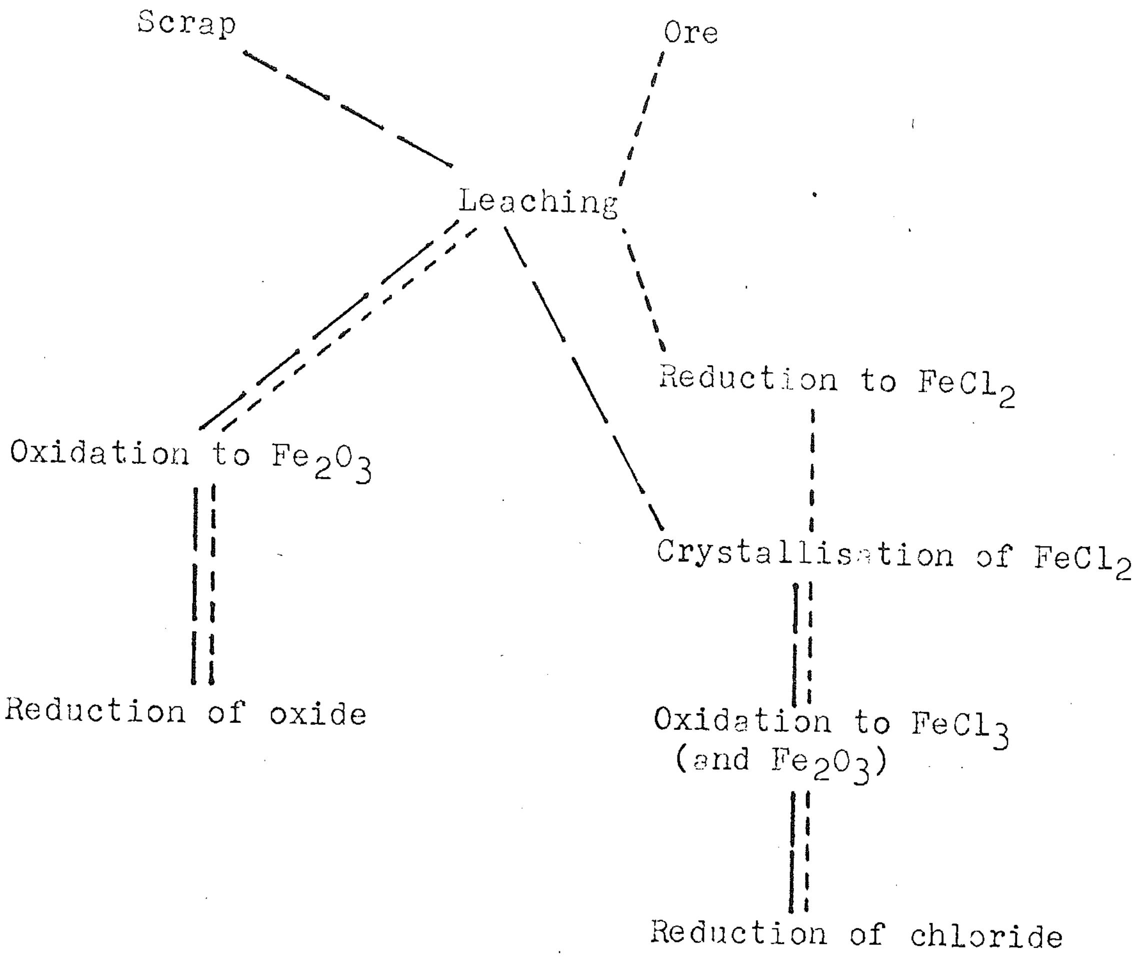


Figure 7.1

Table 7.3

Capital Costs of Process Elements (1970)

(Using Equation 7.5)

"WET"	N	Q	S	T	n	P	n'	£, Capital Cost
Scrap - $FeCl_2$	7	50,000	0.30	200	3	1	-	2,720,000
"	7	350,000	"	"	"	"	"	14,220,000
Ore - $FeCl_2$	10	50,000	0.22	200	3	1	-	4,700,000
"	10	350,000	"	"	"	"	"	24,600,000
Scrap - Fe_2O_3	6	50,000	0.30	300	3	17	1	2,450,000
"	6	350,000	"	"	"	"	"	12,800,000
Ore - Fe_2O_3	6	50,000	0.22	"	"	"	"	2,790,000
"	6	350,000	"	"	"	"	"	14,600,000
$FeCl_2$ - Fe	5	50,000	0.31*	700	3	1(?)	-	1,460,000
"	5	350,000	"	"	"	"	"	7,630,000
H-Iron inc. H_2	-	50,000	-	-	-	-	-	1,600,000**
"	-	350,000	-	-	-	-	-	5,900,000
H-Iron exc. H_2	-	50,000	-	-	-	-	-	1,400,000**
"	-	350,000	-	-	-	-	-	5,000,000
H_2	-	(50,000)	-	-	-	-	-	400,000
"	-	(350,000)	-	-	-	-	-	1,200,000
"DRY"								
Scrap - Fe	9	50,000	0.85(?)	700	7	1(?)	-	1,640,000
"	"	350,000	"	"	"	"	"	8,600,000
by Gore's correlation:								
Scrap - Fe	"	50,000	-	"	"	"	"	470,000
"	"	350,000	"	"	"	"	"	1,600,000

Table 7.3 continued

N, Q, S, T, n, P, n', are as defined earlier in this section.

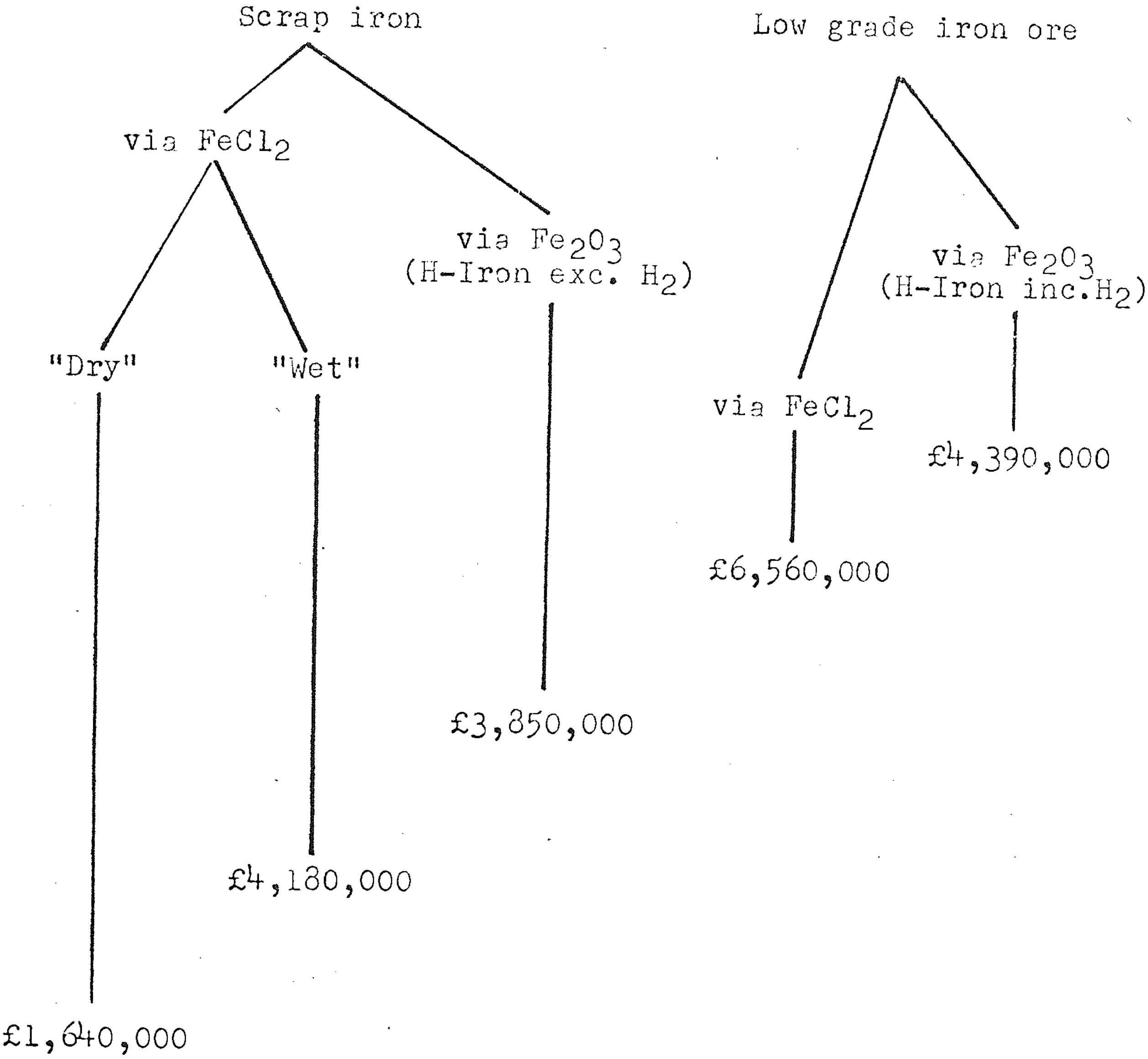
* assuming 15% hydrogen conversion in the reduction reactor.

** obtained by applying the two thirds power law to the larger plant, in the absence of other information.

Table 7.4

Processes producing 50,000 tons per year iron

(1970 costs)



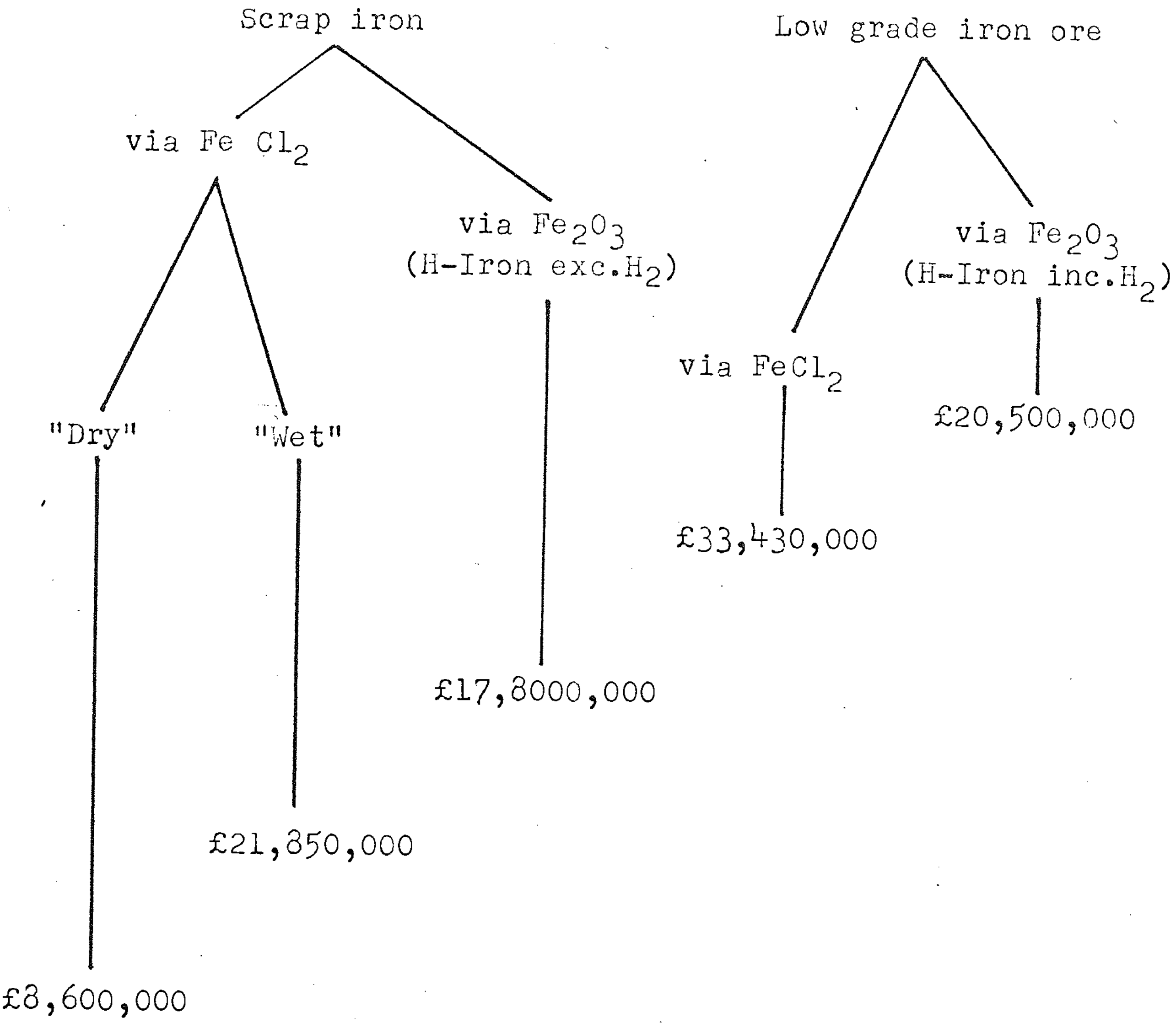
FLOX (impure product) : £5,600,000

R.C.A. (ore or scrap feed) : £6,200,000

Table 7.5

Processes producing 350,000 tons per year iron

(1970 costs)



Current integreated plant to molten steel:	£21,400,000	(2-68)
FLOX (impure product) :	£21,600,000	(2-68)
R.C.A. (ore or scrap feed) :	£23,500,000	(2-68)

in this dissertation. This difference may be explained partly by slightly different definitions of functional units being used and partly by much greater use of solid phase materials than occurred in the processes Gore used to develop his equation. In the case of the former explanation, it is thought that Gore used a more precise and narrower definition of functional unit resulting from a detailed knowledge of the processes he investigated. For novel processes where full information is not available, it is possible that low capital costs would be obtained by using his equation due to under estimation of the number of functional units. Preliminary investigation puts this at 20-40% less than a "true" capital cost. The second explanation is that solids handling is probably more difficult and costly than fluid handling, and processing a solid material and/or producing a solid is likely to increase the cost of a process above that of a fluid based process. Preliminary examination indicates that a factor of around 2 may be involved, and it is likely that a simple additional term could be incorporated into the capital cost correlation, perhaps indicating the fraction of total number of functional units that involve processing a solid. The development of a correlation to estimate the capital cost of any process from minimal information would be both interesting and worthwhile and preceding discussion and conclusions should prove helpful.

The capital costs calculated above are very similar to those predicted earlier (2-68 and appended) based simply on number of process steps, particularly the costs of the "dry" process at 350,000 tons per year and the "wet" process via oxide at 350,000 tons per year. The relevant information is shown in Figure 7.2. The costs of the 50,000 tons per year plants are lower than predicted earlier, due probably to the scale effect of the equation being much less (0.85) than that used in the earlier estimates (0.66). The calculated capital costs also allow for the hydrogen generated by leaching scrap metal, and the lower valence state of the resulting chloride, which was not considered in the earlier estimates. It is thought that within the limitations of the correlation obtained, the costs calculated here are more meaningful.

8 ECONOMICS

The capital costs of the two processes described in this dissertation and other related processes were derived in section 7. Operating costs have been calculated in the way described in section 2.8, and are given in Table 8.1 for the two processes considered, and comparative costs for the other related processes given in Table 8.2.

The production costs are made up of operating or variable costs of £16-£20 per ton of iron product which do not appear to be very dependent on the process employed, and the maintainance and capital (or fixed cost) elements which depend on the process and scale of operation. The method of calculation of the latter in Table 8.1 was taken from the appended paper on iron powder prices in order to effect a comparison. Other methods of discounting capital cost are numerous and include a variety of depreciation allowances. Rate of return on capital employed and payback time are frequently employed as economic criteria, but in the absence of a realistic market price for the product, they are difficult to apply. This difficulty is accentuated by the incomparability of a chemical iron powder to conventional powders in terms of physical and metallurgical characteristics.

The figures provided in Table 8.1 indicate that for an ore based process, heat is likely to be the largest factor in operating costs, and for a scrap based process, feedstock costs are the most significant. Labour costs become a major item in smaller scale processes, particularly those of less than 100,000 tons per year plant capacity. The overall comparative costs quoted in Table 8.2 agree well with those quoted by Gregory (8-1) in his recent paper.

Table 8.1

Costs of Production of Iron Powder

	350,000 tons p.y. iron powder from ore via oxide		50,000 tons p.y. iron powder from scrap via chloride	
	Cost in £ per long ton			
Feedstock:				
ore @ 10/- per ton	1.5			
scrap @ £7 per ton			11.7	
Heat @ 6d. per therm	8.4		1.8	
Electricity @ 1d.per kwh	0.4 (3)		0.4 (3)	
Water	0.3 (3)		0.3 (3)	
Acid make-up	3.5 (5)		0.5 (5)	
Labour	0.8 (4)		6.0 (4)	
Sales costs and overheads	1.0 (3)		1.0 (3)	
Subtotal		15.9		21.7
Maintainance @ 10 % on cap. cost.	5.9		8.3	
Required recovery at say 30% before tax (3)	17.7 (6)		25.1 (6)	
Subtotal		23.6		33.4
TOTAL COST	39.5 (1)		55.1 (2)	

Notes: (1) No credit is allowed for alumina or other byproducts.

(2) No credit is allowed for copper, ferric oxide or other byproducts.

(3) Information taken from appended paper.

(4) Information taken from (8-1).

(5) From mass balances.

(6) Capital costs from section 7

Table 8.2

Comparative Iron Powder Production Costs

	350,000 tons p.y.	50,000 tons p.y.
	£ per long ton iron	
WET		
Ore feed, oxide reduction	39.5	56.2
Ore feed, chloride reduction	46.2	65.6
Scrap feed, oxide reduction	35.2	50.8
Scrap feed, chloride reduction	41.5	55.1
R.C.A. scrap feed, chloride reduction	41.6 (1)	64.4 (1)
DRY		
Scrap feed, chloride reduction	24.9	33.4

Notes: (1) from information in appended paper

The present market price of iron powder is difficult to determine. £107/long ton is quoted in the appended paper for truckload quantities in the U.S.A. in 1968, and a complete cost breakdown is provided for four different non-chemical iron powder processes, in which the production cost ranges from £77 to £120 per long ton iron powder. In the U.K. iron powder of no special quality costs around £80 per ton, and electrolytic and carbonyl powders cost between five and eight times this figure.

The economic analysis indicates that a chemical route to iron powder appears to offer a considerable financial advantage, as well as the technical advantages discussed in Section 2.

9. CONCLUSIONS

The whole field of chemical extraction of iron has been surveyed. Two novel processes for manufacturing iron powder from different feedstocks have been investigated both theoretically and experimentally, and tentative conceptual designs suggested. Economic analyses indicated that iron powder may be manufactured for less than £40 per ton at 350,000 tons per year, or £55 per ton at 50,000 tons per year, but it must be re-emphasized that these figures are in the nature of preliminary estimates and dependent on the work and assumptions laid out in this thesis.

It is clear that more problems have been created than solved which is considered inevitable in a study of this nature. Some of the areas where further work is thought necessary have been summarised:

Ore leaching

(1) Development of mathematical/empirical models to predict extraction.

(2) Adsorption and desorption of iron on ore and silica.

(3) Effect of reaction parameters on the different ore constituents.

(4) Effect of temperatures above 105°C with super-atmospheric pressure.

(5) Technical optimisation of reaction system.

(6) Economic optimisation of reaction system.

(7) Effect of pretreatment on solubility of non-ferrous ore constituents.

(8) Comparative studies of other iron ores.

(9) Possibility of a liquid fluidised bed for ore dissolution.

(10) C.S.T.R. system for ore leaching with air agitation.

(11) Physical properties of reaction mixture including density and viscosity.

(12) Continuous laboratory reactors.

Metal leaching

(1) Effect of different steels.

(2) Effect of nonferrous and non-metallic impurities.

(3) Study of properties of commercial scrap including sizes, qualities, quantities, geometry, surface area and weight characteristics.

(4) Development of mathematical and empirical models, employing analogue or digital computers.

(5) Experimentation at temperatures above 105°C and at super-atmospheric pressure.

(6) Technical optimisation of reaction system.

(7) Economic optimisation of reaction system.

(8) Study of hydraulic seal.

(9) Laboratory investigation of small fixed bed reactor similar to that described for large scale dissolution.

Hydrolysis

(1) Analysis of precipitates at different temperatures.

(2) Control of particle size.

(3) Effect of impurities.

(4) Effect of reaction time.

(5) Effect of reaction temperature and pressure.

(6) Effect of concentration of ferric chloride and impurities.

(7) Purity of product under various conditions.

(8) Prevention of reverse reaction in laboratory experimentation.

(9) Design of laboratory apparatus to investigate continuous hydrolysis.

(10) Optimisation of system.

Crystallisation

(1) Purity of precipitated ferrous chloride.

(2) Effect of impurities.

(3) Conditions for successful precipitation and particle size control.

(4) Separation of crystals.

(5) Optimisation of system.

Oxidation

(1) Quantitative laboratory experimentation.

(2) Linking oxidation stage with reduction stage on laboratory scale.

(3) Effect of impurities in ferrous chloride.

(4) Rate of reaction.

(5) Effect of parameters.

(6) Optimisation of system.

Drying

(1) Feasibility of drying ferrous chloride dihydrate with hydrogen/hydrogen chloride gas mixture.

Reduction of chloride

(1) Quantitative laboratory experimentation.

(2) Determination of time of reaction.

(3) Effect of temperature.

(4) Effect of concentration of hydrogen.

(5) Effect of concentration of inert gas.

(6) Effect of pressure.

(7) Effect of magnetic field.

(8) Control of particle size.

(9) Recirculation of iron particles.

(10) Induction heating of iron particles.

(11) Purity of product.

(12) Magnetic transport.

(13) Gas flow rates and Reynolds number.

(14) Mathematical/empirical models.

(15) Optimisation of system.

Impurities

(1) Selection of suitable operations to remove each deleterious impurity.

(2) Design of operations.

(3) Laboratory experimentation where necessary.

(4) Relationship of impurity removal stages to rest of process, and subsequent optimisation.

(5) Effect on impurities on final product.

Capital cost estimation

(1) Further development of an overall estimating equation.

(2) Inclusion of materials of construction factor.

(3) Inclusion of phase factor.

APPENDIX I

Relevant information on acid extraction of both ferrous and non-ferous metals has been collated and is presented in tabular form below.

Reference .... : Firth et al. (2-12)

Purpose .... : Extraction of Fe from carbonate slate on pilot plant tests.

Ore .... : Carbonate slate

Ore analysis .... : Fe: 26%, Si O_2: 44.0%, Al_2O_3: 1.5%, CO_2: 12.0%, et al.

Comminution .... : - 48 mesh

Roasting - reagent ... : None

- temperature :

Leaching - reagent ... : H_2SO_4 (98%, diluted)

- concn. ... : 10 - 20 % (10% optimum)
- temperature : 50 - 100°C
- pressure .. :
- pH .... :
- time ...... : 2 - 4 hours (multiple stage with low acid concentration) 3 hr. optimum
- losses .... : High

% Fe dissolved .... : 50 - 80%

% others dissolved ... : Mn: 90%, Ca, Mg and Al: 75% each

Next process step .... : Washing

Rest of process ...... : L/S separation, evaporation and crystallisation, calcination, reduction

Final product .... : Fe powder

Purity .... :

Recycle .... : None

Analysis - ore*....... : Yes

- liquor* ... : Part
- product* .. : No

Flowsheet*........... : No

Other information .... : Construction cost for 100 tpd.: $ 4.836m. Total operating cost $ 88.07 per ton

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Six (2-14)

Purpose .... : Preparation of pure ferric oxide

Ore .... : Magnetite, hematite, or other

Ore analysis .... : Magnetite - Fe_3O_4: 91.78%

Comminution .... :

Roasting - reagent ... :

- temperature :

Leaching - reagent ... : HNO_3

- concn. ... : SG: 1.3 - 1.4 45-65% wt.

- temperature : Boiling

- pressure .. : Atmospheric

- pH .... :

- time ...... :

- losses .... :

% Fe dissolved .... : Substantial part (?)

% others dissolved ... :

Next process step .... : Crystallisation

Rest of process ...... : Separation, decomposition of molten salt at 125-150°C, reduction

Final product .... : Fe_2O_3

Purity .... : 99.7% +

Recycle .... : HNO_3

Analysis - ore*....... : Yes (magnetite)

- liquor* ... : No

- product* .. : Yes (Fe_2O_3)

Flowsheet*........... : No

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Primavesi (2-15)

Purpose .... : Production of powdered iron

Ore .... : Unspecified oxides

Ore analysis .... :

Comminution .... :

Roasting - reagent ... :

- temperature :

Leaching - reagent ... : HCl

- concn. ... :

- temperature :

- pressure .. :

- pH .... :

- time ...... :

- losses .... :

% Fe dissolved .... :

% others dissolved ... :

Next process step .... : Reduction of Fe^{+++} to Fe^{++} with Fe

Rest of process ...... : Salting out of $FeCl_2$, hydrolysis, reduction

Final product .... : Fe powder

Purity .... :

Recycle .... : HCl

Analysis - ore*....... : No

- liquor* ... : No

- product* .. : No

Flowsheet*........... : No

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : FLOX 1 (2-16)

Purpose .... : Production of Fe oxides or Fe powder

Ore .... : Low grade

Ore analysis .... : Fe, Al, Ca, Mg, Mn, SiO_2

Comminution .... : None

Roasting - reagent ... : Only if Fe exists as Fe^{++}

- temperature :

Leaching - reagent ... : HCl

- concn. ... :

- temperature : Heating if required

- pressure .. :

- pH .... :

- time ...... :

- losses .... :

% Fe dissolved .... : Most

% others dissolved ... : Most except SiO_2

Next process step .... : Evaporation

Rest of process ...... : Distillation of $FeCl_3$, hydrolysis, reduction

Final product .... : Fe_2O_3 or Fe

Purity .... :

Recycle .... : HCl

Analysis - ore*....... : No

- liquor* ... : No

- product* .. : No

Flowsheet*........... : Yes

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Schaufelberger (2-17)

Purpose .... : Recovery of iron from iron bearing minerals

Ore .... : Lateritic, siliceous (generally any non-sulphide ore)

Ore analysis .... : Fe, Al, SiO_2, plus minor amounts Ni Co Cn Zn Mg Co Pb

Comminution .... : Finely ground

Roasting - reagent ... :

- temperature :

Leaching - reagent ... : HNO_3

- concn. ... : 40 - 50%

- temperature : 90 - 150°C

- pressure .. : O_2 partial pressure: 50 - 150 psi

- pH .... :

- time ...... : 3 - 24 hours

- losses .... :

% Fe dissolved .... : $>$ 80%

% others dissolved ... : Ni: 90%, others 50%

Next process step .... : Pressure precipitation, $>$ 175°C, $>$ 100 psi

Rest of process ...... : Separation of iron oxide.

Final product .... : Fe_2O_3

Purity .... : "Pure" (99%) Fe_2O_3

Recycle .... : HNO_3 + mother liquor

Analysis - ore*....... : Yes on 5 samples

- liquor* ... : Yes on 5 samples

- product* .. : Yes

Flowsheet*........... : No

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Francis (2-18)

Purpose .... : Production of ferrous chloride and sulphate and hence pure iron

Ore .... : Siderite, limonite and hematite ores

Ore analysis .... : Fe: 50%, SiO_2: 7%, Al_2O_3: 2.5%, Traces CaO, MgO, Mn, P.

Comminution .... : $\frac{1}{8}$ - $\frac{1}{4}$ inch

Roasting - reagent ... :

- temperature :

Leaching - reagent ... : HCl

- concn. ... : 35 wt% (22 Be°)
- temperature : 140°F
- pressure .. :
- pH .... :
- time ...... : 1 hour
- losses .... :

% Fe dissolved .... : Most

% others dissolved ... : Some Mg and Mn

Next process step .... : Reduction to Fe^{++} with scrap iron

Rest of process ...... : Evaporation, (crystallisation) sulphation, reduction (of $FeSO_4$)

Final product .... : $FeSO_4$ or Fe powder

Purity .... : Unspecified

Recycle .... : HCl

Analysis - ore*....... : Yes, 4 samples

- liquor* ... : No
- product* .. : No

Flowsheet*............ : Yes

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference	Rao et al. (2-19)	
Purpose	Production of Fe from laterites by leaching and electrolysis	
Ore	Ferruginous laterites	
Ore analysis	19 - 26% Fe.	
Comminution	- 200 to -100 mesh	
Roasting - reagent ...		
- temperature		
Leaching - reagent ...	H_2SO_4	HCl
- concn. ...	Various	Commercial
- temperature	Various	Boiling
- pressure ..		
- pH		
- time		10 minutes
- losses		
% Fe dissolved	28 - 92%	90 - 95%
% others dissolved ...	Unspecified	Unspecified
Next process step	Filtration	
Rest of process	Electrolysis	
Final product	Electrolytic Fe plate	
Purity	Probably > 99.5%	
Recycle	Difficult	HCl or $FeCl_3$
Analysis - ore*.......	No	
- liquor* ...	No	
- product* ..	No	
Flowsheet*...........	No	
Other information	Leaching and electrolysis data given	

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : FLOX 2 (2-20)

Purpose .... : Production of Iron oxide

Ore .... : Low grade ores

Ore analysis .... : Oxides of Fe, Si, Al, Ca, Mg, P, and S

Comminution .... : - 1 inch

Roasting - reagent ... : Yes (unspecified)

- temperature :

Leaching - reagent ... : HCl

- concn. ... : 10- 15%

- temperature : 90°C

- pressure .. :

- pH .... : < 1.0

- time ...... : 1 hour

- losses .... :

% Fe dissolved .... : 100%

% others dissolved ... : SiO_2: none, Al_2O_3: part, rest: all

Next process step .... : Filtration

Rest of process ...... : Reduction of Fe^{+++} to Fe^{++}, precipitation of Al, P, V, Ca, crystallisation, hydrolysis, reduction.

Final product .... : Fe_2O_3

Purity .... : 97.3% wt.

Recycle .... : HCl

Analysis - ore*....... : Yes

- liquor* ... : No

- product* .. : Fe_2O_3 - Yes

Flowsheet*............ : No

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : (R.C.A.) Gravenor et al. (1-5)

Purpose .... : Production of pure Fe powder from low grade ore

Ore .... : Ferruginous oolitic sandstone

Ore analysis .... : Fe: 34.1%, SiO_2:27.0%, Al_2O_3:5.02%, CaO: 1.93%, P, S, Mn, Mg, V

Comminution .... : - ¼ inch

Roasting - reagent ... : Generally all ore reduced. In this case only part. Coal.

- temperature : 900-1000°C

Leaching - reagent ... : HCl

- concn. ... : 20-31% wt.

- temperature : Autothermic, to 100°C

- pressure .. :

- pH .... :

- time ...... : 30 minutes

- losses .... : 0.4% of total acid added

% Fe dissolved .... : Up to 95%

% others dissolved ... : See analysis - liquor

Next process step .... : Filtration and washing

Rest of process ...... : Evaporation, crystallisation, drying, reduction

Final product .... : Fe powder

Purity .... : 99.2% wt.

Recycle .... : HCl

Analysis - ore*....... : Yes as "ore" above: plus P:0.675%, S:0.073%, Mn:0.16%, V_2O_5:0.22%, MgO:1.02%

- liquor* ... : Yes

- product* .. : Yes - Al_2O_3:0.75%, SiO_2:0.17% plus 0.1% Na, K, Cl, P, S, C, Ti, Ca, Mg, Mn, V

Flowsheet*........... : Yes

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : FLOX 3 (2-10)

Purpose .... : Recovery of pure iron or iron oxides from low grade ore

Ore .... : Northants; low grade siliceous, and similar

Ore analysis .... : Fe_2O_3, FeO, Al_2O_3, CaO, P_2O_5, SiO_2, MgO, MnO, S.

Comminution .... : - 1 inch

Roasting - reagent ... : Part of feed only. Unspecified

- temperature : Unspecified

Leaching - reagent ... : HCl

- concn. ... :

- temperature :

- pressure .. : None

- pH .... : 5

- time ...... :

- losses .... :

% Fe dissolved .... :

% others dissolved ... : Al, Ca, Mg, Mn.

Next process step .... : Ca precipitation and filtration

Rest of process ...... : $FeCl_2$ precipitated, dried and hydrolysed to Fe_2O_3 (reduction).

Final product .... : Fe_2O_3, or Fe powder or sponge

Purity .... : 96.8 - 98.7%

Recycle .... : HCl

Analysis - ore*....... : Yes on 4 samples

- liquor* ... : No

- product* .. : Yes on 4 samples corresponding to feedstock (Fe_2O_3)

Flowsheet*........... : Yes

Other information .... : Similar process using waste pickle liquor proposed also

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Tilley et al. (2-11)

Purpose .... : Extraction of Alumina from clays

Ore .... : Clays and other low grade aluminous ores

Ore analysis .... : SiO_2: 40%, Al_2O_3:40%, Fe_2O_3: 3%, Ca, Mg, Na, K.

Comminution .... : 80-100 mesh

Roasting - reagent ... : Roasting

- temperature : Various, optimum for leaching 550°C.

Leaching - reagent ... : H_2SO_4

- concn. ... :

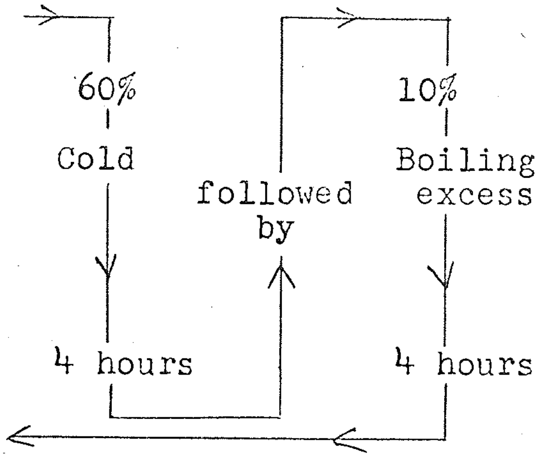
- temperature :

- pressure .. : Atmospheric

- pH .... :

- time ...... :

- losses .... :



% Fe dissolved .... : 40-100% depending on mineral (550 C Roast)

% others dissolved ... : SiO_2:0-0.45%, Al_2O_3:4-86%, TiO_2: 3-100% (550°C Roast)

Next process step .... : Recovery of alumina (various methods)

Rest of process ...... :

Final product .... : Alumina

Purity .... : Dependant on process; > 99% wt.

Recycle .... : Acid gases

Analysis - ore*....... : Yes

- liquor* ... : Yes

- product* .. : Yes

Flowsheet*........... : No

Other information .... : See also Table

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Hoffman et al. (2-24)

Purpose .... : Production of Alumina from Clay

Ore .... : Clay

Ore analysis .... : SiO_2:45%. Al_2O_3:36%, Fe_2O_3:1.0%, TiO_2: 1.4%, + P, Ca, Mg, Na, K.

Comminution .... : Some may be necessary

Roasting - reagent ... : Roasting in air

- temperature : 700°C

Leaching - reagent ... : HCl

- concn. ... : SG 1.07-1.10 (about 20% wt.) in excess

- temperature : 100-105°C (Autothermic)

- pressure .. : 1 Atm.

- pH .... :

- time ...... : 1 hour

- losses .... : Not > 1.0% (0.25-0.57%)

% Fe dissolved .... : Most

% others dissolved ... : > 98% Al

Next process step .... : Concentration by evaporation

Rest of process ...... : Salting out, calcination to oxide

Final product .... : Al_2O_3

Purity .... : 99.6% wt.

Recycle .... : HCl

Analysis - ore*....... : Yes

- liquor* ... : Yes

- product* .. : Yes (part)

Flowsheet*............ : No

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Walthall et al. (2-25)

Purpose .... : Alumina extraction

Ore .... : Clay

Ore analysis .... : Al_2O_3:30%, SiO_2:55%. Fe_2O_3:1.8%, Ti, Mg, Ca

Comminution .... : 4-28 mesh or ½ x ½ inch pellets

Roasting - reagent ... : Roasting

- temperature : 850°C max. for one hour

Leaching - reagent ... : H_2SO_4

- concn. ... : 40% wt.
- temperature : 90°C
- pressure .. : Atmospheric
- pH .... : 2
- time ...... : 1 plus hours
- losses .... : See Table in text (section 2-4)

% Fe dissolved .... : 50% (max. Fe extraction, 90% on dried material)

% others dissolved ... : Al_2O_3 90%, SiO_2: 0.09%

Next process step .... : Electrolytic iron removal

Rest of process ...... : Si O_2 removal, evaporation, calcination, leaching, drying.

Final product .... : Al_2O_3

Purity .... : 99.8%

Recycle .... : H_2SO_4

Analysis - ore*....... : Yes

- liquor* ... : Yes
- product* .. : Yes

Flowsheet*........... : Yes - comprehensive

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Peters et al. (2-26)

Purpose .... : Alumina extraction

Ore .... : Low grade aluminous clay

Ore analysis .... : Fe_2O_3:3%, Al_2O_3:30%, SiO_2:50%, LOI: 15%, Other:2%

Comminution .... : Crushed to - ¼ inch - 20 mesh

Roasting - reagent ... : Dehydration

- temperature : 1300°F

Leaching - reagent ... : HCl

- concn. ... : 20%

- temperature : 200°F

- pressure .. : 1 Atm

- pH .... :

- time ...... : 2 hours

- losses .... : 1%

% Fe dissolved .... : 86.5%

% others dissolved ... : Al_2O_3:87%, SiO_2:0%, Others:75%

Next process step .... : Filtration, concentration

Rest of process ...... : Removal of iron by solvent extraction or precipitation, precipitation calcination

Final product .... : Alumina

Purity .... : 99.4%

Recycle .... : HCl 2-6% make-up

Analysis - ore*....... : as "ore" above plus TiO_2, CaO, MgO, K_2O, Na_2O, P_2O_5.

- liquor* ... : Al_2O_3:5.3%, Fe_2O_3:0.5%, SiO_2:0%, Other: 0.3%, HCl:13.2%

- product* .. : Al_2O_3:99.4%, Cl:0.1%, H_2O:0.5%

Flowsheet*........... : Yes

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Peters et al. (2-27)

Purpose .... : Alumina extraction

Ore .... : Low grade aluminous clay

Ore analysis .... : Fe_2O_3:3%, Al_2O_3:30%, SiO_2:50%, L.O.I: 15%, Other:2%

Comminution .... : Crushed to - ¼ inch   - 20 mesh

Roasting - reagent ... : Dehydration

- temperature :   1300°F

Leaching - reagent ... : H_2SO_4

- concn. ... : 40%

- temperature : 185°F

- pressure .. : 1 Atm

- pH .... :

- time ...... : 2½ hours

- losses .... : 0.44% wt.

% Fe dissolved .... : 8.0%

% others dissolved ... : Al_2O_3:84.5%, SiO_2:0.145%, Others:12.2%

Next process step .... : Thicken and filtration

Rest of process ...... : Electrolysis or precipitation to remove Fe. Production of alumina

Final product .... : Al_2O_3. Fe precipitated

Purity .... : 99.2%

Recycle .... : H_2SO_4:40%. 5.6% make-up (on S)

Analysis - ore*....... : As "ore" above plus Others: TiO_2, CaO, MgO, K_2O, Na_2O, P O

- liquor* ... : Al_2O_3:6%, Fe_2O_3:0.05%, SiO_2:0.02%, SO_4:14.2%, Other:0.07%

- product* .. : SO_4:0.3%, Other:0.5%, Al_2O_3:99.2%

Flowsheet*............ : Yes

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Carlson et al. (2-28)

Purpose .... : Nickel recovery

Ore .... : Cuban laterites

Ore analysis .... : Fe:47.5%, Al:4.5%, SiO_2:3.7%, Ni, Co, Mn, Mg, Cr, Cn, Zn

Comminution .... : Already 85% < 325 mesh. Screening only required

Roasting - reagent ... : None. (Roasting reduces extraction efficiency of Ni)

- temperature :

Leaching - reagent ... : H_2SO_4

- concn. ... : 40-50% (98% feed to slurry)

- temperature : 450-500°F

- pressure .. : 400-600 psi

- pH .... :

- time ...... : 90 mins.

- losses .... :

% Fe dissolved .... : 0.36%

% others dissolved ... : Ni and Co > 95%, Al:11%, Mn, Mg:60%, Cn, Zn:100%, SiO_2:11.6%

Next process step .... : Heat exchange to recover heat

Rest of process ...... : Washing, settling, separation.

Final product .... : (Ni and Co sulphide concentrate)

Purity .... : Low

Recycle .... : Yes - H_2SO_4

Analysis - ore*....... : Yes

- liquor* ... : Yes

- product* .. : No

Flowsheet*............ : Yes

Other information .... : Yes

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

Reference .... : Forward et al. (2-29)

Purpose .... : Extraction of Nickel and Iron from Mayari Ores
Ore .... : Mayari type (la teritic)

Ore analysis .... : Fe:54%, Ni:1.0%, Cr:2.2%, Co:0.15%, Mn:0.5%, SiO_2:5.0%, Al_2O_3:10.0%
Comminution .... : - 65 mesh

Roasting - reagent ... : Roasting in air (helps, but not essential)
  - temperature : 800°F

Leaching - reagent ... : HNO_3

  - concn. ... : 25% (10-70%)

  - temperature : 90°C (40-100°C)

  - pressure .. : Atmospheric

  - pH .... :

  - time ...... :

  - losses .... :

% Fe dissolved .... : "Major part"

% others dissolved ... : Major part of Ni, Co, probably Cr, Mn and Al also
Next process step .... : Autoclaving to precipitate ferric oxide at 185-345 C, 400 psi
Rest of process ...... : Separation of iron oxide and recycling of acid solution
Final product .... : Fe_2O_3

Purity .... : 67.8% Fe (< 1.5% impurities)

Recycle .... : HNO_3 plus nonferrous metals

Analysis - ore*....... : Yes

  - liquor* ... : No

  - product* .. : Yes

Flowsheet*............ : No

Other information .... :

* Where data is too complex to be included, an indication is given as to whether details are in the reference.

APPENDIX II

Relevant data pertaining to the extraction of iron by formation and reaction of chlorides has been collated from a number of sources and presented below. This is not intended as an exhaustive survey of available data, and in some instances the information has been curtailed and the extent of availability indicated. A sub-index is included for ready reference:

1 General Data

	$Fe_{(s)}$	$H_{2(g)}$	$O_{2(g)}$	$Cl_{2(g)}$	$HCl_{(g)}$	Ref.
Molecular weight	55.85	2.016	32.00	70.91	36.47	A2
Melting point ^oK	1803	13.96	54.36	172.16	158.9	A1
Boiling point ^oK	3008	20.39	90.19	239.1	188.1	A1
Density g/cm^3	~7.7	*	*	*	*	A2
H^o $_{298^oK}$ cals/mole	0	0	0	0	-22063	A1
G^o $_{298^oK}$ cals/mole	0	0	0	0	-22750	A1
$S^o_{298^oK}$ e.u.	6.49	31.22	49.01	53.31	44.61	A1
Heat fusion cals/mole	3700	28	106	1531	476	A1
Heat vapourisation cals/mole	84620	216	1630	4878	3860	A1
Heat solution cals/mole					-17787(a)	A2
Free energy soln.(b) cals/mole					-8552	A2
Specific heat (Cp) cals/mole	*	*	*		*	
Solubility in water	nil			very slight	yes,*	A2

Notes: * see information later

(a) dilution 400 moles H_2O / mole

(b) Hypothetical solution of unit molality

General data continued

	$H_2O_{(l)}$	$H_2O_{(g)}$	$FeCl_{2(s)}$	Ref.
Molecular weight	18.016	-	126.76	A2
Melting point °K	273.16	-	950	A1
Boiling point °K	373.16	-	1299	A1
Density g/cm^3	*	*	2.7	A2
$H^o_{298°K}$ cals/mole	-68317	-57798(A2)	-81900	A1
$G^o_{298°K}$ cals/mole	-56720	-54635(A2)	-72600	A1
$S^o_{298°K}$ e.u.	16.75		28.7	A1
Heat fusion cals/mole	1436	-	10280	A1
Heat vapourisation cals/mole	9770	-	30210	A1
Heat solution cals/mole			-18100(c)	A2
Free energy soln.(b) cals/mole			-10400	A2
Specific heat (Cp) cals/mole	*		*	
Solubility in water			yes,*	A2

Notes: * see information later

(b) Hypothetical solution of unit molality

(c) Infinite dilution

General data continued

	$FeCl_{3(s)}$	$Fe_2O_{3(s)}$	FeOCl	Ref.
Molecular weight	162.22	159.70	107.31	A2
Melting point °K	577	Decomp@1740		A1
Boiling point °K	592			A1
Density g/cm^3	2.80	5.12		A2
$H^o_{298^oK}$ cals/mole	-95700	-196800	(-99000(4-9))	A1
$G^o_{298^oK}$ cals/mole	-79500	-177400		A1
$S^o_{298^oK}$ e.u.	32.2	21.5		A1
Heat fusion cals/mole	10300			A1
Heat vapourisation cals/mole	6020			A1
Heat solution cals/mole	-32100(d)			A2
Free energy soln.(b) cals/mole	-17000			A2
Specific heat (Cp) cals/mole	*	*		
Solubility in water	very,*	nil	slight	A2
Heat of association cals/mole	16300(4-9) *			

Notes: * see information later

(b) Hypothetical solution of unit molality

(d) Dilution 2000 moles H_2O / mole

2 Vapour Pressure and Partial Pressure

Vapour pressure (A2):

	mm. mercury								
	5	10	20	40	60	100	200	400	760
	Temperature °C								
H_2O	0.2	11.2	22.1	34.0	41.5	51.6	66.5	83.0	100.0
$FeCl_2$		700	737	779	805	842	897	961	1026
$FeCl_3$	221.8	235.5	246.0	256.8	263.7	272.5	275.0	298.0	319.0

See Figure A1 also.

Vapour pressure (4-9):

$$\log p_{FeCl_2}\ \text{mm} = 8.10 - \frac{6780}{T\ ^\circ K}$$

$$\log p_{Fe_2Cl_6}\ \text{mm} = 15.323 - \frac{7250}{T\ ^\circ K} \quad \text{(over solid, 526-574°K)}$$

$$\text{or} \quad = 55.898 - \frac{10754}{T^\circ K} - 12.642\log T + \frac{133500}{T^2}$$

$$\text{or} \quad = 7.019 - \frac{2444}{T\ ^\circ K} \quad \text{(over liquid)}$$

Partial pressure (A2):

Over aqueous solutions of HCl, the partial pressure of H_2O and HCl is given by:

$$\log p\ \text{mm.} = A - \frac{B}{T}, \quad \text{where } T = \text{temperature, } ^\circ K, \quad A \,\&\, B = \text{constants}$$

	H_2O		HCl	
	A	B	A	B
2% HCl	-	-	11.8037	4736
6% HCl	8.99156	2282	11.2144	4202
10% HCl	8.99864	2295	10.9311	3908
20% HCl	8.97877	2334	10.3833	3245

Values of A and B at other HCl concentrations are given, and also a table of partial pressures which is claimed to be more accurate.

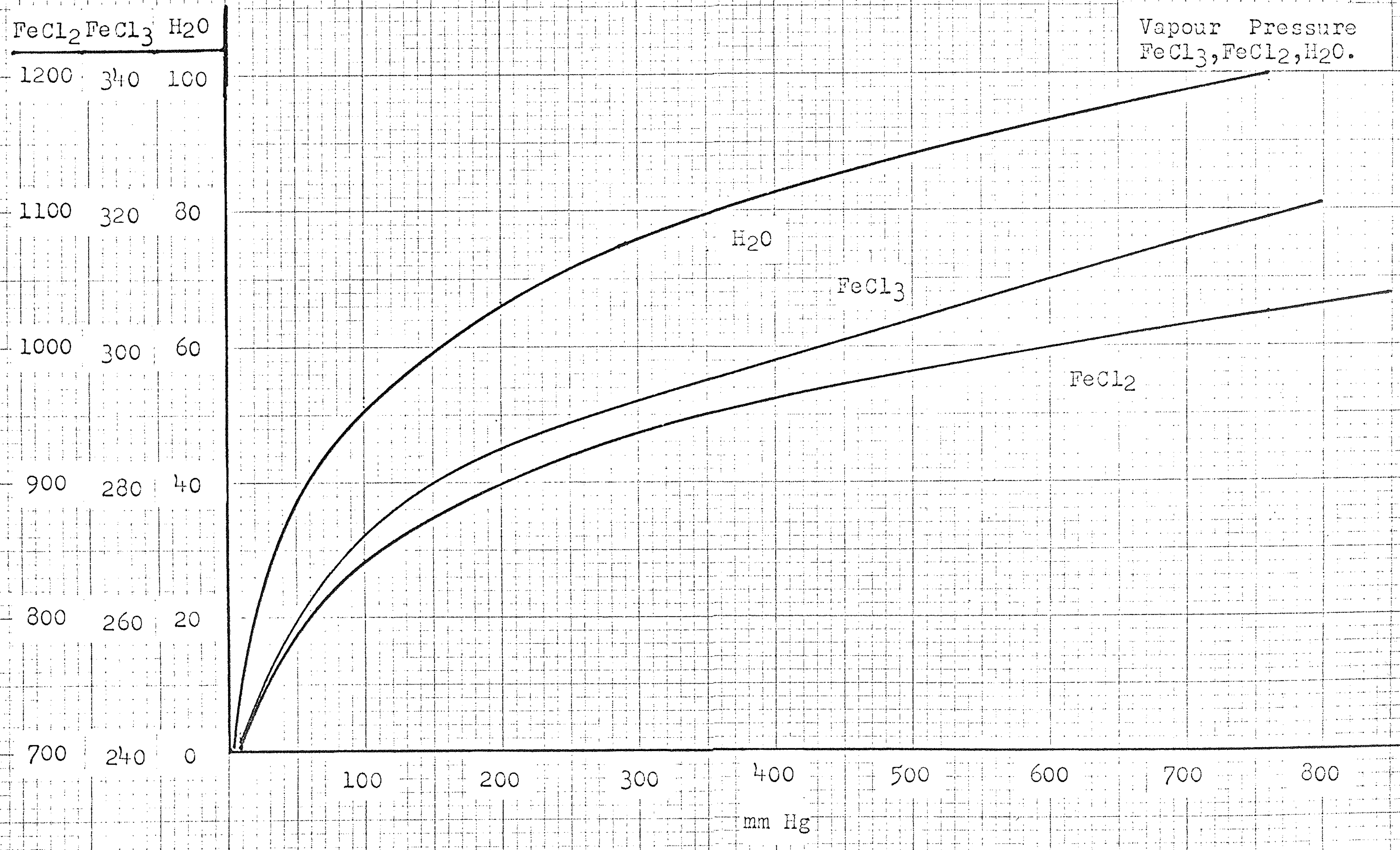

Vapour Pressure
$FeCl_3$,$FeCl_2$,H_2O.
$FeCl_2$
$FeCl_3$
H_2O
1200
1100
1000
900
800
700
340
320
300
280
260
240
100
80
60
40
20
0
H_2O
$FeCl_3$
$FeCl_2$
100
200
300
400
500
600
700
800
mm Hg

Figure A1

Partial pressures of H_2O, HCl, Cl_2, $FeCl_2$, and $FeCl_3$ are given in (4-9) for various systems mentioned in section 9 of this Appendix.

Vapour - liquid equilibrium data is given in (A4) for the system $FeCl_3$ - H_2O - HCl .

3 Density

	%wt.	density g/cm^3	%wt.	density g/cm^3
Aqueous $FeCl_3$ at 20°C (A2)	2	1.0152	25	1.2340
	4	1.0324	30	1.2910
	8	1.0669	35	1.3530
	12	1.1040	40	1.4175
	16	1.1418	45	1.4850
	20	1.1820	50	1.5510

Data at 0°C, 10°C, and 30°C is also available (A2).

	%wt.		density g/cm^3		density g/cm^3
Aqueous HCl (A2)	2	at 20°C	1.0082	at 100°C	0.9688
	6		1.0279		0.9892
	10		1.0474		1.0090
	14		1.0675		1.0286
	18		1.0878		1.0479
	20		1.0980		1.0574
	22		1.1083		1.0668
	26		1.1290		1.0853
	30		1.1493		1.1030
	40		1.1980		

Data at -5°C, 0°C, 10°C, 40°C, 60°C, and 80°C, and for intermediate concentrations is available. (A2)

H_2O density and temperature dependancy data is available in (A2).

	density, g/l at N.T.P.(A2)
H_2	0.0898
HCl	1.6394
Cl_2	3.2204
O_2	1.4289
Air	1.2928

4 Solubility

Aqueous solutions (A2):

	g. anhydrous substance/100 g water			
Temp. °C	HCl	$FeCl_2$ *	$FeCl_3$ *	$AlCl_3$
0	82.3		74.4	
10		64.5	81.9	
15				69.86
20			91.8	
30	67.3	73.0		
40	63.3	77.3		
50	59.6	82.5	315.1	
60	56.1	88.7		
70				
80		100	525.8	
90		105.3		
100		105.8	535.7	

See Figure A2

* see below also

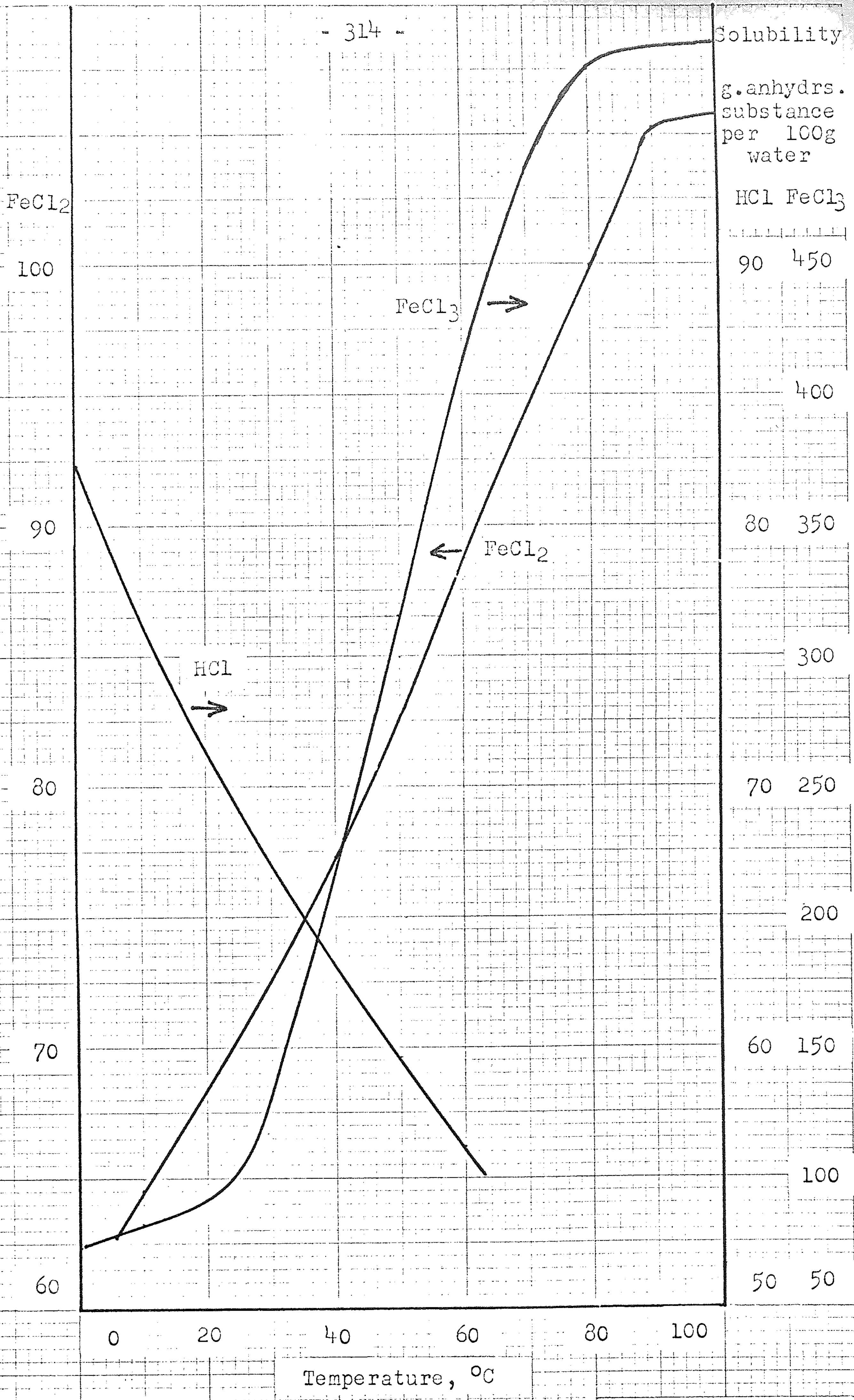

Solubility
g.anhydrs. substance per 100g water
HCl FeCl$_3$
90 450
400
80 350
300
70 250
200
60 150
100
50 50
FeCl$_2$
100
90
80
70
60
FeCl$_3$ →
← FeCl$_2$
HCl →
0
20
40
60
80
100
Temperature, °C

Figure A2

Aqueous $FeCl_2$ (4-2):

Temp. °C	Solid phase	g. $FeCl_2$ per 100 g. saturated solution
117.5	$FeCl_2.2H_2O$	50.4
100	"	48.7
96	"	48.3
86	"	47.7
76.5	$FeCl_2.2+4H_2O$	47.4
70.5	$FeCl_2.4H_2O$	45.8
63.0	"	44.4
60.0	"	43.9
52.0	"	42.6
40.0	"	40.7
36.2	"	40.4
35.0	"	40.2
25.0	"	39.2/39.6
20.5	"	38.6
20.0	"	38.5

Systems:

Information is available for the following systems:

$FeCl_2$ - HCl - H_2O	see section 4.2
$FeCl_3$ - $AlCl_3$ - H_2O	(A3)
$FeCl_3$ - $AlCl_3$ - KCl - HCl - H_2O	(A3)
$FeCl_3$ - H_2O	(A3), very extensive
$FeCl_3$ - HCl - H_2O	(A3), very extensive; (4-4)
$FeCl_3$ - $AlCl_3$ - HCl - H_2O	(A5) at -10°C

5 Heat of Solution

	Temp. °C	Moles of water dissolving 1 g mole	Hs cals/g mole	Ref.
$FeCl_3$	18	2000	-32100	A2
"	"	1000	-31700	"

Heat of solution continued

	Temp. °C	Moles of water dissolving 1 g mole	Hs cals/g mole	Ref.
$FeCl_3.2\frac{1}{2}H_2O$	18	1000	-21000	A2
$FeCl_3.6H_2O$	"	1000	- 5600	"
$FeCl_2$	"	infinite	-18100	"
"	"	400	-17900	"
$FeCl_2.2H_2O$	"	400	- 8700	"
$FeCl_2.4H_2O$	"	400	- 2700	"
$AlCl_3$	"	600	-77900	"
$AlCl_3.6H_2O$	"	600	-13200	"
HCl	"	400	-17787	"
"	25	3.221	-13870	4-9

6 Specific Heats

	Cp, kcals/g.mole	Temp.range °K	Ref.
Fe, α	$3.90+6.8x10^{-3}T$	273-1000	A7
	$4.13+6.38x10^{-3}T$	273-1000	A2,4-9
	$3.37+7.10x10^{-3}T+0.43x10^{5}T^{-2}$	298-1033	A1
Fe, β	$6.12+3.36x10^{-3}T$	1060-1180	A2,A7
	10.40	1033-1179	A1
	11.8		4-9
Fe, γ	$4.06+3.6x10^{-3}T$		A7
	8.40		A2,4-9
	$4.85+3.00x10^{-3}T$	1179-1674	A1
Fe, δ	10.0		A2
	10.30	1674-1803	A1
$FeCl_{2(s)}$	$18.27+1.06x10^{-3}T$		A7
	$18.94+2.08x10^{-3}T-1.17x10^{5}T^{-2}$	298- 950	A1,4-9
$FeCl_{2(l)}$	24.40	950-1110	4-9

Specific heats continued

	Cp, kcals/g mole	T. range °K	Ref.
$FeCl_{2(g)}$	14.0		4-9
$FeCl_{3(s)}$	$18.53+15.7x10^{-3}T+1.5x10^{-6}T^2$		A7
	$29.56-6.11x10^5T^{-2}$	298- 577	A1,4-9
$FeCl_{3(g)}$	$14.00+4.5x10^{-3}T$		A7
	$19.4+0.5x10^{-3}T-1.7x10^5T^{-2}$	298-1000	4-9
$Fe_2Cl_{6(g)}$	$30.25+5.0x10^{-3}T+3.0x10^{-6}T^2$		A7
	$44.0-20.0x10^5T^{-2}$	700-1100	4-9
H_2	$6.62+8.1x10^{-4}T$	273-2500	A2,A7, 4-9
	$6.52+0.78x10^{-3}T+0.12x10^5T^{-2}$	298-3000	A1
HCl	$6.70+8.4x10^{-4}T$	273-2000	A2,A7, 4-9
	$6.34+1.10x10^{-3}T+0.26x10^5T^{-2}$	298-2000	A1
Cl_2	$8.28+0.56x10^{-3}T$	273-2000	A2,A7
	$8.82+0.06x10^{-3}T-0.68x10^5T^{-2}$	298-3000	4-9
O_2	$8.27+2.58x10^{-4}T-1.877x10^5T^{-2}$	300-3000	A2,A7

7 Entropy

Units : cl or e.u.

Temperature : 298 °K, unless otherwise indicated

	Ref.A1	Ref.A7	Ref.4-9
Fe,α	6.49	6.60	6.49
$FeCl_{2(s)}$	28.7	29.3	28.7
$FeCl_{2(g)}$			89.0@1289°K
$FeCl_{3(s)}$	32.2	36.95	
$FeCl_{3(g)}$		105.7@932°K	
$Fe_2Cl_{6(g)}$		142.2	171.5@700°K
$Fe_2O_{3(s)}$	21.5		21.5
H_2	31.22	31.23	31.22
$H_2O_{(l)}$	16.75		
$H_2O_{(g)}$			45.13

Entropy continued

	Ref. A1	Ref. A7	Ref. 4-9
HCl	44.61	44.66	44.66
Cl_2		53.31	53.31

8 Enthalpy and Free Energy

Data is given in (A1) for change in enthalpy and free energy with temperature for the following:

Fe, $FeCl_2$, $FeCl_3$, H_2, HCl, Cl_2, O_2.

9 Equilibrium Constants

Schäfer (4-9) gives expressions for equilibrium constants and their temperature dependency for the following reactions:

$Fe_2O_3 + 2HCl = 2FeOCl + H_2O$

$Fe_2O_3 + 6HCl = 2FeCl_{3(g)} + 3H_2O_{(g)}$

$Fe_2O_3 + 6HCl = Fe_2Cl_{6(g)} + 3H_2O_{(g)}$

$2FeOCl + 4HCl = 2FeCl_{3(s)} + 2H_2O$

$2FeOCl + 4HCl = Fe_2Cl_{6(g)} + 2H_2O$

$FeCl_{2(l)} + H_2 = Fe + 2HCl$

$FeCl_{2(g)} + H_2 = Fe + 2HCl$

$2FeCl_3 = Fe_2Cl_6$

$Fe_2Cl_{6(g)} = 2FeCl_{2(s)} + Cl_2$

10 Chemical Reactions and Heats and Free Energies of Reactions

A) Calculated from data in section 1 of this Appendix

		Heat of Reaction	Free Energy of reaction
		ΔH^o	ΔG^o
		cals/mole	Fe product
$Fe_{(s)} + 2HCl_{(g)}$	$= FeCl_{2(s)} + H_{2(g)}$	-37,774	-27,100
$Fe_{(s)} + 2HCl_{(aq)}$	$= FeCl_{2(aq)} + H_{2(g)}$	-20,300	-20,396
$Fe_{(s)} + 2FeCl_{3(s)}$	$= 3FeCl_{2(s)}$	-18,100	-19,600
Fe + 2FeCl	= 3FeCl	-14,800	-18,670

Chemical reactions continued

		ΔH^o	ΔG^o
		cals/mole	Fe product
$Fe_2O_{3(s)} + 6HCl_{(aq)}$	$= 2FeCl_{3(aq)} + 3H_2O_{(l)}$	-12,325	+ 1,026
$Fe_2O_{3(s)} + 6HCl_{(g)}$	$= Fe_2Cl_{6(g)} + 3H_2O_{(g)}$	- 1,488	- 4,502(a)
$Fe_2O_{3(s)} + 6HCl_{(g)}$	$= 2FeCl_{3(g)} + 3H_2O_{(g)}$	-14,812	- 4,502(a)
$2FeCl_{3(g)}$	$= Fe_2Cl_{6(g)}$	+16,300	

(also $FeO_{(s)} + HCl_{(g)}$ or (aq))
(& $Fe_3O_{4(s)} + HCl_{(g)}$ or (aq))

		ΔH^o	ΔG^o
		cals/mole	for reaction named
$12FeCl_{2(s)} + 3O_{2(g)}$	$= 4Fe_2Cl_{6(g)} + 2Fe_2O_{3(s)}$	-45,840	-119,600(a)
$4FeCl_{2(s)} + 3O_{2(g)}$	$= 2Fe_2O_{3(s)} + 4Cl_{2(g)}$	-66,000	- 6,400
$8FeCl_{2(s)} + 4Cl_{2(g)}$	$= 4Fe_2Cl_{6(g)}$	+20,160	- 55,200(a)
$2Fe_2Cl_{6(g)} + 3O_{2(g)}$	$= 2Fe_2O_{3(s)} + 6Cl_{2(g)}$	-76,080	-104,800(a)
$4FeCl_{2(s)} + O_{2(g)}$	$= 2FeOCl_{(s)} + 2FeCl_3$ (or Fe_2Cl_6)	-	-
$6FeOCl_{(s)}$	$= 2Fe_2O_{3(s)} + 2FeCl_3$ (or Fe_2Cl_6)	-	-
$2FeCl_{2(aq)} + O_{2(g)} + H_2O_{(l)}$	$= Fe_2O_{3(s)} + 2HCl_{(aq)}$	-108,183	

Chemical reactions continued

		ΔH^o	ΔG^o
		cals/mole	Fe product
$2FeCl_{2(s)} + 2H_{2(g)}$	$= 2Fe_{(s)} + 4HCl_{(g)}$	+37,774	+ 27,100
$Fe_2Cl_{6(g)} + H_{2(g)}$	$= 2FeCl_{2(s)} + 2HCl_{(g)}$	-24,583	- 15,850(a)
$Fe_2Cl_{6(g)} + 3H_{2(g)}$	$= 2Fe_{(s)} + 6HCl_{(g)}$	+13,191	+ 11,250(a)
$2FeCl_{3(g)} + H_{2(g)}$	$= 2FeCl_{2(s)} + 2HCl_{(g)}$	-40,883	-
$2FeCl_{3(g)} + 3H_{2(g)}$	$= 2Fe_{(s)} + 6HCl_{(g)}$	- 3,109	-

Notes: (a) calculated with $FeCl_3$ (or Fe_2Cl_6) in the solid phase

B) Other reactions quoted by Schäfer et al. (4-9), and based on his enthalpies etc.:

		ΔH^o cals/mole for reaction given
$2FeCl_{3(s)} + O_2$	$= 2FeOCl + 2Cl_2$	- 4,400
$Fe_2O_3 + FeCl_{3(s)}$	$= 3FeOCl$	+ 3,570
$2FeCl_3$	$= Fe_2Cl_6$	+32,550
$Fe_2Cl_{6(g)}$	$= 2FeCl_{2(g)} + Cl_2$	-62,400
$2FeCl_{3(g)}$	$= 2FeCl_{2(g)} + Cl_2$	-29,800
$Fe_2Cl_{6(g)}$	$= 2FeCl_{2(s)} + Cl_2$	+13,600
$2FeCl_{3(g)}$	$= 2FeCl_{2(s)} + Cl_2$	+46,200
$2FeCl_{3(s)}$	$= 2FeCl_{2(s)} + Cl_2$	-24,600

		ΔG cals.
$Fe_2O_3 + FeCl_{3(s)}$	$= 3FeOCl$	$3{,}572 - 9.73 x T^oK$ (around 600^oK)

APPENDIX III

The results of the best capital cost equation obtained in section 7 (equation 7.5) are reproduced. The computer programs and techniques employed in the derivation of the estimation equations are also included.

Results from equation 7.5

Capital quoted	Cost, £ Calculated	$\frac{\text{Calculated}}{\text{quoted}}$ %
5350000.0	5211821.6	97.417226
17300000.	17722082.	102.43978
28629000.	30291539.	105.80718
35895000.	28838590.	80.341523
44574000.	37031927.	83.079658
33310000.	33696145.	101.15924
34892000.	28838590.	82.651008
37615000.	35240903.	93.688430
33072000.	32598896.	98.569472
31018000.	31680217.	102.13494
6288000.0	6812413.3	108.33990
7841000.0	8440271.1	107.64278
11212000.	12312222.	109.81239
13599000.	15254284.	112.17210
19470000.	22252145.	114.28939
24016000.	27569399.	114.79596
31250000.	28553012.	91.369638
1727000.0	1399466.9	81.034562
26786000.	31110719.	116.14544
15000000.	16651518.	111.01012

Computer program to produce a matrix, the solution of which gives values of A, b, c, d, to equation = $y = Av^{b}w^{c}x^{d}$

```
PR5461
1 001 INP                    1 002 C000 GO
1 003 L000 GO                1 004 S017 GO
1 005 C019 GO                1 006 L020 GO
1 007 C001 GO                1 008 C002 GO
1 009 C003 GO                1 010 C004 GO
1 011 C005 GO                1 012 C006 GO
1 013 C007 GO                1 014 C008 GO
1 015 C009 GO                1 016 C010 GO
1 017 C011 GO                1 018 C012 GO
1 019 C013 GO                1 020 C014 GO
1 021 C015 GO                1 022 C016 GO
1 023 C018 GO                1 024 C033 GO
1 025 INP                    1 026 C021 GO
1 027 INP                    1 028 C022 GO
1 029 INP                    1 030 C023 GO
1 031 INP                    1 032 JMP 166
1 033 INP                    1 034 C025 GO
1 035 INP                    1 036 C026 GO
1 037 INP                    1 038 C027 GO
1 039 INP                    1 040 C028 GO
1 041 INP                    1 042 C029 GO
1 043 INP                    1 044 C030 GO
1 045 L021 GO                1 046 M031 GO
1 047 D022 GO                1 048 D029 GO
1 049 D030 GO                1 050 LOG
1 051 C001 GO                1 052 L023 GO
1 053 D024 GO                1 054 LOG
1 055 C002 GO                1 056 L025 GO
1 057 M026 GO                1 058 D022 GO
1 059 LOG                    1 060 C003 GO
1 061 L024 GO                1 062 JMP 064
1 063                        1 064 LOG
1 065 C004 GO                1 066 L033 GO
1 067 A001 GO                1 068 C033 GO
1 069 L005 GO                1 070 A002 GO
1 071 C005 GO                1 072 L006 GO
1 073 A003 GO                1 074 C006 GO
1 075 L007 GO                1 076 A004 GO
1 077 C007 GO                1 078 L002 GO
1 079 M002 GO                1 080 A008 GO
1 081 C008 GO                1 082 L003 GO
1 083 M003 GO                1 084 A009 GO
1 085 C009 GO                1 086 L004 GO
1 087 M004 GO                1 088 A010 GO
1 089 C010 GO                1 090 L002 GO
1 091 M003 GO                1 092 A011 GO
1 093 C011 GO                1 094 L002 GO
1 095 M004 GO                1 096 A012 GO
1 097 C012 GO                1 098 L003 GO
```

```
1 099 M004 GO
1 101 C013 GO
1 103 M002 GO
1 105 C014 GO
1 107 M003 GO
1 109 C015 GO
1 111 M004 GO
1 113 C016 GO
1 115 A018 GO
1 117 S019 GO
1 119 L019 GO
1 121 L005 GO
1 123 L006 GO
1 125 L007 GO
1 127 L033 GO
1 129
1 131 L005 GO
1 133 L008 GO
1 135 L011 GO
1 137 L012 GO
1 139 L014 GO
1 141
1 143 TYPE
1 145 TYPE
1 147 TYPE
1 149 TYPE
1 151 TYPE
1 153
1 155 TYPE
1 157 TYPE
1 159 TYPE
1 161 TYPE
1 163 TYPE
1 165
1 167 M040 GO
1 169 C024 GO
1 171 RET
```

```
1 100 A013 GO
1 102 L001 GO
1 104 A014 GO
1 106 L001 GO
1 108 A015 GO
1 110 L001 GO
1 112 A016 GO
1 114 L017 GO
1 116 C018 GO
1 118 IF - JMP 025
1 120 TYPE
1 122 TYPE
1 124 TYPE
1 126 TYPE
1 128 TYPE
1 130
1 132 TYPE
1 134 TYPE
1 136 TYPE
1 138 TYPE
1 140 TYPE
1 142 L006 GO
1 144 L011 GO
1 146 L009 GO
1 148 L013 GO
1 150 L015 GO
1 152 JMP 153
1 154 L007 GO
1 156 L012 GO
1 158 L013 GO
1 160 L010 GO
1 162 Lo16 GO
1 164 JMP 165
1 166 LOG
1 168 EXP
1 170 JMP 033
```

Computer program to calculate capital costs from data supplied (indicated in brackets), and calculate percentage agreement.

```
PR5461
3 001 INP                          3 002 C100 GO (A)
3 003 INP                          3 004 C096 GO (b)
3 005 INP                          3 006 C094 GO (c)
3 007 INP                          3 008 C092 GO (d)
3 009 INP                          3 010 C101 GO (Cap. Cost Quoted)
3 011 INP                          3 012 C102 GO (N)
3 013 INP                          3 014 C103 GO (Q)
3 015 INP                          3 016 JMP 070 (S)
3 017 INP                          3 018 C105 GO (T)
3 019 INP                          3 020 C106 GO (n)
3 021 INP                          3 022 CL07 GO (P)
3 023 INP                          3 024 C108 GO (n')
3 025 INP                          3 026 C109 GO (Fm)
3 027 INP                          3 028 C110 GO (ENR)
3 029 L100 GO                      3 030 JMP 031
3 031 C100 GO                      3 032 L100 GO
3 033 M102 GO                      3 034 JMP 035
3 035 M110 GO                      3 036 D098 GO
3 037 LOG                          3 038 C097 GO
3 039 L103 GO                      3 040 D104 GO
3 041 LOG                          3 042 M096 GO
3 043 C095 GO                      3 044 L105 GO
3 045 M106 GO                      3 046 D102 GO
3 047 LOG                          3 048 M094 GO
3 049 C093 GO                      3 050 L107 GO
3 051 M108 GO                      3 052 D102 GO
3 053 LOG                          3 054 M092 GO
3 055 C091 GO                      3 056 L097 GO
3 057 A095 GO                      3 058 A093 GO
3 059 A091 GO                      3 060 EXP
3 061 C090 GO                      3 062 L101 GO
3 063 TYPE (Quoted Cap.Cost)       3 064 L090 GO
3 065 TYPE (Calculated Cap-        3 066 L090 GO
           ital Cost)
3 067 D101 GO                      3 068 M120 GO
3 069 TYPE (Percentage             3 070 JMP 009
           agreement)
3 071 LOG                          3 072 M080 GO
3 073 EXP                          3 074 C104 GO
3 075 JMP 017                      3 076 RET
```

APPENDIX IV

The following papers are appended as supporting material:

"Long Range Process Design and Morphological Analysis"
Chemical Engineer, April 1968.

"Morphological Methods - Principles and Practice"
in 'Technological Forecasting' ed. R.V.Arnfield, pub.
Butterworths, 1970.

"Iron Powder: Prices, Costs, and Possibilities"
Powder Metallurgy, November 1968.

"Electrolysis of Iron - A Bibliography"
University of Aston.

"Chemical Alternatives to the Conventional Manufacture of
Iron and Steel" presented to I. Chem. E. meeting,
Swansea, 1969.

A.V. Bridgwater B.Sc. (Tech), M.Sc., AMCST

Electrolysis of Iron - A Literature Survey and Bibliography

Introduction

A survey of the literature pertaining to the electrolysis of iron from every aspect has been carried out in connection with the O.S.C.A.T. project. This project is investigating chemical alternatives to the conventional manufacture of iron and steel, and the survey therefore, is orientated toward the economic and technical viability of electrolysis as a unit operation in any proposed hydro-metallurgical process.

The paper is intended to provide a reference to the source of any required information, rather than to provide such information. It is considered to be as complete as practicable. Information has been tabulated where convenient, and a comprehensive index provided.

INDEX

1 Introduction

1.1 Historical

An early commercial application of electrodeposition of iron was in the manufacture of Russian banknote printing plates around 1860 (reported in 2, 4, 21). Not until after 1900 were several processes for manufacturing pure iron devised and put into industrial operation: iron ore was leached, and the resulting solution electrolysed to give pure iron (2, 4-7 and para 12). In some cases a shaped iron product, such as tubes, were obtained. Interest in these processes was not maintained due to technical difficulties (4) and costs (see also sect. 12.1). After then, electrolysis was only used to produce high purity iron for experimental purposes, and powder for powder metallurgy work. In the last twenty years the Russians have evinced considerable interest in the building up of worn machine parts by electrodepositing iron. The literature is very extensive (see also sect. 12.2). Pure iron powder continues to be made electrolytically from conventionally-produced cast iron and steel (22); the only other commercial application of iron plating in this country is the plating of contacts in the heavy electrical engineering industries (23), as far as is known.

1.2 Reviews

An interesting paper was written by Hughes (66) in which he critically reviews the important researches on iron plating up to 1921. Mellor's (21) inorganic text-book of 1932 very comprehensively reviews the electrolysis of iron, and contains over 300 references on the subject, from the earliest recorded deposition of iron in 1831, to 1932. Many of these references were concerned with investigating the conditions of electrolysis in relation to the quality and quantity of iron deposit obtained. Since Mellor's book, however, the interest in electrodepositing iron has waned and few general articles have been written. Of particular interest is Goldmann's (24) recent annotated bibliography on iron plating (unfortunately not available), Clark's (25) paper, and other general reviews on electroplating (26-28).

A monograph on the electrodeposition of iron was written by Hughes (29) in 1922. More recent general textbooks are by Blum and Hogaboom (30), Mantell (31), Lowenheim (32), and Bockris and Conway (33). Bridgwater (296) has recently reviewed all previous proposals for the chemical extraction of iron, which includes electrolytic processes.

2 Aqueous Solid Electrodeposition

2.1 Theory

Of particular practical interest is Pourbaix's (34) atlas of electrochemical equilibria, which provides a general view of the limits of possibility of corrosion by means of pH versus potential diagrams. Also covered is the formation and stability of oxides, and other topics concerned with the electrochemical behaviour of iron. A number of books have been written on electrochemical theory and corrosion, for example West (35). The following references are all concerned with the theories and fundamental studies of the electrolysis of iron, and have been grouped under specific headings.

Anion effect: 36, 37

Crystal structure: 38-42, 64

Kinetics: 43-51, 63

Mechanism of deposition: 49, 50, 52, 53, 62, 70

Passivity: 54, 55

Polarisation: 34, 51, 54, 56-58, 65, 69, 96

Potential: 34, 48, 56, 59

Redox system Fe (II) - Fe (III): 60, 111

Use of Ultrasonics: 61

2.2 Baths and Conditions

There are a large number of references on the composition of electrolysis baths and conditions of operation. These are summarised below and arranged by the iron salt anion. All give satisfactory deposits of iron.

2.2.1 Ferrous chloride

a) Alone: 21, 29, 30, 65-70

b) $FeCl_2$ + $NaCl$ or KCl as main additive: 30, 64-85

c) $FeCl_2$ + NH_4Cl as main additive: 66, 71, 75, 76, 85, 86

d) $FeCl_2$ + $CaCl_2$ as main additive: 30, 66, 67, 84, 88, 89

e) $FeCl_2$ + $MnCl_2$ as main additive: 71, 75, 76, 87, 90

f) $FeCl_2$ + $NiCl_2$ as main additive: 91

2.2.2 Ferric chloride: 92, 93

2.2.3 Ferrous sulphate

a) Alone: 30, 66, 94-97

b) $FeSO_4$ + $Al_2(SO_4)_3$ as main additive: 71, 94, 96, 98, 99

c) $FeSO_4$ + $(NH_4)_2SO_4$ as main additive: 30, 66, 94, 100, 101

d) $FeSO_4$ + $MgSO_4$ as main additive: 66, 94

e) $FeSO_4$ + K_2SO_4 as main additive: 94, 95, 99, 102, 103

f) $FeSO_4$ + $NaHSO_4$ as main additive: 63

g) $FeSO_4$ + Na citrate as main additive: 104, 105

h) $FeSO_4$ + Urea as main additive: 106

The "main additive" is the other major component, comprising at least 20% of the total solutes.

2.2.4 Ferric sulphate: 97, 107, 108

2.2.5 Mixed iron chlorides and sulphates

a) $FeCl_2$ + $FeSO_4$: 30, 66, 109, 110

b) $FeSO_4$ + $Fe_2(SO_4)_3$: 97, 111

2.2.6 Other iron salts

a) $Fe(NO_3)_3$: 112 (gives maghemite)

b) $Fe(BF_4)_2$: 113-115, 165

c) Fe salts of fluoro-acids: 116

d) $Fe(C_6H_5SO_4)$: 117-119

e) $Fe(NH_2SO_3)_2$: 120, 121

All of the above electrolysis baths are known as "acid baths", having usually a pH of less than 6. Some work has been done on electroplating iron from an alkaline bath. For iron in solution, the references are given below; and for iron as a solid suspension, or paste, this is covered in sect. 11 as "electro-reduction".

2.2.7 Fe salts in alkaline medium

a) Pyrophosphate: 122

b) Fe chelates (TEA and EDTA): 123

One of the most comprehensive investigations into electroplating iron from solutions of different salts was by Watt (124). He tested 21 inorganic salts and 22 organic salts of iron and his work is of considerable importance for its completeness: although published in 1887 there are surprisingly few references to this work in the literature.

2.3 Additives

A considerable amount of work has been done on the effect of different additives to the electrolysis bath in iron plating. This has been summarised in Table 1.

TABLE 1

ADDITIVE	EFFECT ON DEPOSIT	REFERENCE
Acetic acid	Decreases iron powder size	125
Alkylarene sulphonate	Increases brightness of deposit	103, 126
Aluminium chloride	Increases buffer capacity of bath	127
Aluminium sulphate	Moves steady state potential. Increases rate of iron dissolution	57
	Rate of dissolution increases linearly with increasing current	94
Ammonium chloride	Increases buffer capacity of bath	127
Ammonium fluoride	Acts as buffer in bath and improves deposit	82
Ammonium sulphate	Increases hardness. Reduces ductility	128
	Increases cathodic polarisation	56
	Current efficiency decreases as current density increases. Rate of deposition increases linearly with applied current	103
Arene sulphonate	Acts as brightener. Gives smooth even deposit	103
Ascorbic acid	Gives stability to bath. Prevents reduction Fe (III) to Fe (II)	79
	Decreases cathodic polarisation	139
	Gives hard, durable deposit	129
	Reduces layering	64
Boric acid	Favourable	106
	Acts as a buffer	130
	Decreases Fe (II) activity. Decreases rate of $Fe(OH)_2$ sol formation. Improves quality, and brightens deposits.	127
Calcium chloride	Increases microhardness. Gives coarse deposit in large amounts	131
Carbon dioxide	When solution saturated, prevents Hydrogen impregnation in Fe	128
Cellulose	Improves adherence and structure	132
Citric acid	Gives hardness	71
	Increases hardness to near Chromium	128
	Increases cathodic polarisation	87
	Increases wear resistance	133, 140
	Decreases fatigue limit and decreases cathode polarisation	134
Dextrin	Increases cathode polarisation	87, 129
	Decreases wear resistance	133
	Increases hardness, decreases wettability of cathode	137
	Decreases fatigue limit	134
	Codeposits with metal	136, 137
	Improves wear resistance	75
	Reduces adsorbed Hydrogen on cathode	139
	Increases wear resistance	140
Dextrose	Improves wear resistance	75
Diethylamine	Decreases formation $Fe(OH)_2$ sol.	127
Dihydric alcohols	Increases brightness of deposit	126
Fatty acid sulphate	Increases brightness of deposit	126
Fluoborate ions	Increases adhesion, increases hardness and combats cathode passivation	128
	Improves electrolysis	165
Gelatin	Increases cathode polarisation	87
	Increases wear resistance	133
	Increases contact angle and adherence of Hydrogen bubbles causing porosity	137
	Decreases fatigue limit	134
	Decreases cathode polarisation	134

Glycerin	Increases cathode polarisation	128
Glycerol	Gives high wear resistance and micropores which retain lubricant	83
	Improves wear resistance	75, 76
	Reduces adsorbed Hydrogen on cathode	139
	Increases fatigue limit	134
	Increases current efficiency	135
	Increases hardness	77, 137
	Gives hardness	71
Glycine	Acts as buffer, gives smooth shiny deposit, enables deposition over wider pH range	141
Hexa methylene-tetramine	Reduces Hydrogen in deposit	142
Iron (II) bicarbonate	Improves throwing power	143
Iron glycerate	Gives hard durable coating	129
	Gives fine crystalline deposits with high mircrohardness	138
Iron methyl sulphate	Gives hard durable coating	129
	Gives fine crystalline deposit with high microhardness	138
Iron sulphosalicylate	Gives hard durable coating	129
	Gives fine crystalline deposit with high microhardness	138
Lauryl sulphate	Anti-pitting agent	114
Magnesium sulphate	Increases hardness and brittleness	128
	Increases cathodic polarisation	56
	Current efficiency decreases as current density increases above 2.5 asd	94
Manganese chloride	Decrease in microhardness. Increased ductility	73
	Increases fatigue limit	134
	Increases cathodic polarisation	139
	Increases hardness. Improves appearance of deposit	77
	Controls grain size, improving ductility	150
Methallylamine	Improved coating	144
Monohydric alcohols	Increases brightness of deposit	126
136 Naphthalene tri-sulphonic acid	Improved coating	144
Pulsating current	Increases polarisation and rate of deposition	164
Phenol	Decreases microhardness. Increases ductility	73
Phosphate ions	Forms complex ions on the cathode	145
Phthalimide	Levelling agent	146
Polyoxyethylene sorbitan monooleate	Gives uniform metal powder	147
Poly vinyl alcohol	Improves appearance and structure of deposit	132
Potassium chloride	Increases cathode polarisation	139
Potassium sulphate	Increases hardness of deposit	128
	Current efficiency decreases as current density increases above 2.5 asd	94
	Limiting current reduced	95
Quinoline	Increases Hydrogen voltage, does not improve deposits	127
Saccharin	Levelling agent	146
Safranine	Increases Hydrogen over voltage, does not improve deposits	127
Secondary alcohol sulphates	Increases brightness of deposit	126
Sodium arsenate	Inhibitor	148
Sodium chloride	Increases fatigue limit	134
	Increases cathode polarisation	139

Sodium fluoride	Improves hardness Enables thick adherent deposits to be obtained Gives fine silvery appearance	92 28 28
Sodium lauryl sulphate	Improves coating	144
Sodium sulphate	Increases hardness slightly Increases cathode polarisation Current efficiency decreases as current density increases above 2.5 asd	128 56 94
Sugar	Increases contact angle and adherence of Hydrogen bubbles, causing porosity Decreases fatigue limit Codeposits with metal Improves wear resistance Increases wear resistance Increased current efficiency	137 134 136, 137 75, 140 137 135
Sulphated coconut hydroxyalcohol	Gives ductile deposit	146
Sulphonated phenol	Increases hardness and ductility	128
Sulphonic acid amide salts	Increases brightness of deposit	126
Thiorea cournarin	Levelling agent	149
Tribenzylamine	Throwing power of bath increased. Appearance improved.	78
Triethanolamine	Reduces adsorbed Hydrogen on cathode. Increases cathodic polarisation	139
Triethylamine	Improves quality and brightness of deposit. Decreases formation of $Fe(OH)_2$ sol.	127
Ultrasound	Increases deposition rate and current efficiency Work capacity increased fivefold	129 61
Urea	Improves quality and brightness of deposit Decreases formation of $Fe(OH)_2$ sol. Brightens deposit Favourable	127 130 106
Urotopine	Appearance improved. Throwing power increased. Current density range increased.	78

2.4 Electrolysis with Insoluble Anodes

Of particular interest to the O.S.C.A.T. project are those references where the iron is removed from solution, and not transferred from anode to cathode. This is called "electrowinning", and is a method used for removing iron from a leach liquor for example. Most of the references refer either to the recovery of iron from spent pickle liquor, or to complete processes as discussed in sects. 1 and 12. Both Liebscher (166) and Krudryavtseva (86) investigated the deposition of iron from a chloride bath using inert anodes; and Stender and Ksenzhek (157) discussed the electrolysis of aqueous chloride solutions with a graphite anode. This method has also been used to try and separate dissolved impurity iron, for example, from zinc chloride solution (152) - unsuccessfully; and aluminium chloride (261) - successfully. Other applications include the preparation of ultra pure iron by electrolysing the eluate from an ion exchange column (153), a patent by Juda (154) where the insoluble solid anode is replaced by Hydrogen anode, recovery of iron from grinding dust (155), and another patent for precipitating copper from solution with iron and recovering the iron by electrolysis (156). Whenever an insoluble anode is used, the applied voltage is usually higher and the current efficiency lower.

2.5 Electrorefining

Some work has been done on the purification of pig-iron by electrolysis, mainly to remove copper (157, 158), aluminium (159); or produce graphite (160); or just to purify the iron generally (161-163).

3 Aqueous Powder Electrodeposition

Metal powders can be produced electrolytically in two ways: direct precipitation on the cathode; and deposition of a brittle sponge, which is later ground to powder. Due to electrochemical characteristics, iron powder is made by the second method. (167, 168). Some commercial processes produce powder instead of bar or sheet (see sect. 12); but the form the product takes usually depends on the conditions of electrolysis. Powder manufacture by deposition on a mercury cathode with subsequent removal of the mercury is covered in sect. 6.

3.1 History and Reviews

One of the earliest commercial production processes was for the manufacture of coils for the U.S. telephone services (169). Iron powder for powder metallurgical purposes generally has been made from then, up to the present day (22), although in relatively small quantities. Granberg (185) describes such a plant using scrap iron and steel as raw material, making 4000 tons/year. Reviews on iron powder are by Shafer and Harr (170), Ljungberg (168) and Mantell (171).

3.2 Theory

Investigations into:

a) Concentration of electrolyte: 172, 173, 175

b) Crystal structure: 172-174

c) Current density: 132, 171-173, 175-177

d) Mechanism of deposition: 62, 173, 176, 177

e) pH: 178

f) Physical constraints: 175

g) Polarization: 173

h) Temperature: 132, 172, 173, 175

3.3 Electrolysis baths

a) $FeSO_4$ alone: 148, 171, 178, 179

b) $FeSO_4 + Al_2(SO_4)_3$ as main additive: 94

c) $FeSO_4 + (NH_4)_2SO_4$ as main additive: 94, 100, 169, 170, 180

d) $FeSO_4 + MgSO_4$ as main additive: 94, 148

e) $FeSO_4 + K_2SO_4$ as main additive: 173, 178, 181

f) $FeSO_4 + Na_2SO_4$ as main additive: 94, 181

g) $FeSO_4$ + NaCl as main additive: 181

h) $FeSO_4$ + Na citrate as main additive: 104

i) $FeCl_2$ alone: 185

j) $FeCl_2 + NH_4Cl$ as main additive: 167, 182

k) Unspecified: 183, 184

Levin and Pushkareva (181) stated that the ferrous sulphate bath is very unsatisfactory on account of its instability and changes in ionic composition during electrolysis. They found that the best additive was sodium chloride.

4 Use of Membranes in Aqueous Electrolysis

Membranes or diaphragms have been widely used in electrolysis to separate the anode and cathode components. They may act either physically, ie. as a filter; or chemically by ion exchange. Here, again, much of the relevant work has been on regenerating spent pickle liquor: since the acid content is relatively high without a membrane the iron redissolves almost as soon as it is plated giving hydrogen; acid is continuously produced at the anode with evolution of oxygen, and the overall effect is the electrolysis of water to hydrogen and oxygen. These pickling references are discussed briefly below, with the other references, and also in (1). Katz (186) evaluated electric membrane processes for industrial chemical applications.

4.1 Physical membranes

When electrodepositing iron from impure solutions or anodes, a membrane is used to prevent these impurities being transported through the bath and deposited on the cathode. Agladze and Gongliashvili (97) and LaCroix and Belcier (187) used membranes in refining pig iron and Kerti (155) in reclaiming iron from grinding dust. Both Krudryavtseva et al (86) and Parsi (188) used membranes to prevent oxidation of ferrous to ferric iron in the anode compartment. Several patents specify membranes as a safety precaution (109, 156). The use of membrane in regenerating pickle liquor is specified in several patents (154, 188-190), and Aravamuthan et al (191) used a diaphragm cell to regenerate pickle liquor in the cathode compartment, and precipitate manganese dioxide from manganese salts in the anode compartment.

4.2 Ion exchange membranes

These have been widely used in investigations into regenerating spent pickle liquor (179, 192-196), and patents have been taken out on the subject (197, 198). Neal et al (199) produced sulphur free iron by electrolysis with a cation exchange membrane, and Davey and Scott (113) produced maghemite by electrolysing ferric nitrate across an ion exchange membrane.

5 Electrodeposition from a Non-aqueous Solvent

Very little work has been performed on the electrolysis of non-aqueous iron solutions. Mellor (21) reviewed this up to 1932, and Gutmann and Schöber (200) had nothing further to add up to 1958. In 1964, the polarization of electrodes during deposition of iron from methyl sulphate, glycerate and sulphosalicylate was investigated by Dushevskii (201); and in 1966, the migration of water and solvent was studied in the solvent extraction of ferric chloride, by electrolysing the organic phase. (202). The investigations may be summarised:

> $FeCl_3$ in methyl chloride (21), in acetone (21, 66), alcohol (21, 66), acetone and alcohol (21, 66), diethyl ether (21, 202), chlorex (202), dibutyl ether (202), dimethyl ketone (202), $FeBr_2$ in pyridine (21), Fe salts in liquid ammonia (21, 200).

Mellor, however, is not altogether reliable: for example the electrodeposition of iron in liquid ammonia by Booth and Merlub-Sobel (256) was reported by him to be unsuccessful, yet in fact they obtained "perfect deposition". In all cases the conditions of electrolysis were very important and critical, otherwise carbon, iron oxide, or ferrous chloride was precipitated. There thus seems little application to the large scale production of iron, since aqueous electrolysis is more successful and cheaper in terms of solvent.

6 Mercury Cathodes

A considerable amount of work has been done on the production of iron powder by deposition on mercury. This is particularly suitable for continuous processes; and is also claimed to give superior iron powder; both in purity, and properties for metallurgical applications (1). Mundowicz (203) and Emert (204) have reviewed the deposition of iron on mercury cathodes, and Csizi (205) the application of this method to purify wastes.

6.1 Theory and conditions

The theory of the mercury cathode is still largely speculative. Mundowicz (206) found that it behaved as a heterogeneous electrode, with spontaneous electrochemical corrosion. The transport of metals beneath the mercury surface was investigated by Gladyshev (207) who proposed an energy barrier, related to overvoltage, to help or hinder the solution of metals in the mercury. The kinetics of the deposition of iron and the effect of surfactants was investigated by Prikhodchenko et al (208); who found that anionic agents increased iron deposition, and cationic and molecular agents decreased it. No explanation was suggested for this. Popkov et al (58) also were at a loss to account for non-ideal behaviour of iron deposition on a mercury cathode.

Conditions necessary for successful deposition of iron on mercury have been investigated (209-214), and also electrolyte baths (208, 210, 212, 215, 216) and additives (208, 213).

6.2 Applications

Some work has been done on regenerating spent pickle liquor by depositing the iron onto mercury (218-220), but there has been more interest in producing iron powder. Iron is relatively insoluble in mercury, and on electrolysis forms either a suspension or a layer on the surface. The most complete removal of mercury is by distillation, usually after concentration by filtration (215, 217, 218, 222) or magnetically (210, 224, 226); or distillation alone (1, 223). Brannland et al (216) oxidised the iron with air to expel it from the mercury, then reduced the oxide with hydrogen, at the same time evaporating the remaining mercury. All the workers reported that the iron was non pyrophoric although sometimes highly reactive (1). The iron has also been removed by "leaching" with ferric sulphate (218, 221, 225), giving a solution of ferrous sulphate. Apart from purifying iron, it is difficult to see the purpose of this. The iron has also been "extracted" into benzene for analysis (227, 228). Luborsky (229) and Razniewska et al (228) both produced elongated iron particles instead of the more usual asymmetrical shape, which have a particular application in powder metallurgy.

7 Fused Salt Electrolysis

The lack of interest in producing iron by electrolysis of fused salts is explained by Ljungberg (168) who states that although the iron powder produced is of very high quality, high production costs and difficulties of obtaining a completely salt-free powder, make this method quite uneconomic compared with electrolysis from aqueous solution. Kroll (230, 255) reviews the production of metals by fused salt electrolysis, with emphasis on iron. He states that electrorefining of iron (i.e. soluble anode) is relatively straightforward requiring 2 Kwh/lb iron produced, but electrowinning (insoluble anode) proves most difficult due to internal oxidation-reduction reactions, and the energy consumption is around 16 Kwh/lb iron powder produced. This inefficiency could be overcome by using a "membrane" but it would be extremely difficult to find a suitable material, capable of withstanding the operating conditions of fused salt electrolysis. Mellor (21) only gives a few references in his comprehensive review. Solid iron is always deposited in a pulverent form (168) and no claims to the contrary have been met in the literature. Apart from some investigations into the electrolysis of iron silicates and slag by Esin et al (231-237), no work on the production of molten iron by electrolysis appears to have been done.

The theory of iron deposition from a fused salt system has been studied (233, 235-242). The most popular bath has been ferrous chloride, usually with an alkali metal chloride, to increase the conductivity and lower the melting point, such as sodium (240, 243, 244), potassium (240), lithium-potassium (241, 243, 245-247), and unspecified (248-250). Iron has also been deposited from a ferric chloride - sodium chloride bath (251, 252); sodium nitrate and sodium nitrite bath (241), cryolite bath (239) and pure iron oxide (253). A review by Kroll (254) on

Of particular interest to the O.S.C.A.T. project is the recovery of iron from a fused salt bath using insoluble anodes. In spite of the difficulties reported by Kroll above, several authors report the successful manufacture of iron powder although with low efficiency (230, 234, 237, 239, 242, 245, 253, 255) and patents have been taken out (244, 248, 249).

8 Electrodialysis

Electrodialysis has been almost exclusively applied to demineralisation of dilute solutions, and very little work has been done on separation of iron bearing solutions. Of particular interest is Lewis and Tye's (262) paper on the regeneration of spent pickle liquor, which was investigated in considerable detail, and design data presented. No economics are given, although the costs are suggested to be high. This process is similar to those using ion exchange membranes in sect. 4. The general theory and design equations are well developed (263-265) although orientated towards water desalination. Forward and Halpern (266) patented a general method for treating metallurgical pulps continuously or batchwise. No evidence of commercial application has been found.

9 Electroforming

The production of bank-note printing plates was one of the earliest applications of electroforming, and is still practised (see sect. 12). Much work on the production of pure iron tubes was done in the early part of this century; initiated by Cowper-Coles in 1906 (267), and patented (268). His process was investigated in great detail by Palmaer and Brinell (2) who reported on the economics without comment, and postulated leaching an iron ore with acid and electrolysing this with insoluble anodes (Cowper-Coles used pig-iron anodes) to give iron tubes or sheets. This latter electrowinning process was estimated to consume 3.4 - 3.8 Kwh/lb iron, as opposed to 0.75 Kwh/lb iron for electroplating. However Belcher (4) considers Boucher's (269) work more important for manufacturing iron tubes, although the process is essentially the same. The Eustis process described in sect. 12.1 also produces tubes. There are many reports of these processes, (21, 4, 30, 66).

Since this work, there has been little interest in electroforming iron; probably on account of cost. Bull et al (270) described a commercial process for electroforming iron in many fields. General articles of interest are by Hamilton (271),also (272, 273, 278). Montan Union (84) patented a process for the continuous manufacture of electrolytic iron sheet; see (274, 275) for electroforming iron. Many other general patents on electroforming, which could be applied to iron have been taken out (e.g. 276).

10 Electrophoresis

Metals are only deposited by electrophoresis when conventional techniques cannot be used. Metal powders and oxides (including iron) are reported to have been successfully deposited by this method (277). However, in view of the very successful deposition by straightforward electrolysis, there seems very little application for the large scale manufacture of iron. Fundamentals and theory are covered in (31) and (277).

11 Electro-reduction

The mechanism and kinetics of the cathodic reduction of a suspension iron oxides in an alkaline medium has been investigated in detail (279-286). The efficiency ranged from 4% to a maximum of 71% (281), but not usually more than 50%; and the conditions were more critical than for acid solutions. These may be explained by the very low solubility of iron in alkalis. In spite of this, both LeDuc et al (287) and Yampol'skaya (288) have considered the production of iron powder by electrolysis in alkaline medium; and Czech (289) and Mehl (290) have patented processes. There does not appear to be any advantage over electrodeposition from acid solutions.

There is very little known iron electrolysis practised in this country at the time of writing: only for the production of high grade iron powder, and in the heavy electrical engineering industries (see sect. 1.1). Although many schemes for regenerating spent pickle liquor electrolytically have been proposed, there is no evidence of their being practised. Some interest has been shown in the following fields:

a) Complete processes to recover metal from ore.
b) Building up worn machine parts.
c) Manufacturing bank-note printing plates.
d) Specialist studies e.g. computer components.
e) Electroforming. This is discussed in sect. 9.
f) Pickle liquor regeneration, see sects. 4 and 12.
g) Powder production. See above and sect. 3.

12.1 Complete Processes:

Of particular interest are those references which deal with the electrowinning of iron, especially from leach liquors. Palmaer and Brinnell (2) in their report on the Cowper-Coles electroforming process, suggested leaching iron ore and depositing the iron from the leach solution. They were very pessimistic about the cost however. The Eustis process aroused considerable interest a few years later when it was patented (3) and introduced commercially (4-8). It is, in fact, the only proposed electrolytic process manufacturing iron from ore, that has been successfully practised on an industrial scale. The patent specifies hydrochloric and/or sulphuric acid leaching to dissolve the iron values, but all subsequent commercial work was performed on ferric chloride leaching of sulphide ore (4-8), which may be due to a much earlier patent by Siemens (293), specifying this leaching agent. Ferrous chloride solution and elemental sulphur were the products. Any copper, as chloride, was precipitated by cementation, remaining ferric chloride reduced with sulphur dioxide, and the ferrous chloride electrolysed in a diaphragm cell to give iron, and ferric chloride which was recycled. The corrosivity of hot ferric chloride caused the eventual shut-down and loss of interest. The power consumption was approximately 1.5 - 2.4 Kwh/lb iron (which corresponds to £18 - 29/ton on present day prices). A patent by Konrad and Eustis (9) improved this to 1.2 - 1.25 Kwh/lb Fe (corresponding to £14 - 15/ton) by using an improved graphite anode. This processing method was studied by Pike et al, (10), and Aravamuthan (11) also mentions a ferric chloride leaching of pyrrhotite and electrolysis process, but with no details. Konrad (294) put forward a very enthusiastic proposal in 1953 for a commercial plant to manufacture electrolytic iron along very similar lines to the Eustis process. Full technical and economic details are given in the paper, but nothing apparently materialised and no commercial plant seems to have been built.

Other processes for acid-leaching iron oxide ores, followed by electrolysis have been put forward (12-14) but not practised. Iron has also been removed electrolytically from leach liquors of mixed ores: chromium - iron (15, 16); titanium - iron (17-19); and nickel matte (20). In these examples, iron is the undesirable impurity. Electrolytic recovery of iron from spent pickle liquor is covered in (1).

The electrowinning and deposition of iron from aqueous solution has been shown to be successfully practised. Recent interest has been slight, however, due to high costs. This is mainly due to expensive raw material in electroplating (pig iron costs circa £20 per ton, and steel ingot £27 per ton) and electrolysis costs; giving a product not directly usable on a large scale. The problems experienced by Eustis are also, no doubt, partly responsible for lack of interest in electrowinning.

A major advantage of electrolysis is the inherent separation due to varying migration rates of different ions, and their different deposition potentials. It is thus possible to deposit certain metals preferentially from a mixed solution. The cost of electrolysis at a theoretical 100% energy efficiency may be expressed as 974 V kwh per ton of iron produced from ferrous solution, where V = applied voltage. (1) This is approximately equivalent to £5 V per ton of iron produced, with electricity costing 1.25 d per kwh. (1461 V kwh per ton of iron from ferric solution). In practice, current efficiencies of 95-100% are realised. By careful design, therefore, electrolysis could be made economic. There is also the advantage of stationary ion separation which is an added "bonus".

Attempts to produce iron by electrowinning from a fused salt bath of iron chlorides, with usually alkali metal chlorides, have proved costly due to the very low current efficiency of the system. This has been found to be 29% at best, see sect. 7. The operating costs then become 3360 V kwh per ton of iron produced where V = applied voltage, which is at least double that required for aqueous electrolysis. Thus the cost of the inefficiency alone renders this method uneconomic, apart from the costly further purification required and high temperature considerations, both of which add weight to the above conclusion.

Critical discussion of the various electrolytic recovery processes may be found in (295).

12.2 Building up Worn Machine parts

This was developed by MacFadyen (257) around 1920 to meet a war need. There was not much interest in this application, however, until recently, when a considerable amount of work was done in Russia (70, 71, 73, 75-77, 79, 81, 83, 87, 90, 93, 117, 118, 129, 131, 133-135, 137, 138, 140, 141). The effect of additives for such work was also investigated (see sect. 2.3). In all cases, a soluble anode is used, and there is no recovery from solutions.

12.3 Manufacture of bank-note printing plates

One of the earliest recorded commercial applications of iron plating was the production of printing plates in Russia by Klein, (258) in 1868. 60 years later Thomas and Blum (259) reported that this method was in general use in the United States, although in a more sophisticated form; and still is (32). The iron is either used as a protective coating to prevent wear on the face; or the whole printing plate is built up by an electroforming process. (see sect. 9).

12.4 Specialist applications

There has been limited interest in the production of thin ferromagnetite films by electrolysis e.g. (260). This is stated to give superior results to thermal decomposition of carbonyls or acetylacetonates. Although iron alone has been used, iron-nickel co-deposits are usually used, which is outside the scope of this study. The crystal structure of thin iron films has been studied in detail (85).

13 Electroless Plating

Brenner (291) reports that in spite of papers and patents claiming electroless deposition of iron, he has not been able to deposit it. This process has been quite well developed for nickel, and there is no obvious reason why this should not be applied to iron also. A brief history and theory is given. Hallsworth (292) also has written a review on recent work.

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