A PRELIMINARY EVALUATION OF NEW PROCESSES FOR THE MANUFACTURE OF IRON BY WAY OF LIQUID/SOLID PHASE SYSTEMS.

Anthony Victor Bridgwater

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SUMMARY

A general selection procedure has been developed in an attempt to establish the most feasible and economic process for manufacturing a shaped iron product from an iron-bearing feedstock such as a low grade home iron ore.

The criteria used in making this selection were information availability, technical feasibility, and economics of a rudimentary nature. A computer programme based on simple compatibility rules was developed to assist in the early elimination of many of the alternatives.

As a result of this selection, six processing routes are recommended.

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1. O.S.C.A.T

O.S.C.A.T. is the acronym derived from "Ore to Steel, Chemical and Associated Techniques".

1.1 History

The O.S.C.A.T. project originated in 1964 when the Iron and Steel Board Report of 1963 (A 1) suggested that it might be profitable to look at alternative processes to the existing methods of manufacture of iron and steel. S.A. Gregory was awarded two grants for this investigation: one from the British Iron and Steel Research Association, and the other from the Science Research Council, both for a two year period initially.

1.2 Aims

Although many individual processing routes have been put forward as alternatives to the blast furnace (see sect. 8.1.10), the whole field has not been comprehensively covered in one study. It is the aim of this project to investigate all possible methods for the production of iron and steel; and from this overall picture, select the method or methods which will produce a useful product at the lowest cost.

2. METALLURGY

Any metallurgical operation of extracting metal from an ore involves three basic steps:

1)	Separation	- extracting and purifying the metal values from the gangue.
2)	Reduction	- reducing the metal compound to metal.
3)	Shaping	- Forming the metal into a useful and acceptable shape.

Although most processes have these steps in the order given above, theoretically any arrangement is possible:

a) Separation - Reduction - Shaping.

This is the most usual arrangement, for example the Iron and Steel Industry (see sect. 3.4).

b) Separation - Shaping - Reduction.

The metal compound is concentrated and purified, formed into a useful shape (e.g. as a powder), and finally reduced. This is found in the manufacture of "cermets".

c) Reduction - Separation - Shaping

The crude ore is reduced to metal; the metal values separated e.g. sponge iron magnetically; and finally shaped, by grinding to powder in the example cited above.

d) Reduction - Shaping - Separation.

A refined, or high quality ore is reduced, shaped into a required form, and the impurities separated, e.g. volatilisation of sulphur as the hydride.

e) Shaping - Reduction - Separation.

This is similar to d), where a refined or high quality ore is shaped, then reduced and finally the impurities removed, for example by distillation or sublimation.

f) Shaping - Separation - Reduction.

After shaping, the impurities are leached, distilled or thermally decomposed etc.; followed by a final reduction to the metal.

High grade ore is necessary for (d), (e) and (f), as large amounts of gangue cannot be handled. Arrangements (b), (d), (e), (f) and possibly (c) involve powder metallurgy, since an open structure is required for intimate contacting of reducing agent or for separation. It is also possible that two of these basic steps may be fused into a single step (see sect. 5.1.4). For example, reduction of an iron oxide powder to give iron powder involves both reduction and shaping - iron powder being considered a minimum useful shape.

3. INTRODUCTION

As stated in sect. 2 there are three main subjects to be investigated of which the largest is separation methods. Reduction is relatively straightforward, and shaping is being considered at a later stage of the project (see sect. 5.1.4 also).

3.1 Separation

A comprehensive list of all known separation methods was compiled from the A.S.M. Review of Metals 1959-1964. The result is summarised in Table 1. Topliss (A 2) and Gregory (A 3) compiled similar lists from other sources, which were compared with Table 1 to ensure that all known separation methods were included. The separation methods in parentheses in Table 1 are not being considered (see sect. 5.1.2).

3.2 Reduction

The reduction methods may be classified by the phases of the material to be reduced and the reducing agent respectively.

a) Solid - Gas.

this is found in conventional iron and steel making, and is well established.

b) Solid - Liquid.

ferric chloride reduced to iron powder by an aluminium alkyl compound is an example.

c) Solid - Solid.

for example iron oxide plus carbon to give

TABLE 1

(Absorption	G-L)
Adsorption	G-S, L-S
Amalgamation	L-S
Biological leaching	L-S
(Carbonylation	G-L, G-S)
Centrifugation	G-L, G-S, L-L, L-S
Chromatography	G-G, L-L
Clathration	L-S
(Condensation	G-L, G-S)
Crystallization	L-S
Cyclone	G-L, G-S, L-L, L-S, S-S
Dialysis	L-L
(Diffusion	G-G)
Distillation	G-L
Electrodialysis	L-S
Electrolysis aqueous	L-S
Electrolysis fused	L-L, L-S
Electrophoresis	L-S
Electrostatic separation	G-L, G-S, L-S, S-S
Evaporation	G-L
Filtration	G-S, L-S
Flotation	L-S
Fluidisation	G-S, L-S

TABLE 1 (Contd.)

Foam	G-L
Gravity	G-L, G-S, L-L, L-S, S-S
(Halogenation (non-aqueous)	G-G, G-L, G-S, S-S)
(Ion beam	G-G)
Ion exchange	L-L, L-S
Ion exclusion	L-S
Leaching	L-S
Magnetic separation	S-S
Organometallic	G-L, L-L, L-S,
Osmosis	L-S,
Oxidation	G-G, G-L, G-S, L-L, L-S, S-S
Precipitation chemical	G-S, L-S
Precipitation electrodeposition	L-S
Precipitation electrostatic	G-S, L-S
Reduction	G-G, G-L, G-S, L-L, L-S, S-S
Solvent extraction	L-L
(Sublimation	G-S)
Sweating	L-S
Thermal decomposition	G-S, L-S, S-S
(Volatolisation	G-G, G-L, G-S)
Zone melting	L-S

iron powder or sponge iron.

d) Liquid - Gas.

hydrogen pressure precipitation is an example (see sect. 8.2.1).

e) Liquid - Liquid.

this is found in the reaction between an aqueous solution of an iron salt and sodium borohydride giving an iron powder precipitate (see sect. 8.2.2).

f) Liquid - Solid.

iron powder is obtained by reducing ferric chloride solution with a sodium suspension (see sects. 8.2.2 and 8.2.3).

g) Gas - Gas/Liquid/Solid.

not considered, (see sect. 5.1.2).

h) Aqueous electrolysis.

i) Organic solvent electrolysis.

j) Fused salt electrolysis.

Reduction from high to low valency is not considered here. For the purpose of route selection (see sect. 5.1.3) reduction has been classified as a separation method.

3.3 Shaping

It is important to produce a "useful" iron product; i.e. one that can be used directly, without the need for further forming operations, as in the manufacture of:

a) Iron powder.

b) Electroformed articles.

c) Iron whisker crystals.

d) Conventional methods (for comparison).

Only liquid and solid phase reactions are considered above. It is possible, for example, to deposit iron by vapour plating, which is discussed elsewhere (A 2).

3.3.1 Iron powder

There is a large potential market for this, if it is available at a price comparable to iron and steel prices. The present market is of the order of 5000 tons per year, and iron powder costs about three times as much as solid steel in billet form. If the unit cost is reduced by about 50%, the market might be expected to increase at least tenfold, since there is large scope for cheap iron powder, either as such for powder metallurgy, or feedstock for precision casting. The Motor Industry is a typical market.

There is also the possibility of large scale manufacture of steel sheet by powder rolling if it is cheaper in operating costs than conventional steel sheet. Stainless steel sheet could be made by powder blending followed by rolling, or rolling followed by metal vapour diffusion.

Marketing and Shaping is outside the scope of this thesis and is to be thoroughly investigated by other members of the project (see A 4).

3.3.2 Electroforming

Apart from conventional shaping, this is the other probable major outlet of shaped iron products. The iron may be formed:

a) into useful articles directly, as either pure iron or alloy, e.g. to gauze or tubes.

b) continuously into strip; again either as pure iron or alloy.

c) into powder.

This is discussed further in sects. 8.1.6 and 8.3.

3.3.3 Iron whisker crystals

These are important on account of their very high strength which is attributed to an unbroken crystal formation. A forseeable use for these is for reinforcement of a plastic matrix, in much the same way as glass fibre is used with a resin. Iron whisker crystals, of any appreciable size, have only been grown from the vapour phase to date, although microscopic whiskers of many metals other than iron have been electrodeposited, (A 11).

3.3.4 Conventional methods

This section has been included to afford a comparison. Molten iron and steel is shaped in essentially one of two ways:

a) Casting into ingots followed by progressive rolling or forging to shapes and plate products.

b) Direct casting to shapes, followed by machining where necessary.

An important development of (a) above is continuous casting, This new steel casting technique is already successfully practised at several plants. The molten steel is directly and continuously formed into billets or slabs, which are cut into required lengths prior to rolling. It might be advantageous to develop this method to produce the final shape directly, but the mechanical properties may be poor, and therefore some degree of mechanical working would probably be required.

3.4 Conventional iron and steel making

3.4.1 Manufacturing process

As a comparison, the conventional route from iron ore to steel sheet or bar is given stepwise:

a) Comminution.

b) Pretreatment.

this depends entirely on the type and grade of ore and includes such operations as sintering and pelletising. Alternatively, it may also follow (c) below.

c) Separation.

an optional step also, depending on the grade of ore.

1) If this step follows pretreatment, the iron values may be concentrated magnetically for example.

2) If this precedes pretreatment, the iron values may be concentrated by flotation for example, or gravity concentration.

d) Reduction and melting.

iron oxides are reduced in the blast furnace by gases formed from oxidation of coke, which also supplies heat for melting. This gives a "pig-iron" containing about 94% Fe.

e) Purification.

otherwise known as steelmaking, when the undesirable impurities are removed, and possibly alloying elements added.

f) Shaping.

the molten steel is cast, and rolled into shapes or sheets. The casting and rolling are usually quite separate operations.

g) Ancillaries

the coke ovens produce coke for the blast furnace, gas which is used as a fuel, and coal tar.

3.4.2 Observations

Both economical and technical opportunities exist for alternative methods of manufacture. Some of the economic opportunities are indicated by considering the following disadvantages of the conventional process:

a) The capital cost of both iron and steel making, and the subsequent shaping operations is very high. This can exceed £100 per ton year total, for steel sheet or girders, rails etc., - shaping accounting for approximately one third of this. Further discussion is in (A 4).

b) The reducing agent (coke, indirectly) is very costly.

c) There is no heat recovery after the pretreatment step, the casting or rolling operations. A vast amount of energy in the form of heat is thus lost.

d) Iron is produced intermittently from the blast furnace, and from this point the whole process is batchwise.

e) While it is possible to treat practically all iron ores by this method, some require special pretreatment, or blast conditions; and may considerably reduce the throughput of the furnace in terms of quantity of iron made. A typical example of this kind of ore is Northants ore (see sect. 5.1.6).

3.5 Existing alternatives to the blast furnace

There are a number of these processes, all of which involve the direct reduction of iron ore to metal. The most well known of these is probably the H - Iron process., (A 5, A 6, A 7, A 8). This is the fluidised reduction of iron ore fines with hydrogen: the resulting high metallic content powder (circa 90% Fe.) being fed to the steel furnace. This use requires a high grade ore for feed as all the gangue contained in the ore is also fed to the steel furnace, which is not designed to handle large quantities of slag. Another important fluidised iron ore reduction process is ESSO'S FIOR (A 9), and there are many more such as HyL, S-L R-N, Purofer and Krupp-Renn. These are comprehensively covered by Roger (A 6), Sibakin and Fraser (A 7) and Brown (A 8).

It is important to appreciate that in all these direct reduction processes, the product is fed into the conventional iron and steel making process at an intermediate point, thus leaving the usual purification (steel making) and shaping steps still to be performed. Therefore these new processes still suffer from the same disadvantages discussed in sects. 3.4.1 and 3.4.2.

4. SELECTION PROCEDURE PRINCIPLES

The general principles of the processing route selection procedure are given below. These may be applied to any problem of selection.

It has been shown in sect. 2 that there are a large number of possible processing routes made up of combinations of separation, reduction and shaping methods. It is essential to consider all possible alternatives. These are obtained by permutation of possible processing methods from the three general classes discussed above. This operation is termed "divergence". Once these alternatives have been collated, the "undesirables" can be eliminated, firstly on a simple criterion, then progressively by more involved and detailed criteria, until only a few choices remain. This elimination procedure is "convergence". The whole operation may be depicted diagrammatically as in Figure 1 which shows how the field of study broadens then narrows.

The literature review consists of about 900 references, (see sect. 8 et seq.) which establishes the knowledge and feasibility of the various methods of separation, reduction and shaping. The next step is to fix arbitrarily the number of stages in each processing route at an upper limit. It is then possible to eliminate many of the routes obtained by permutation of the above methods on grounds of compatibility. Since the field of study at the widest point consists of over 200 million routes of six stages or less, this initial

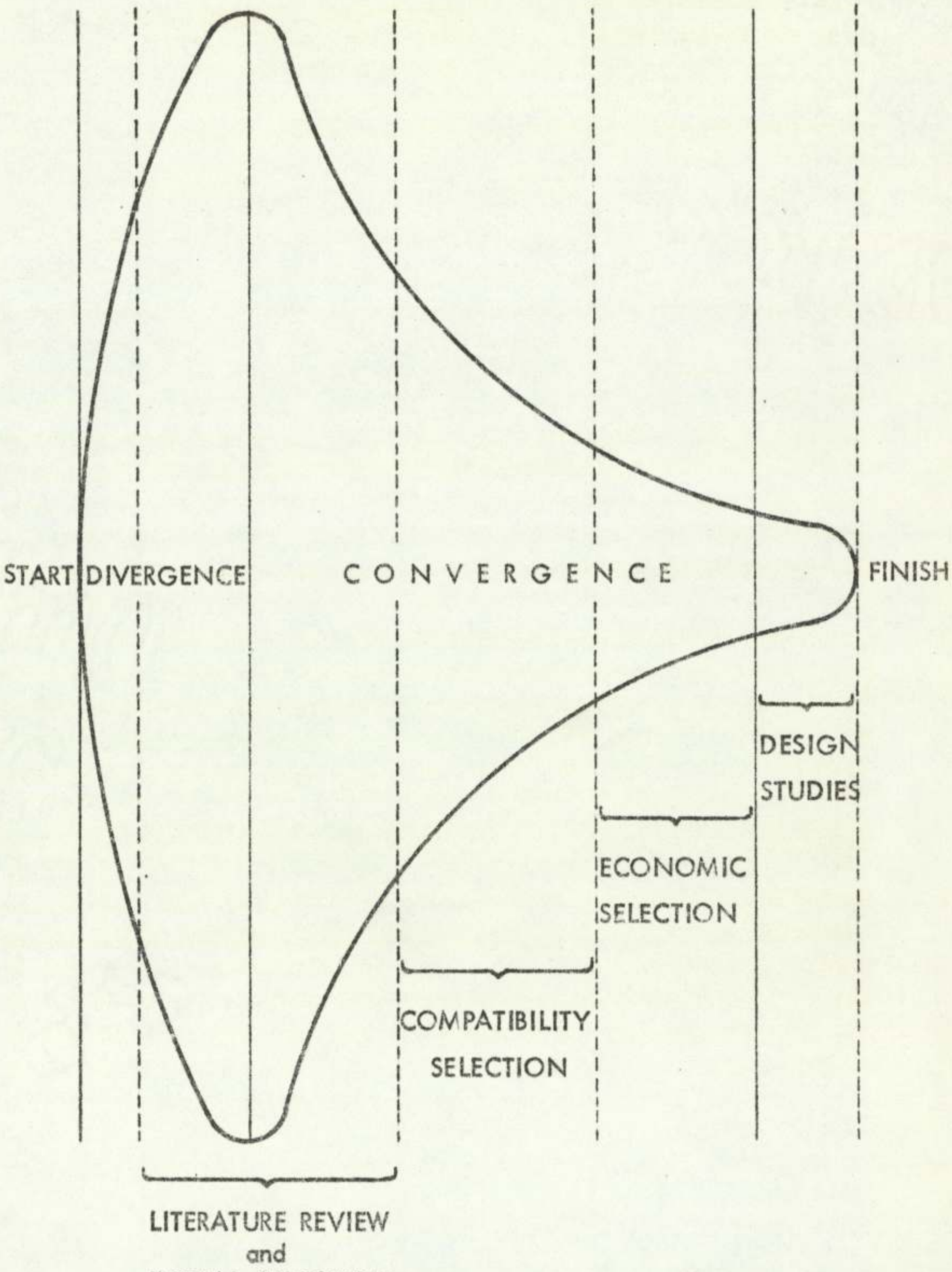
START
DIVERGENCE
CONVERGENCE
FINISH
DESIGN STUDIES
ECONOMIC SELECTION
COMPATIBILITY SELECTION
LITERATURE REVIEW and INITIAL SELECTION

Figure 1

selection may be solved by computer, based on simple rules. The closer the convergence becomes, the more detailed and complicated are the selection criteria until there are sufficiently few processing routes remaining for detailed design studies to be made.

The following section shows how the principles outlined above are applied to finding the optima processing routes from iron ore to metal.

5. SELECTION OF OPTIMA PROCESSING ROUTES

5.1 Introduction

5.1.1 Definition

A processing route is defined as a combination of separation, reduction, and shaping operations, starting with an iron bearing feedstock and finishing with a useful, pure iron product. This is discussed more fully in sect. 2.

Initially, the various separation methods of Table 1, together with reduction, were grouped together as routes in the form of a network (Figure 2), starting with iron feedstock at the top and giving metal at the bottom. It became obvious that a vast number of routes were possible, and therefore a strictly methodical approach was required, whose logic could be transferred to a computer. In order to do this, assumptions and rules must be made, which are discussed in sects. 5.1.2 - 5.1.7 below.

5.1.2 Separation methods

The separation methods tabulated in sect. 3.1 were initially classified by phases. For example solvent extraction is a liquid - liquid separation, and is denoted by "L - L". Leaching is denoted by "L - S". This is shown in Table 1 where each separation method has been classified in this way.

This dissertation covers the "wet" processing routes, which are defined as those processes in which the iron is always in a solid state; or liquid state, i.e. in solution, as fused salt or

POSSIBLE PROCESSING ROUTES

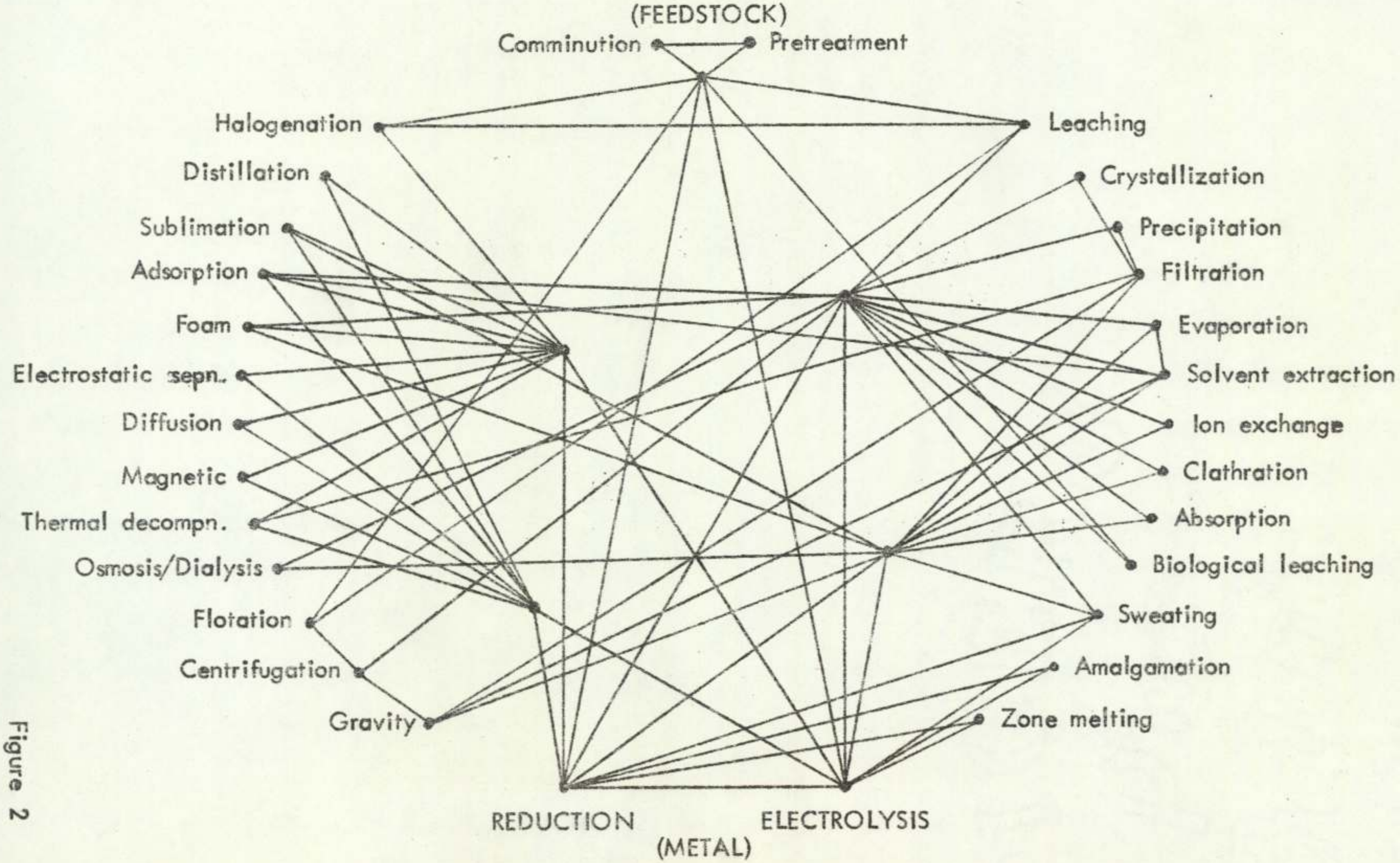

Figure 2

molten metal. Table 2 lists the separation methods which fall into this classification.

There are a number of separation methods in Table 2 which are termed "Mechanical aids" and labelled "M". These are standard mechanical (i.e. non-mass transfer) separation methods which are well documented and generally applicable (see also sect. 8.1). In some cases they may be understood to be an integral part of another separation method; for example filtration with precipitation. Filtration may also be replaced by centrifugation, cyclone, gravity settling etc., depending on circumstances. As such therefore, these methods are not considered in the following processing route planning and selection (see also sect. 5.1.5).

TABLE 2

Adsorption	
Amalgamation	
Biological Leaching	
Centrifugation	M
Chromatography	
Clathration	
Crystallisation	
Cyclone	M
Dialysis	
Distillation	
Electrodialysis	
Electrolysis Aqueous	
Electrolysis Fused	
Electrophoresis	
Electrostatic separation	M
Evaporation	
Filtration	M
Flotation	
Fluidisation	M
Foam	
Gravity	M
Ion Exchange	
Ion Exclusion	

TABLE 2 (Contd.)

Leaching		
Magnetic separation	M	
Organometallic		
Osmosis		
Oxidation		
Precipitation Chemical		
Precipitation Electrodeposition		See Electrolysis Aq.
Precipitation Electrostatic		See Electrostatic
Reduction		
Solvent Extraction		
Sweating		
Thermal Decomposition		
Zone Melting		

M: "Mechanical aid" (see sect. 5.1.2).

5.1.3 Reduction

For the purpose of route selection, reduction will be treated as a separation method. As explained in sects. 5.1.4 and 5.1.5.4, the shape of the final product will be that obtained from the reduction step; thus obviating the necessity of inclusion of shaping in route selection, as the inclusion of reduction covers this step. In the later stages of the selection, reduction may be subdivided by phases and methods (see also sect. 8.2 et seq.).

5.1.4 Shaping

The importance of producing a useful product has already been discussed (see sect. 3.3). If it were possible to carry out a shaping operation at the same time as reduction; using only operating costs and capital necessary for this reduction step, there might be an advantage. In fact electrolytic reduction is readily adapted to produce either iron powder or electroformed articles, and chemical reduction, within the limits of study, (see sect. 8.2), also invariably produces powder (this being regarded as a "minimum shape", see sect. 3.3.1). Conventional gaseous reduction, which is discussed elsewhere (A 4) may also be adapted to produce iron powder or plate in many instances, but this depends to a large extent on the pre-reduction state of the iron and the conditions of reduction.

Since one of the aims of this study is to produce a shaped iron product, the following route selection is orientated in this direction, and shaping as a distinct operation is not considered (see also A 4).

5.1.5 Assumptions and Rules

5.1.5.1 Order of working

This will be: separation,
reduction,
shaping

(see sect. 2). It is probable that the primary feedstock will be low grade ore (circa 30% Fe; see sect. 5.1.6), when it might be advantageous to separate the iron values first, before reduction and shaping, to minimise the heat, energy and plant size requirements of treating large amounts of non-iron bearing materials (gangue). Sect. 2 shows that a high grade ore is required if either reduction or shaping is the first of the three steps.

5.1.5.2 Pretreatment

The raw ore will require crushing and grinding to increase the surface area; and a prereduction or roasting operation may be necessary, but this depends on the first separation method of the processing route. The routes which are derived later are based on the assumption that one or two pretreatment steps may be necessary, such as prereduction or sintering. These have been a part of the iron and steel industry for the greater part of its history, and are thus standardised and well documented.

5.1.5.3 Impurity removal

In all of the processing routes considered, each separation method refers only to the iron bearing stream. The selection of the routes will take into account the likely impurities (see sects. 5.1.6 and 5.3.2.3), but additional purification stages will not be added until detailed investigation has proved them necessary.

5.1.5.4 Conflation

As explained in sect. 5.1.4, it is possible to perform two or more operations as one - reduction and shaping being the example cited. This is termed conflation, and if technically possible, would probably be more economic than the separate operations. Another example is pressure leaching of pyrite (see sects. 8.1.10 and 8.1.12), where the sulphur is oxidised to sulphate, which is simultaneously leached: this is conflation of leaching and oxidation. In subsequent route selection such operations are regarded as a single method.

5.1.5.5 Mechanical aids

As discussed in sect. 5.1.2, these are understood to be an integral and essential part of several separation methods; for example precipitation requires filtration. This differs from conflation in the previous paragraph, in that precipitation and filtration need not be carried out at the same time in the same apparatus.

5.1.5.6 Product

This will be pure iron (>99.0%), in a useful, i.e. shaped, form (see sects. 5.1.4 and 5.1.5.4).

5.1.5.7 Recycling

In many chemical processes, non-product reagents are frequently recycled for reuse, unless exceptionally cheap. It is anticipated that one or more recycling operations will be required in any successful processing route, but these will not be considered in the initial route selection (see sect. 5.1.5.8).

5.1.5.8 Number of stages

Each processing route is made up of a number of separation methods (including reduction). If there are 27 possible methods, complete permutation gives:

27 routes of 1 stage
729 routes of 2 stages
19,683 routes of 3 stages
531,441 routes of 4 stages
14,348,907 routes of 5 stages
387,420,489 routes of 6 stages etc.

Of course, many of these alternatives are highly improbable, if not impossible, technically; and may therefore be easily eliminated. There is strong evidence that the capital cost of a chemical plant is related to the number of individual steps involved (U 1), so, in view of the fact that neither pretreatment nor recycling steps are to be included in the initial selection, it was decided to limit arbitrarily the number of stages considered to four. As there are such a large number of alternatives, any initial selection procedure should eliminate the largest number of unlikely routes by the simplest criteria to avoid time and work wastage.

5.1.6 Feedstock

The choice of feedstock for processes is considered elsewhere (A 4). The most likely alternatives are:

a) Light scrap iron

b) Low grade siliceous iron ore as found in Northamptonshire.
A typical analysis is given in Table 3 (U 5).

5.2 Initial selection of processing routes

5.2.1 Literature selection

Since the first part of the O.S.C.A.T project is a "paper study", separation methods are eliminated on the following grounds:

a) No information in the literature on the particular method.

b) References state that the method does not work for iron separation.

c) References state that there is no forseeable application for iron separation.

The separation methods given in Table 2 are shown below with cross references to the literature review, and with comments on their suitability as an iron separation method, as indicated from the literature. This is based on technical feasibility only, and where the separation method is a primary one; i.e. concerned with the iron bearing stream (see sect. 5.1.5.3).

TABLE 3

Cottesmore Ore

Raw ore:

Fe	33.08% (weight)
H_2O	17.7%

Ore dried at 100°C

(Fe	40.1%)
FeO	0.45%
Fe_2O_3	56.08%
SiO_2	17.90%
Al_2O_3	8.05%
MnO	0.32%
CaO	1.70%
MgO	0.35%
P	0.75%
S	0.06%

Loss on ignition 12.70%

Traces V, Cu.

Adsorption: (sect. 8.1.1). Very little information and doubtful application.

Amalgamation: Does not work as iron is practically insoluble in mercury. May be used as a cathode in electrolysis (see G 1).

Biological Leaching: (sect. 8.1.2) Satisfactory. Classified as leaching.

Chromatography: (sect. 8.1.3). Not applicable

Clathration: No information.

Crystallisation: (sect. 8.1). Satisfactory.

Dialysis: (sect. 8.1.4). Very little information, and doubtful application.

Distillation: (sect. 8.1.5). Useful aid, but no application to iron separation.

Electrodialysis: (see G 1). Generic term for electrolysis through a membrane. Satisfactory (covered by Electrolysis)

Electrolysis - Aqueous: (sect. 8.1.6). Satisfactory. (see also G 1).

Electrolysis - Fused: (see G 1). Satisfactory.

Electrophoresis: (see G 1) No application.

Evaporation (to dryness): (sect. 8.1) Satisfactory.

Flotation: (sect. 8.1.7) Apart from ore dressing, very little information.

Foam: (sect. 8.1.8) Virtually no information.

Ion exchange: (sect. 8.1.9). Satisfactory.

Ion exclusion: (sect. 8.1.9). Very little information.

Leaching: (sect. 8.1.10) Satisfactory.

Organometallic compounds: (sect. 8.1.11). Very little application.

Osmosis: No information.

Oxidation: (sect. 8.1.12) Satisfactory, but with certain limitations. Conflated with leaching or precipitation, q.v.

Precipitation (chemical): (sect. 8.1.13). Satisfactory.

Reduction: (sect. 8.2) Satisfactory and essential (except for electrolysis).

Solvent extraction: (sect. 8.1.14). Satisfactory.

Sweating: No information.

Thermal decomposition: (sect. 8.1.15). Satisfactory.

Zone melting: (sect. 8.1.16) Only very small scale application. Serious technical difficulties of scale-up.

This leaves as possible separation methods:

Crystallisation

Electrolysis, aqueous and fused

Evaporation

Ion exchange

Leaching (including biological)

Precipitation

Reduction

Solvent extraction

Thermal decomposition

In many cases these are not single separation methods, but rather unit operations. Crystallisation for example includes either cooling or evaporation - evaporation as quoted in the list above as a separation method is taken as evaporation to dryness.

5.2.2 Computer selection

It is possible to eliminate unlikely processing routes by computer before the literature selection, based on all the separation methods of Table 2. This gives well over 1000 alternatives, each of which would have required inspection, with regard to the literature, for elimination. By performing the literature selection first, as in the previous paragraph, then using essentially the same computer programme, it is possible to arrive at 56 routes which are relatively easy to inspect individually.

In order to distinguish between the very different reductive systems; electrolysis is divided into aqueous and fused, and reduction into reduction of a solid phase and of a liquid phase. The possible stages then become:

Crystallisation

Electrolysis Aqueous

Electrolysis Fused

Evaporation (to dryness)

Ion exchange

Leaching

Precipitation

Reduction - L (of a liquid phase)

Reduction - S (of a solid phase)

Solvent extraction

Thermal decomposition

"Compatibility" rules have been devised for 2, 3 and 4 stage routes made up of combinations of the above 11 methods; and subject also to the assumptions and rules laid down in sect. 5.1.5.

a) As the feedstock is a solid, the first stage can only be leaching.

b) The last stage is reduction or electrolysis, and no further purification is required. This may be expressed as:

Electrolysis Aqueous cannot be followed immediately by: crystallisation, electrolysis aqueous, electrolysis fused, evaporation, ion exchange, leaching, precipitation, reduction - L, reduction - S, solvent extraction, or thermal decomposition. In other words, electrolysis aqueous cannot be followed by any other method. The same applies to electrolysis fused, reduction - L, and reduction - S.

Similar expressions may be derived for the other separation methods:

c) Crystallisation cannot be followed immediately by crystallisation, evaporation, leaching or precipitation.

d) Evaporation by: crystallisation, electrolysis aqueous, evaporation, ion exchange, precipitation, reduction - L, solvent extraction.

e) Ion exchange by: electrolysis fused, ion exchange, reduction - S, thermal decomposition.

f) Leaching by: electrolysis fused, leaching, reduction -S, thermal decomposition.

g) Precipitation by: crystallisation, evaporation, precipitation.

h) Solvent extraction by: electrolysis fused, leaching, reduction - S, solvent extraction.

i) Thermal decomposition by: crystallisation, electrolysis aqueous, evaporation, ion exchange, precipitation, reduction - L, solvent extraction.

The above "compatibility" rules are based on the phase relationship of adjacent stages, and with no repetition of any method. The programme is designed to calculate firstly 2 stage routes, then 3 stage, and finally 4 stage routes; based on the above rules. The result is printed out on the lineprinter simultaneously with the computation in the form given in Table 4. This shows the 56 routes thus obtained. The computer programme is presented in

TABLE 4

LEACHING	ELECTROLYS AQ
LEACHING	REDUCTION -L

(2)

LEACHING	CRYSTALLISATN	ELECTROLYS AQ
LEACHING	CRYSTALLISATN	ELECTROLYS FU
LEACHING	CRYSTALLISATN	REDUCTION -L
LEACHING	CRYSTALLISATN	REDUCTION -S
LEACHING	ION EXCHANGE	ELECTROLYS AQ
LEACHING	ION EXCHANGE	REDUCTION -L
LEACHING	PRECIPITATION	ELECTROLYS AQ
LEACHING	PRECIPITATION	ELECTROLYS FU
LEACHING	PRECIPITATION	REDUCTION -L
LEACHING	PRECIPITATION	REDUCTION -S
LEACHING	SOLVENT EXTRN	ELECTROLYS AQ
LEACHING	SOLVENT EXTRN	REDUCTION -L
LEACHING	EVAPORATION	ELECTROLYS FU
LEACHING	EVAPORATION	REDUCTION -S

(14)

LEACHING	CRYSTALLISATN	ION EXCHANGE	ELECTROLYS AQ
LEACHING	CRYSTALLISATN	ION EXCHANGE	REDUCTION -L
LEACHING	CRYSTALLISATN	SOLVENT EXTRN	ELECTROLYS AQ
LEACHING	CRYSTALLISATN	SOLVENT EXTRN	REDUCTION -L
LEACHING	CRYSTALLISATN	THERMAL DECMP	ELECTROLYS FU

TABLE 4 (Contd.)

LEACHING	CRYSTALLISATN	THERMAL DECMP	REDUCTION -S
LEACHING	ION EXCHANGE	CRYSTALLISATN	ELECTROLYS AQ
LEACHING	ION EXCHANGE	CRYSTALLISATN	ELECTROLYS FU
LEACHING	ION EXCHANGE	CRYSTALLISATN	REDUCTION -L
LEACHING	ION EXCHANGE	CRYSTALLISATN	REDUCTION -S
LEACHING	ION EXCHANGE	PRECIPITATION	ELECTROLYS AQ
LEACHING	ION EXCHANGE	PRECIPITATION	ELECTROLYS FU
LEACHING	ION EXCHANGE	PRECIPITATION	REDUCTION -L
LEACHING	ION EXCHANGE	PRECIPITATION	REDUCTION -S
LEACHING	ION EXCHANGE	SOLVENT EXTRN	ELECTROLYS AQ
LEACHING	ION EXCHANGE	SOLVENT EXTRN	REDUCTION -L
LEACHING	ION EXCHANGE	EVAPORATION	ELECTROLYS FU
LEACHING	ION EXCHANGE	EVAPORATION	REDUCTION -S
LEACHING	PRECIPITATION	ION EXCHANGE	ELECTROLYS AQ
LEACHING	PRECIPITATION	ION EXCHANGE	REDUCTION -L
LEACHING	PRECIPITATION	SOLVENT EXTRN	ELECTROLYS AQ
LEACHING	PRECIPITATION	SOLVENT EXTRN	REDUCTION -L
LEACHING	PRECIPITATION	THERMAL DECMP	ELECTROLYS FU
LEACHING	PRECIPITATION	THERMAL DECMP	REDUCTION -S
LEACHING	SOLVENT EXTRN	CRYSTALLISATN	ELECTROLYS AQ
LEACHING	SOLVENT EXTRN	CRYSTALLISATN	ELECTROLYS FU
LEACHING	SOLVENT EXTRN	CRYSTALLISATN	REDUCTION -L
LEACHING	SOLVENT EXTRN	CRYSTALLISATN	REDUCTION -S

TABLE 4 (Contd.)

LEACHING	SOLVENT EXTRN	ION EXCHANGE	ELECTROLYS AQ
LEACHING	SOLVENT EXTRN	ION EXCHANGE	REDUCTION -L
LEACHING	SOLVENT EXTRN	PRECIPITATION	ELECTROLYS AQ
LEACHING	SOLVENT EXTRN	PRECIPITATION	ELECTROLYS FU
LEACHING	SOLVENT EXTRN	PRECIPITATION	REDUCTION -L
LEACHING	SOLVENT EXTRN	PRECIPITATION	REDUCTION -S
LEACHING	SOLVENT EXTRN	THERMAL DECMP	ELECTROLYS FU
LEACHING	SOLVENT EXTRN	THERMAL DECMP	REDUCTION -S
LEACHING	SOLVENT EXTRN	EVAPORATION	ELECTROLYS FU
LEACHING	SOLVENT EXTRN	EVAPORATION	REDUCTION -S
LEACHING	EVAPORATION	THERMAL DECMP	ELECTROLYS FU
LEACHING	EVAPORATION	THERMAL DECMP	REDUCTION -S

(40)

TOTAL: 56 ROUTES

Appendix I.

5.2.3 Results of initial selection

Thus it has been shown how 27 separation methods may be permuted to give 551,880 theoretical processing routes of up to 4 stages (divergence); see sect. 5.1.5.8. By two relatively simple operations, using simple criteria as discussed in sect. 4, 99.99% of the total possible theoretical alternatives have been eliminated; leaving 56 likely routes (convergence).

5.3 Final selection of processing routes

5.3.1 Initial economic evaluation

Each method concerned in the 56 routes obtained from the computer selection is individually examined from an economic aspect. In order to make a selection it is necessary to fix arbitrarily a maximum operating cost per stage, including recycle, which has been set at £10 per ton of iron produced. This figure has been chosen because at any stage of operation it is substantial in relation to the value of the iron or steel product, which may be worth £30 - 80 per ton. Clearly any stage costing much more than this would have to be automatically excluded from consideration.

5.3.1.1 Crystallisation

Inherent in the unit operation of crystallisation is one of the following:

- a) evaporation
- b) cooling
- c) addition of organic solvent for "salting out"

(see also sect. 5.3.1.7).

The energy requirements for:

a) Evaporation; are dependent on the concentration and solubility of the dissolved salt.

b) Cooling; are dependent on the concentration and solubility - temperature characteristics of the system.

c) Salting-out by addition of organic solvent; are dependent on the concentration and solubility of the dissolved salt.

While all these alternatives may be both feasible and economic in principle, it is the characteristics of the iron salt concerned that determine the best method. This will depend on the leaching agent employed; so that it is necessary to consider both leaching and crystallisation together, within any limitations imposed by the choice of leaching agent (see sect. 5.3.2).

5.3.1.2 Electrolysis aqueous

The electrowinning and deposition of iron from aqueous solution has been shown to be successfully practised (see sect. 8.1.6). Recent interest has been slight, however, due to high costs. This is mainly due to expensive raw material in electroplating (pig iron costs circa £21 per ton, and steel ingot £28 per ton) and electrolysis costs; giving a product not directly useable on a large scale. The problems experienced by Eustis (see sect. 8.1.6) 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. In the electrowinning of iron, however, from the leach liquor of the envisaged feedstock (see sect. 5.1.6), it is difficult to forecast the degree of separation of iron as there is no information on the solubility of the constituent metals. 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. (see Appendix II). This is approximately equivalent to £5 V per ton of iron produced, with electricity costing 1.25d per kwh. (1461 V kwh per ton of iron from ferric solution). In practice, current efficiencies of 95-100% are realised. By careful design, this could fall within the cost limit of sect. 5.3.1. There is also the advantage of migrationary ion separation for which "credit" must be allowed.

5.3.1.3 Electrolysis fused

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 G 1). The operating costs then become 3360 V kwh per ton of iron produced (see Appendix II), 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.

5.3.1.4 Evaporation to dryness

The prime disadvantage of this method is that no separation takes place. From the final list of routes in Table 4 therefore, it is necessary for the leaching stage to be highly selective to iron dissolution to give a pure iron product on reduction, (not considering those routes otherwise eliminated). Although this might require a relatively complicated leaching stage, there is no evidence to show that this is likely to be uneconomic.

5.3.1.5 Ion exchange

The conclusions of sect. 8.1.9.5 are that ion exchange is almost certainly not economic for recovery of metals less valuable than copper from their leach liquors. These have been affirmed by two other independent authors (U 2, U 3).

5.3.1.6 Leaching

Leaching is the first stage of all the processing routes of Table 4. It is evident from sects. 8.1.2 and 8.1.10 that biological or alkaline leaching is not satisfactory for iron extraction.

Both acid leaching, and chemical roasting followed by water leaching are technically feasible, and may be made economic by suitable recycling operations. This is discussed at length in sect. 5.3.2 below.

5.3.1.7 Precipitation

There are four classifications:

a) Chemical.

b) Oxidative.

c) Physical: i.e. "salting out", see sect. 5.3.1.1.

d) Reductive: this is discussed in sect. 5.3.1.8

Chemical precipitation necessitates either total loss of reagent or reagent recycle. The former alternative is unacceptable as there are no suitable precipitating agents costing under £10 per ton; Soda ash, the cheapest alkali, costs £14 per ton or £26.5 per ton iron equivalent; and caustic soda costs £34.5 and £49.5 respectively (U 4). For reagent recycle considerations, the common insoluble iron compounds suffer from the following disadvantages: difficulty of filtration - hydroxide and sulphide; impurity introduction - sulphide and phosphate; difficulty of recycling phosphate and carbonate; cost of regeneration chemicals - hydroxide (lime for causticiser). Reagent losses and recycling problems also add considerably to the cost.

Oxidative precipitation is a successful method of removing iron from waste pickling acids (see sects. 8.1.13.1 and 8.4.2), using waste alkalis and/or aeration or oxygenation. In this study however, waste alkalis cannot be used due to purity considerations, and any chemicals used must be able to be recycled. Although additional reduction is necessary, this is not likely to seriously affect the economics of the process; except in the case of electrolysis, which does not arise in the routes considered.

5.3.1.8 Reduction - L

Reduction of iron in the liquid phase has been shown to be possible, but very uneconomic except for gaseous reductive precipitation, for example with hydrogen or carbon monoxide. However, the technical feasibility of such a process is very doubtful; and costly reagents, difficult to recycle, would also probably be required (see sect. 8.2.1). Investigations are being carried out at Imperial College, London, but so far without success. This method is therefore eliminated.

5.3.1.9 Reduction - S

The economics of reduction of solid iron compounds have been discussed and shown to be quite satisfactory (A 4).

5.3.1.10 Solvent extraction

It is shown in sect. 8.1.14 that solvent extraction is unlikely to be economic for recovery of iron from leach solutions. This is also borne out by Warner (U 2) who states that it is usual for commercial solvent extraction processes to lose between 0.2 and 2.0% of the solvent by dissolution and entrainment losses. A suitable solvent such as tributylphosphate costs about £700 per ton, in which case, the cost of solvent losses alone could exceed £50 per ton of iron produced apart from the chemicals required for stripping etc. Chapman (U 6) confirms that solvent extraction for metal recovery usually costs about £80 per ton of metal produced, which appears high on initial estimating by Chapman himself. (U 6). It is possible that solvent extraction may prove a borderline case as far as economics are concerned.

Solvent extraction would be used to separate iron from other dissolved metals in the leach solution. If selective leaching is employed (see sect. 5.3.2.3) a further separation may not be required. In any case, the first five routes of the final six (see sect. 5.3.1.12), involve crystallisation, and/or precipitation and/or electrolysis, all of which are selective and likely to be cheaper than solvent extraction. This last method is to be held "in reserve", should serious difficulties be encountered during subsequent design studies on the final selected routes.

5.3.1.11 Thermal decomposition

The cost of thermally decomposing compounds is usually relatively low, even including treatment and/or recycling of off-gases, and may easily fall within the cost limit.

5.3.1.12 Results of initial economic evaluation

Those routes containing methods found to be uneconomic in the above sections have been eliminated from Table 4, leaving a total of 6 processing routes set out in Table 5. The most important step in each case is the first, leaching stage, as all the subsequent stages are directly dependent on the products. It is significant to

TABLE 5

LEACHING	ELECTROLYSIS AQ		
LEACHING	CRYSTALLISATION	ELECTROLYSIS AQ	
LEACHING	CRYSTALLISATION	REDUCTION -S	
LEACHING	CRYSTALLISATION	THERMAL DECOMPN	REDUCTION -S
LEACHING	PRECIPITATION	THERMAL DECOMPN	REDUCTION -S
LEACHING	EVAPORATION	THERMAL DECOMPN	REDUCTION -S

to note that the Peace River process (see sect. 8.1.10.11) appears in the final list. This serves as a useful cross check on the selection criteria.

5.3.2 Examination of the leaching stage

Leaching of low grade siliceous ore (see sect. 5.1.6), may be carried out either by acid leaching, or roasting the ore with a suitable chemical to render the iron content water soluble, to be followed by water leaching.

5.3.2.1 Acid leaching

There are several hundred well known acids, from which a leaching agent may be chosen. Since it is envisaged that only large scale commercial interest will be taken in the results of this evaluation, only those acids are considered which are freely available commercially in large quantities,(see Table 6).

Acids may be eliminated from Table 6 on the following grounds:

a) Insolubility of acid in water.

b) Insolubility of iron salts of the acid in water.

c) Low reactivity.

d) Cost and/or difficulty of recovery of iron salts.

e) Cost and/or difficulty of recovery of acid for recycling (excepting electrolysis).

f) Other criteria specific to certain acids:

Maleic acid: addition of strong mineral acid

TABLE 6

	Elimination criteria					
Acetic acid		b(Fe^{+++})	c		e	
Acetylsalicylic acid	a					
Benzoic acid	a	b				
Butyric acid	a					
Carbonic acid (i.e. carbon dioxide)		b	c			
Citric acid			c		e	
Formic acid			c		e	
Fumaric acid	a					
Hydrobromic acid						
Hydrochloric acid						
Hydrofluoric acid		b				
Lactic acid		b(Fe^{++})	c		e	
Maleic acid	(a)		c		e	f
Monochloracetic acid			c		e	
Naphthenic acids	a					
Nitric acid				d		f
Oleic acid	a	b				
Phosphoric acid		b				
Phthalic acid	a					
Propionic acid			c		e	
Stearic acid	a					
Sulphuric acid		(b(Fe^{+++}))				

TABLE 6 (Contd.)

	Elimination criteria	
Sulphurous acid (i.e. sulphur dioxide)	b	f
Tartaric acid	b	

Parentheses indicate partial applicability of the criterion.

readily converts this to insoluble fumaric acid.

Nitric acid: this acts as a strong oxidising agent at economic concentrations for leaching. Only at low concentrations does nitric acid behave primarily as a mineral acid when iron recovery would be very costly.

Sulphurous acid: both sulphite and thiosulphate are formed, the latter giving rise to possible impurity introduction. Sulphurous acid is also readily oxidised to sulphuric acid, and it is uneconomic to pay about five times more for sulphur dioxide, which, as sulphurous acid, only oxidises to sulphuric acid.

The above reasons for elimination of unsuitable acids are indicated in Table 6 by the prefix letter.

The above elimination leaves the following suitable acids, with their cost on a bulk supply, 100% basis, at the time of writing (U 4).

Hydrobromic acid	50.00d/lb.
Hydrochloric acid	4.57d/lb.
Sulphuric acid	1.37d/lb.

(the price of sulphuric acid is subject to wide fluctuations due to problems of raw sulphur supplies).

If a 5% iron loss in acid equivalent is assumed arbitrarily, then the cost of the acid loss per ton of iron is:

	Ferrous salt	Ferric salt
Hydrobromic acid	£67.5	£101
Hydrochloric acid	£2.8	£4.2
Sulphuric acid	£1.12	£1.68

(see Appendix III)

Hydrobromic acid is thus eliminated.

Examination of the processing routes of Table 5 shows which acids may be used in the routes.

L. E.	HCl and	H_2SO_4
L. C. E.	HCl and	H_2SO_4
L. C. R.	HCl	
L. C. T. R.		H_2SO_4
L. C. T (as hydrolysis). R.	HCl	
L. P. T. R.		H_2SO_4
L.Ev. T. R.		H_2SO_4
L.Ev. T (as hydrolysis). R	HCl	

Key

L = Leaching.
R = Reduction of solid.
E = Electrolysis.
T = Thermal decomposition.
C = Crystallisation.
P = Oxidative precipitation.
Ev = Evaporation.

It is unlikely that any pretreatment of the ore, apart from comminution, will be required.

5.3.2.2 Water leaching of reacted ore

The chemical added to form the iron soluble compound may be either gaseous or solid:

Gaseous: sulphur dioxide (see sect. 8.1.15.2.1), chlorine or chlorinating agents (A 2).

Solid: sulphate (e.g. ammonium or sodium)
chloride (e.g. sodium) (A 2).

Excluded are those chemicals about which nothing has been found in the literature pertaining to roasting of ore, with subsequent recovery of low cost metal values. Chlorination is discussed in detail in (A 2), where iron is separated and recovered by subliming the chloride. It is possible to alter the conditions such that the chloride is not sublimed. Little work has been carried out on sulphation of iron ores however, either by gaseous or solid reagents. As in acid leaching, the result is an aqueous solution of iron chloride or sulphate. In order to ensure that the iron salts do not hydrolyse in neutral solution, slightly acid solutions would be used.

5.3.2.3 Separation of feedstock impurities

The probable feedstock (see sect. 5.1.6) contains Fe, Si, Al, Ca, P, Mg, Mn, in descending order of quantity, all present as oxides. It is impossible to forecast the action of either final acid on the ore without actual tests, except that most of the metal present will be dissolved to a substantial extent. Thus with acid leaching, the impurity elements have to be removed in one of the post - leaching operations.

In the case of water leaching of roasted ore, both chlorides and sulphates of the different metals present in the ore, form and decompose at different temperatures and a separation may thereby be effected. Advantage may be taken of the fact that ferrous sulphate decomposes at a lower temperature than any of the other metal sulphates; and also ferric chloride forms at a lower temperature than any of the other metal chlorides, although separation in this case may not be complete.

Iron may be selectively leached therefore in several ways. Ore may, for example, be sulphated with sulphur dioxide at 600°C, when ferrous sulphate has decomposed to the oxide but the other metals remain in sulphate form. These sulphates may be water leached, leaving insoluble silica and calcium sulphate, and iron oxides which may then be leached with sulphuric or hydrochloric acid. Another example is the formation of iron chlorides which may be water leached, leaving other metals behind as oxides. There is more information on this latter system than the sulphation described previously. In either sulphation or chlorination, gaseous reaction provides better contact and easier recycle. Also there is much more information in the literature on gaseous reaction than solid reaction. Therefore only gaseous chemical treatment is considered.

6. CONCLUSIONS

By examining the pertinent literature and economics of the relevant process stages, six processing routes have been selected as possible methods for the manufacture of a pure, shaped iron product from iron ore. These are given in Table 5. The first stage in each case is leaching, and four leaching methods are proposed: acid leaching using hydrochloric acid or sulphuric acid; or neutral, partially selective leaching with water after gaseous chlorination or sulphation.

7. FUTURE WORK

The future programme recommended for the O.S.C.A.T. project is to carry out design studies on the six processing routes named earlier, based on commercial processes to manufacture 5,000, 50,000 and 500,000 tons of iron per year. These rates were arrived at by simple market considerations (U 5). Design studies are required to forecast all the areas where subsequent experimentation is to be applied, although it will be very difficult to make accurate estimates of the proportion of each element that dissolves in the leaching stage and the quantity of leaching reagent lost, both of which affect the subsequent process steps.

It is recommended that the second part of the O.S.C.A.T. project, which follows the design studies, should follow two lines of investigation:

a) Practical experiments following the routes selected in this dissertation to produce metallic iron.

b) Theoretical studies to determine process and design parameters necessary for final large scale plant design. The information obtained may be used to modify the earlier designs.

8. LITERATURE REVIEW

The literature review has been arranged into four sections:

a) Separation methods.

b) Reduction methods.

c) Shaping methods.

d) Established processes.

The first three sections follow the procedures specified in sects. 3.1, 3.2, and 3.3 respectively; while the last section covers processing routes - i.e. combinations of the above - which have been postulated or practised.

8.1 Separation methods

The methods considered are given in Table 2 (see sect. 5.1.2). There are however some methods pertaining to the separation of iron and its compounds for which no references could be found, and which do not appear to have any future application. These are:

a) Amalgamation (except in electrolysis).

b) Clathration.

c) Electrostatic separation (except as a "Mechanical aid": see below and sect. 5.1.2).

d) Osmosis.

e) Sweating.

There are also some methods which are standard chemical engineering operations, well covered in the standard references e.g. (A 10). These are:

a) Crystallisation.

b) Evaporation.

and also what are termed "Mechanical aids" (see sect. 5.1.2) which include:

c) Centrifugation.

d) Cyclone.

e) Electrostatic separation.

f) Filtration.

g) Gravity.

h) Magnetic.

There is still one more separation method which may be described as an "aid" but which is not, in fact, a separation method, This is fluidisation. It is a universal processing aid that can be applied to many operations, e.g. iron ore reduction (see sect. 3.5). Where fluidisation arises, it will be discussed in the appropriate subsection.

Most of the following separation methods are chemical engineering unit operations; and the general theories and applications are well covered in standard textbooks. The following references only apply to the separation of an iron compound, where applicable, and only cover liquid and solid phase separations (see sect. 5.1.2).

8.1.1 Adsorption (from the liquid phase)

The principles and theories of adsorption are covered by

Perry (B 1), Monet (B 2), and Mantell (B 3). Although no single theory has been postulated, Stuart and Coull (B 4) derived equations for predicting selective adsorption from the liquid phase Jones and Stuart (B 5) continued this work proving the validity of the equations for many organic systems. Their work, unfortunately, did not extend to inorganic solutes. In a review paper, Barry (B 6) cites many commercial examples of liquid separation, but again with no mention of inorganic solute separation.

Vargha (B 7) investigated the adsorption of ferric chloride in trace quantities on Hungarian bentonites (activated clays) in the natural state, but formed no conclusions on the mechanism of adsorption. However Martynov (B 8) showed that the adsorption of aluminium, ferric and copper chlorides on silica gel from silicon tetrachloride solution was physical adsorption, by calculating the heats of adsorption. This, in fact, is the only reference to the separation of inorganic compounds by physical adsorption as opposed to ion exchange.

Other references to the adsorption of iron include Scallet's (B 9) work on the corrosion of iron in corn syrup liquor, in the presence of activated charcoal. He found that the corrosion effect of the metal - semimetal couple was offset by adsorption of iron on to the activated charcoal. The adsorption of iron (Fe^{59}) on to copper, aluminium, stainless steel, and glass was measured by Herczynska (B 10) for instrument accuracy measurements, and the adsorption of iron onto cellulose as a discolouration in paper making was investigated by Pozin and Yur'ev (B 11). These last three references are only of academic interest as the separation of iron is not investigated, only the mechanism of its adsorption.

8.1.2 Biological leaching

8.1.2.1 Introduction

A large number of elements have been shown to be biologically affected with regard to availability, solubility or oxidation state. These are K, Mn, Se, Te, As, Zn, Ca, Mg, Al, Mo, Fe, Cu, S, and halogens (C 1). Butler and Postgate (C 3) include hydrogen, oxygen and "most elements of biological importance". The bacteria that are most important in this field are those that obtain their energy by oxidising inorganic compounds, obtaining the carbon for the cell structure from carbon dioxide. There are a large number of organisms responsible for these biological reactions, details of which go far beyond the scope of this dissertation. Full information on the biological processes involved may be found in suitable references (C 1, C 2, C 4 - C 7).

8.1.2.2 Historical

One of the earliest isolations of an iron oxidising microorganism was reported by Winogradsky (C 8) in 1888. Waksman (C 9), 34 years later, undertook the first serious experiments on the oxidation of sulphur and sulphides to sulphuric acid. There was an investigation by Beckwith and Bovard (C 10) into the disintegration of sulphur - containing sealing compound in pipe joints, and by Beckwith (C 11) into the corrosion of iron by bacterial oxidation of sulphides; but it was not until around 1950 that any real interest in the field of inorganic microbiology arose.

8.1.2.3 Developments

There has long been a problem of acid mine-waste water polluting streams, particularly in the U.S.A. Colmer and Hinkle (C 12) investigated this, coming to the conclusion that micro-organisms were mainly responsible for oxidising sulphur and sulphides to sulphuric acid and acid sulphates, together with some help from atmospheric oxidation. They also reviewed previous work on this subject. This was further investigated extensively by Leather et al.(C 13 - C 17); but it was not until 1954 that Bryner et al. (C 18) applied this bacterial oxidation of sulphide to extracting iron and copper, and proved that it was possible. They performed valuable experiments on pyrite (empirical formula FeS_2), chalcopyrite (empirical formula $CuFeS_2$), and copper sulphide in natural and synthetic form. The mechanism was thought to be oxidation of lower valent sulphur to sulphate. Bryner and Anderson (C 19) then tried this out on molybdenite (MoS_2) with partial success; addition of pyrite increasing the yield approximately 50%.

The bacteria responsible for these oxidations were the cause of an investigation by Bryner and Jameson (C 20) who conclusively identified them as Thiobacillus ferro-oxidons (genus

Thiobacillus; oxidation of ferrous to ferric iron), and Thiobacillus thio-oxidans (same genus; oxidation of sulphur to thiosulphate to sulphate), although this latter organism was the subject of one of the earlier inconclusive papers by Leather et al. (C 13).

Due to considerable interest in this field several workers investigated the reaction parameters and mode of attack, (C 21 - C 25). The general conclusions reached were:

a) the sulphur is oxidised by the bacteria to sulphuric acid.

b) the metal (copper and/or iron) sulphide is oxidised bacterially to the metal sulphate.

c) the acid from (a) attacks the metal sulphide to give the sulphate.

d) the ferrous sulphate is oxidised to ferric sulphate.

e) the ferric sulphate dissolves the metal (e.g. copper) sulphide to give metal sulphate and ferrous sulphate which then recycles to (d).

The latter two mechanisms explain the increased yield of molybdenum in the presence of pyrite, as stated above (C 19). Ito et al. (C 26) also arrived at similar conclusions as to the mechanism. Biologically orientated studies have been performed on the bacteria responsible for these reactions (C 31 - C 33).

Therefore metallurgical extraction using bacteria is not straightforward. Biological reactions, chemical reactions and atmospheric oxidation all contribute to the leaching effect, and the complete mechanism has still not been worked out, or the proportion of reaction attributable to the bacteria.

A series of articles by Sutton and Corrick on biological leaching of sulphide minerals first outline the field (C 28) then consider the application of individual bacteria to leaching specific non-ferrous ores (C 29, C 30).

8.1.2.4 Yields and Conclusions

The rate of reaction is very slow: Bryner et al. C 18) released only 2.8% of the copper from one chalcopyrite sample in 70 days, and 6.6% from another in 56 days; and Malouf and Prater(C 27) leached 50% of the copper in chalcopyrite in 170 days with a maximum of 60% in 470 days. Many similar examples are given in the literature (C 13, C 19 - C 23), which, as Duncan et al. (C 23) point out, limits the practical application of microbiological leaching due to the unreasonably long leach time and poor yield.

However, two patents have been taken out. The first by Simon Carves (C 34) uses the sulphur oxidising and iron oxidising bacteria to regenerate alumina catalysts, and the second by Zimmerley et al. (C 35) utilises a cyclic leaching process with ferric sulphate as the solvent, using iron oxidising bacteria to regenerate the ferric iron after leaching. No examples were cited, and only a few results given which might indicate only limited success.

There is no evidence of serious industrial interest in employing this form of leaching in extractive metallurgy.

8.1.3 Chromatography

Chromatography is the very small scale application of adsorption and ion exchange, and by definition therefore, is of no practical use. Lederer and Lederer (D 1) cover the whole field of chromatography very comprehensively with 3814 references, including at least 38 on the identification of iron. The field of paper chromatography is very well covered by Hais and Macek (D 2) again with a considerable number of references on iron separation. Other references include Zechmeister and Cholnoky's book, (D 3); and Savidan (D 4) who includes a section on chromatography in mineral chemistry.

The field of continuous preparative chromatography may be of more interest, but again is only practised on a very small scale. Large scale application is found in sect. 8.1.9.6.

8.1.4 Dialysis

Lane and Riggle (E 1) performed experiments with a wide range of membranes, and solutes including the chlorides of hydrogen, sodium, potassium, lithium, magnesium, calcium and barium. Equations were derived for dialysis on a general basis which appeared to agree with all their experimental results. The authors point out however, that dialysis is usually used to separate a colloid from an electrolyte, and only mention the possibility of separating different sized molecules. This latter idea was the subject of a not very successful (processwise) patent by Signer (E 2) employing dialysis and evaporation to separate and purify one constituent from a mixture. The lack of success may be attributed to the high capital and running costs of handling very large quantities of liquid.

Chamberlin and Vromen (E 3) were quick to point out the possibilities of using dialysis in the acid extraction of metals. Only a mention of this being practised is made - the separation of nickel sulphate from sulphuric acid, (no reference given). They state that mineral recoveries up to 90% can be achieved; and data on several ions are presented, but with no mention of iron. Vromen's paper (E 4) of three years later again mentions many interesting metallurgical possibilities, but again nothing materialised in spite of great enthusiasm, and an advanced theory and design equations.

Fundamental studies into the separation of metal ions including iron were carried out by Kamii et al. (E 5) from tartaric acid solution, and Kumar and Bhattacharya (E 6) from chloride solution. There is no suggestion of industrial utilisation in either paper.

8.1.5 Distillation and allied operations

Gaseous treatment and handling of iron is discussed elsewhere (A 2), and this review only considers the removal of reagents or undesirable impurities from iron and its compounds, all of which is subsidiary to the separation of iron.

Some work has been performed on leaching ores with solutions of acid gases (see also sect. 8.1.10.1) Bogatsky (F 1) investigated the use of an aqueous solution of sulphur dioxide to leach nickel and cobalt ores, and Fox et al. (F 2) developed the nitrogen dioxide leaching of manganese ores to a semi pilot plant scale, based on previous work by Dean et al. (F 3). The gases are recovered for recycling by stripping, and thermal decomposition. No similar work has been performed on iron ores, but this is investigated later in this dissertation (see sects. 8.1.10.1.1/2 and 5.3.2.2).

In the treatment of spent pickling liquor, ferrous sulphate may be precipitated by adding a miscible organic solvent, e.g. acetone, separating the precipitated salt, and recovering the solvent from the regenerated acid by distillation (F 4, F 5, F 6).

There has been a considerable amount of work on the electrodeposition of iron onto a mercury cathode (G 1). Iron powder is obtained from the resulting amalgam by distilling off the mercury (F 7, F 8, F 9). The powder thus obtained is claimed to be far superior to that made in any other way (F 8).

A freeze-drying technique for making ultra fine metal powder was proposed by Landsberg and Campbell (F 10), who successfully prepared tungsten and tungsten-rhenium alloy powders.

A considerable amount of work has also been done on the removal of impurities in molten steel by distillation (F 11, F 12). The commercial interest in this form of purification is limited due to the relatively high cost. Interest has increased recently in the plasma field:- ultra-high temperatures. Goldberger (F 13) discusses this in relation to separation and purification.

There is, thus, wide application of these vapourising operations in the separation and extraction of iron.

8.1.6 Electrolysis

A complete summary of references (circa 300) on the electrolysis of iron has been written (G 1). This includes the theory and practice of electrodepositing from aqueous, non aqueous and fused-salt baths, and related phenomena.

Of particular interest are those references which deal with the electrowinning of iron, especially from leach liquors. Palmaer and Brinell (G 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 (G 3) and introduced commercially (G 4 - G 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 (G 4 - G 8), which may be due to a much earlier patent by Siemens (G 21), 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 considerable trouble; and, together with the doubtful economics of the process, 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 Eustic (G 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. (G 10), and Aravamuthan (G 11) also mentions a ferric chloride leaching of pyrrhotite and electrolysis process, but with no details.

Other processes for acid-leaching iron oxide ores, followed by electrolysis have been put forward (G 12 - G 14) but not practised. Iron has also been removed electrolytically from leach liquors of mixed ores: chromium - iron (G 15, G 16); titanium - iron (G 17 - G 19); and nickel matte (G 20). In these examples, iron is the undesirable impurity

8.1.7 Flotation

Flotation has long been a major ore - dressing technique. The literature on this is very extensive for general principles, and specific applications (e.g. H 1 - H 4). This aspect will not be discussed further, only those references in which a manufactured iron compound is selectively removed by flotation are considered.

Separation of metal salts in solution by ionic flotation is a recent interesting development in which high efficiency extraction, and recovery of surface active agent are claimed by Poltoranina et al. (H 5). Jangg (H 6) separated the residues after alkaline pressure leaching of pyrite by flotation; and Chumachenko and Kiselev (H 7) first roasted their pyrite, leached the copper and zinc, and floated the iron cakes, obtaining better than 90% extraction.

However, the surfactants necessary for successful flotation are expensive, and difficult to recover, which renders this separation method unattractive for commercial exploitation and investigation; as shown by the dearth of literature.

8.1.8 Foam

Most work on foam fractionation has been carried out on sewage purification. A very recent paper on this subject by Brunner and Stephan (I 1) only quotes three references. The results of experiments and design data are given by Brunner and Stephan, and although their work applies to surface active solute removal from sewage; the possibility of selectively extracting iron as a chelate or clathrate complex remains. Such a process would probably prove expensive, however, unless a simple and cheap suitable iron compound could be found, where the complexing agent is recycled.

A development of foam fractionation by Lemlich (I 2) is called "bubble fractionation" in which the active constituent is adsorped onto the surface of the bubble, which rises, and hence

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concentrates the solute. This suffers from the same limitations as foam fractionation.

8.1.9 Ion exchange

The principles of ion exchange are well covered in standard textbooks such as Mantell (J 1), Nachod and Schubert (J 2), and Perry (J 3). An annual review is published (J 4) giving details of activity in this field, although there is no mention of iron separation in either of the references cited under (J 4). Ion exchange may be conveniently divided into six sections for the purpose of reviewing.

a) Solid Anion exchange) Fundamental and analytical
)
b) Solid Cation exchange) interests.
c) Liquid ion exchange
d) Commercial operation - practice and potential.
e) Economics
f) Related topics

A comprehensive list of ion exchange materials is given by Perry. (J 3).

8.1.9.1 Solid anion exchange

A number of authors have reported the separation of heavy metal complex ions by ion exchange. D'Amore and Curro (J 5) indicate how Fe^{+++} in a lactate complex may be separated from solutions containing other metal ions (i.e. Cu, Mn, Co, Zn, Cd.). Pitstick (J 6) investigated the tartaric acid complexes along similar lines. Both Anders (J 7), and Reents and Kahler (J 8) report on the removal of iron as the $FeCl_4$ - complex ion from spent hydrochloric acid pickling liquor, based on original work by Kraus and Moore (J 9). The potential separation of the heavy metal ions of Ti, Cr, Mn, Fe, Co, Ni and Cu from hydrochloric acid solution was investigated by Tsitovich (J 10), and Suvorovskaya (J 11) partially separated complex chloride ions of copper and iron from aluminium chloride solution, by exchange on a synthetic petroleum tar. The separation and concentration of impurity iron cyanide complexes is reported by Mindler (J 12) and Sussman et al. (J 13). With the exception of the work on pickle liquor regeneration, there appears to have been no unified approach to this subject.

8.1.9.2 Solid cation exchange

Dolmatov (J 14) investigated the removal of impurity iron in substantial quantities from titanium sulphate solutions. The separation of a number of metal cations including Fe^{++} and Fe^{+++} was investigated by both Emel'yanov and Tarkov'skaya (J 15), and Rosset (J 16), who both state that the cation must be exchanged for H^+, otherwise the metal hydroxide is precipitated on to the resin. Tsitovich (J 10) compares the effect of several resins on a number of metal ions including Ti, Cr, Mn, Fe, Co, Ni and Cu, but reached no conclusions on preferential separation of iron. Ferrous and ferric sulphates were separated by Marti and Herrero (J 17); and Potter and Moresby (J 18) developed an ion exchange technique for estimating copper and iron at concentrations down to 0.0001 ppm.

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As concluded in the previous section also, there is very little interest in separating iron by ion exchange. This is no doubt due in part to the cost (see sect. 8.1.9.5), but also because most work has been on recovery of those metals which are difficult to extract by any other method.

8.1.9.3 Liquid ion exchange

Agers and House (J 19) discuss amine liquid ion exchange generally in terms of operation and economics. A basic study of the extraction of several metals in acid solution, including iron, with a liquid ion exchanger was carried out by both Abe and Yazawa (J 20) and Ishimori et al.(J 21, J 22), who compare the ease of extraction of the different metal ions. The removal of iron and nickel as impurities in the purification of uranium with organic phosphorus esters was investigated by Gianotti (J 23). None of the references give any indication of commercial application. Other references on liquid ion exchange may be found in sect. 8.1.14, solvent extraction, when the mechanism of extraction is not made clear in the reference.

8.1.9.4 Commercial application

One of the main reasons for the lack of interest in ion exchange in ferrous metallurgy is the high cost. This is discussed in the next section. Many references also point out that ion exchange is ideal for removing impurities in low concentration from process streams (e.g. water demineralization), but when it comes to handling solutions of greater concentration than 0.5% (5000ppm) ion exchange is not economical (J 1, J 8, J 12,)

In spite of these assertions, Dolmatov (J 14) considered removing iron from titanium sulphate solution, and Poliskin (J 24, J 25) devised an involved process for recovering waste pickle acids by adsorbing the iron onto resin, recovering it as the nitrate on elution with nitric acid, then thermally decomposing the nitrate to give iron oxide and recycled nitric acid. Another process for the regeneration of spent pickle liquor was patented by Horton and Serfass (J 26) in which iron is taken up by the resin, which is regenerated when fully loaded by immersion in sulphuric acid. The iron free resin floats and $FeSO_4.H_2O$ precipitates and sinks. It is not known whether any one of these methods is, in fact, practised.

8.1.9.5 Economics

Dasher et al. (J 27) point out in their paper on uranium separation, that even using cheaper resins, higher loadings and increased sorption rates, the cost per pound of metal recovered is not likely to fall below £65 - 93/ton (in 1957). They summarise by saying that the use of ion exchange to recover metals less valuable than copper from their leach solutions would probably not be economical. Anderson (J 28) does not entirely agree, pointing out that their prediction is only valid if the complete cycle of processing used by Dasher is followed. However, Everest and Wells (J 29) support Dasher's ideas; saying that aluminium; zinc and magnesium are not likely to be recovered economically from leach liquors derived from ores. (These metals are worth approximately £200, £100, and £300 per ton respectively). Everest and Wells base their figures on uranium production like Dasher, although derived in a different way. Hatch et al. (J 30) also state that the costs of regenerative chemicals become very important where large concentrations of ions are to be removed, and prove prohibitively high for many applications.

8.1.9.6 Related topics

Hatch and Dillon (J 31) give the name "Acid Retardation" to the separation of strong acid from its metal salt, by absorbing the acid into an ion exchange resin. The separation of iron chlorides from spent pickle liquor to regenerate the acid was investigated in some detail, the operation resembling large scale chromatography. The authors however, come to the conclusion that the method is not economic for regenerating pickle liquors on account of the low cost or value of materials processed. Nelson and Kraus (J 32) performed similar investigations in separating hydrochloric acid from lithium and magnesium chlorides.

"Ion Retardation" is a similar process; except that ions of metals may be separated by preferential absorption into a modified ion exchange resin known as a "snake cage polyelectrolyte". A description is given by Hatch, Dillon and Smith (J 30). The economics of ion retardation are said to be similar to those for ion exchange, except that chemical regeneration costs are sometimes reduced.

These snake cage polyelectrolytes have also been used to separate polar and non-polar mixtures, which was investigated by Hatch and Smith (J 33). A similar separation is also performed by "Ion Exclusion" methods, as described by Bauman et al. (J 34). The non-ionic materials are less excluded from inside the resin particle than are ionic solutes. No work has been carried out on specific metal separation by either "Ion Retardation" or "Ion Exclusion"; and there is insufficient evidence so far that the latter has any potential usefulness.

8.1.10 Leaching

There has been very little work performed on hydrometallurgy, solely for the production of iron. Since many non-ferrous ores contain a large percentage of iron, hydrometallurgical processing of these ores involves the treatment of the iron present; either to discard it as an unwanted impurity (possibly for conventional processing), or to recover it as a "valuable" by product. Irrespective of the purpose of separating the iron, the processes may be divided into:

a) Acid leaching.
b) Alkaline leaching.
c) Neutral leaching.
d) Biological leaching which is discussed in sect. 8.1.2.
e) Oxidative leaching which is discussed in sect. 8.1.12.

A large number of practical references have been included, while those of lesser importance are tabulated. The theory and operation of standard leaching operations may be found in standard textbooks.

8.1.10.1 Acid leaching

8.1.10.1.1 Sole production of iron

One of the most recent developments in the manufacture of iron is the "Peace River Project" based upon the Alberta Research Council process: low grade iron ore is leached with hydrochloric acid, the ferrous chloride purified by crystallization and iron powder produced by reduction of the dried crystals with hydrogen, the hydrogen chloride being recycled, Gravenor, Govett and Rigg describe, (K 1) and have patented (K 2) this process. Similar schemes are suggested by Primavesi (K 3) where the ferrous chloride is hydrolysed to oxide for reduction; and Francis (Q 46) who obtains ferrous sulphate from the chloride, which is heated to give the oxide. Reeve (K 4) suggests leaching low grade ore with hydrochloric acid. He did not pursue this, although a patent was taken out (N 36). The process is similar to that of Primavesi. The Eustis process, described in sect. 8.1.6, was patented (G 3) as a hydrochloric and/or sulphuric acid leach, followed by electrolysis to iron; although the commercial application leached sulphide ore with neutral ferric chloride solution, followed by electrolysis. Rao et al. (G 12) suggested a process similar to Eustis' patent, but without putting it into practice. The production of electrolytic iron as a by-product from titanium ore by sulphuric acid leaching was patented by Nakazawa et al. (G 19), and from nickel matte by hydrochloric acid leaching is described by Kryukova (G 20). "Red mud" from the aluminium industry is mostly iron oxide, which may be purified by acid or alkali leaching, then reduced to iron powder (K 5). Iron oxides are also prepared from natural sulphides by acid leaching and precipitation by alkali (K 29, Q 48, Q 59), which must be very costly.

8.1.10.1.2 Non-ferrous metal production - iron dissolved

Iron is present as an impurity in many ores and may either be dissolved prior to processing the other metal values, dissolved along with the other metal values and rejected later, or left as solid while the metal values are leached. This latter alternative is discussed in the next section. All the alternatives are important as they give indications of the conditions necessary for successful leaching of iron from a low grade ore, such as will probably be used as feedstock in this project. (see sect. 5.1.6).

Iron may be selectively leached from other ores only in special circumstances, depending on the non-ferrous metal, acid, and physical conditions. This has been applied to the concentration of chromium ores using sulphuric acid (K 6, K 7) or sulphurous acid (K 6, K 8); to the upgrading of complex ores (K 9 - K 12, K 35); processing iron residues from the aluminium industry (K 13); and removing iron from titania (G 19, K 14 - K 23). The latter application is interesting due to the wide variety of conditions employed; and also because preferential dissolution of iron and titanium is claimed under similar conditions (K 24 - K 28, P 61). These conditions are summarised in Table 7 for comparison. Titania is relatively insoluble in hydrochloric acid (K 14, K 15, K 17, K 21 - K 23), except for the extreme conditions of (K 28), see Table 7; and soluble only in concentrated (90%) sulphuric acid (K 18 - K 21, K 25 - K 27). The ore is often prereduced (K 16, K 17, K 19), or roasted (K 18, K 20), to render the iron values more soluble. It is important to note that the iron content is readily soluble in medium strength mineral acids, even without pretreatment.

The hydrometallurgical treatment of mixed ores to recover all the metal values covers a wide range of metals. The references are conveniently summarised in Table 8. In all cases the iron is recovered from the leach liquor by precipitation. It is seen that iron is only soluble in dilute mineral acids after some method of pretreatment; and is generally one of the most soluble metallic elements.

8.1.10.1.3 Ferrous and non-ferrous metal production - iron not dissolved.

The following references describe processes to produce a purified iron ore for conventional iron - making, as well as valuable non-ferrous metal solutions in some cases. These are summarised in Table 9.

TABLE 7

Acid	Strength	Iron Dissolved	Titanium Dissolved	Temp. °C	Pressure Atm.	Reference
HCl	20%	Yes	No	Boil	-	K 14
HCl	20%	Yes	No	220	13.3	K 15
HNO_3	20-40%	Yes	No	Cold	-	K 16
HCl	-	Yes	No	-	-	K 17
H_2SO_4	Dilute	Yes	No	100-120	Yes	K 18
H_2SO_4	-	Yes	No	-	-	K 19
H_2SO_4	Various	Yes	No	Various	-	K 20
HCl	-	Yes	No	-	-	K 21
H_2SO_4	95%	-	Yes	-	-	K 21
HCl	Conc.	Yes	No	175-300	35	K 22
HCl	Conc.	Yes	No	-	-	K 23
H_2SO_4	75%	Yes	Yes	140-150	Yes	K 24
H_2SO_4	Conc.	Yes	Yes	High	-	K 25, K 26
H_2SO_4	91-98%	Yes	Yes	150-200	Yes	K 27
HCl	32%	Yes	Yes	95	-	K 28
HCl	-	Yes	Yes	60-75	-	P 61

TABLE 8

Metals dissolved	Acid	Strength	Pretreatment	Temp. ^{o}C	Pressure Atm.	Ref.
Fe,Ni,Co	HCl	Various	No	Various	No	G 20
Fe,Mn	HCl	Conc.	No	-	-	K 30
Fe,Ni	HCl	Dilute	Yes	-	-	K 31
Fe,ni	HCl	Various	-	Various	-	K 32
Fe,Pb,Zn	HCl/H_2SO_4	Dilute	Yes	100	-	K 33
Fe,Ni	H_2SO_4	Various	-	Various	-	K 32
Fe,As,Bi,Co,Cu,Ni	H_2SO_4	Dilute	No	-	-	K 34
Fe,Co,Cu	H_2SO_4	V.Dilute	Yes	60-70	No	(K 36 (K 37
Fe,Co,Cu	H_2SO_4	-	-	High	High	K 38
Fe,Mn,P	H_2SO_4	-	Yes	-	No	K 39
Fe,Ni	H_2SO_4/NaCl	Dilute	Yes	-	-	K 40
Fe,Zn	H_2SO_4	-	No	Low	-	K 41
Fe,Zn	H_2SO_4	Conc.	No	High	-	K 42
Fe,Mn	spent pickle liquor	-	Yes	Various	-	K 43
Fe,Ni	HNO_3	Various	-	Various	-	K 32
Fe,Cr,Ni	H_2SO_4	0.5-3.0%	Yes	-	No	K 44
Fe,Cu	unspecified	Various	No	High	Yes	K 45
Fe,Cd,Co,Ni,Pb,Zn	unspecified	-	-	-	No	K 46
Fe,Ag,Au,Cu,Pb,Zn	unspecified	-	Yes	-	No	K 47
Fe,Al,Cr,Ni	HNO_3	-	No	90-150	Yes	M 27
Fe,Ni,Co	unspecified	Dilute	Yes	-	-	M 37
Fe,Ni,Co	H_2SO_4	Dilute	Yes	-	No	M 38

TABLE 8 (Contd.)

Metals dissolved	Acid	Strength	Pretreatment	Temp. °C	Pressure Atm.	Ref.
Fe, Cd, Cu, Pb, Zn	HNO_3	-	No	Low	-	M 44
Fe, Cd, Cu, Pb, Zn	H_2SO_4	-	No	Low	-	M 44
Fe, Al, Co, Mg, Ni	HCl	30%	Yes	90	-	N 22
Fe, Co, Ni	H_2SO_4	-	No	250-300	26-40	N 28
Fe, Co, Mg, Ni	H_2SO_4	25-50%	No	High	-	Q 47

TABLE 9

Metals dissolved	Acid	Strength	Pretreatment	Temp. °C	Pressure	Reference
Ni, Co	H_2SO_4	-	Yes	240	Yes	K 48, K 49
Al, Ni, Co	HNO_3	30%	No	100	No	K 50
As	H_2SO_4	Dilute	Yes	-	-	K 51
"Natural Cements"	H_2SO_4	-	No	-	-	K 52

8.1.10.2 Alkali leaching

Whereas in acid leaching the iron is usually dissolved leaving the solid impurities; with alkaline leaching, the impurities are dissolved leaving an enriched iron ore. The literature is summarised in Table 10. Caustic soda leaching successfully removes aluminium and silicon from low grade iron ores, as will probably be used as feedstock in later designs (see sect. 5.1.6). The caustic soda may be recovered from the aluminium relatively easily, but not from the silica. The cost of caustic soda lost in this way might exceed £20/ton of iron produced, which together with the cost of producing high temperature and pressure makes the process uneconomic. The ammonia leaching processes only remove copper, cobalt and nickel as complex ammines which are not likely to occur in the feedstock (see sect. 5.1.6). Ammoniacal ammonium carbonate leaching is not selective, nor will there be any significant quantities of manganese in the feedstock envisaged. Sodium ferrite is formed on fusion of iron ores with caustic soda; but this is very easily hydrolysed and is unstable in aqueous solution, giving hydrated iron oxides and sodium hydroxide. Such a solution may in fact be successfully electrolysed (G 1).

8.1.10.3 Neutral solvent leaching

Some work has been carried out on roasting mixed ores with salts to convert the metal values to a soluble form, then leaching with water. This has been applied to iron - titanium ores roasted with ammonium sulphate to give the double sulphate (K 74),

TABLE 10

Dissolved	Not dissolved	Alkali	Strength	Pretr-ment	Temp. $^{\circ}$C	Press. Atm.	Ref.
Al, Ca	Fe, Na, Ti	NaOH	-	No	High	High	K 53
Al, Si	Fe	NaOH	4-44%	No	110-250	Yes	K 54
Al, Si	Fe	NaOH	10%	-	100	-	K 55
Ba, Cr, Ti, W, V	Fe	NaOH	F	-	750	-	K 56
Al, P, Si	Fe, Ca	HaOH	45%	-	100	-	K 57
Al, Cr	Fe	NaOH	50%	-	135	Yes	K 58
Unspecified	Fe	NaOH	44%	-	135	Yes	K 59
Various	Fe	NaOH	Various	-	Various	-	K 60
Al, P, Si	Fe, Ca, Mg	NaOH	40%	-	125-135	Yes	K 61
Ti	Fe	NaOH	F	-	-	-	K 62
Co, Cr, Ni	Fe	NaOH	F	-	800-1200	-	K 63
Al, Cr	Fe	NaOH	F	-	900-1100	-	K 64
Al, Cr	Fe	$NaHCO_3$	F	-	900-1100	-	K 64
Al, Cr	Fe	Na_2CO_3	F	-	900-1100		K 64
Co, Cr	Fe, Ni	NaOH	Dilute	-	Low	-	K 65
Co, Cu, Ni, S	Fe, S, Si	NH_3	Dilute	Yes	65-100	5	K 66 - K72
Mn	Fe	$(NH_4)_2CO_3$	-	Yes	-	-	K 73

F: Fusion with alkali, followed by leaching with water.

and to complex concentrates roasted with sodium chloride to give zinc, iron, and indium chlorides (K 75). Sulphates formed by selective sulphation (K 76, M 1, M 2) may also be extracted by water leaching.

Iron has been successfully leached with ferric chloride from titaniferous ores (G 17, G 18), pyrite and chalcopyrite (K 77) and nickel matte (K 78). The iron is recovered from the resulting ferrous chloride solution by electrolysis, which also gives ferric chloride for recycling (G 17, G 18, K 77. See also sect. 8.1.6). Ferric sulphate, and copper chloride and sulphate have also been used with some success (K 77, K 79). The ore is sometimes pre-reduced (G 17, G 18, K 78), and dissolution at high temperatures (105-115°C) and pressures employed (K 77, K 79).

No references have been found on leaching iron containing ores with organic solvents.

8.1.11 Organometallic compounds

Those organo-iron compounds which vapourise before decomposing are reported in detail elsewhere (A 2). Included in that category are ferrocene, carbonyls, acetoacetonates, hexaethynyls, alkyls and aryls. There is no information on the thermal stability of bis-arene complexes (L 1) or alkoxides and aryloxides (L 2, L 3), which probably decompose to oxides. A literature survey on methods of recovering metals from organo-metallic compounds was carried out by Graham (L 4) with practically no mention of iron. The iron salts of carboxylic acids readily thermally decompose to iron and iron oxides. This is discussed in sect. 8.1.15.1. Iron chelate complexes (L 2, L 3) appear to be chemically and thermally stable as they are used as additives in oils, fuels and rubber. Apart from the acid salts, there appears to be little application of organo-iron compounds for separation or recovery of iron.

8.1.12 Oxidation

Iron may be separated by an oxidation reaction which either

a) dissolves the iron, or oxidises it to a soluble form

b) precipitates the iron; ferric salts being usually less soluble than their ferrous counterparts for example.

8.1.12.1 Dissolution oxidation

Sulphide ores may be oxidised to the metal sulphates by roasting in air, or air plus sulphur dioxide, or by pressure oxidation leaching. The former was investigated by Stephens (M 1), and in much greater detail for selective extraction by Smithson and Hanway (M 2), on the basis of whose work a pilot plant was built (M 3). The process concerned has also been patented (M 45). More usually however, roasting of iron sulphide goes via sulphate to oxide, (e.g. M 4, M 5) which is then fed to a blast furnace for conventional treatment.

The oxidation of pyrite by pressure leaching has been studied in much more detail. Forward et al. (M 6, M 7) have written very comprehensive reviews with over 240 references, and McKay and Halpern (M 8) describe this process as one of the most important hydrometallurgical developments in recent years. Some of the more important theoretical studies have been performed on suspensions of pyrite in water, under high oxygen partial pressures. (M 8 - M 10), which gives a mixture of sulphuric acid and metal sulphate. This process has been patented (M 11). The aqueous oxidation of pyrite in alkaline medium under similar conditions has been reviewed (M 46), investigated (H 6, M 12, M 13), and patented for general sulphide minerals (M 14). Insoluble sulphide is converted to insoluble oxide with production of some sulphate. The conditions are more critical for successful operation than in neutral, or acid medium as diffusion is the principal mechanism.

Acidic oxidation has been paid more attention by Russian workers, who have investigated the extraction of iron, copper, nickel, cobalt and a few other metals from mixed sulphide ores (M 15 - M 21). Separation is achieved by "under-oxidising" when only iron goes into solution as sulphate, or "over oxidising" when iron is reprecipitated as basic sulphate, leaving copper, nickel etc. in solution as sulphates. Patents have been taken out on these latter processes (M 22 - M 24). Oxidation of a mixed sulphide ore has also been carried out successfully with nitric acid (M 25, M 44) and nitric acid and oxygen (M 26, M 27).

8.1.12.2 Precipitative oxidation

Oxidation to ferric salt, basic salt, and/or oxide will precipitate iron, as these salts usually become progressively less soluble. The mechanism and kinetics of oxidation by molecular oxygen of aqueous ferrous sulphate (M 28 - M 30) and ferrous chloride (M 30, M 31) have been studied. Some commercial examples are found in the regeneration of spent pickle liquor (M 32 - M 34, Q 31 and sect. 8.4.2).

In view of the lower solubility of most ferric salts, many iron precipitation reactions are carried out under oxidising conditions for higher efficiency. This is also found mainly in the spent pickle liquor industry (M 35, N 5, N 7, N 13, N 15, N 25) when the acid is neutralised for disposal. A similar method is used to remove impurity iron from leach liquors of mixed ores (M 36, M 37). Other oxidising agents have also been used to effect precipitation: copper sulphide (N 29), hydrogen peroxide (N 22, Q 38), nitrous acid (Q 38), nitric acid (Q 38), potassium permanganate (M 38) and sodium nitrate (M 39).

8.1.12 3 Oxidative roasting

Ferrous chloride from pickle liquor is commercially converted to oxide by roasting, and recovering the hydrogen chloride or chlorine for re-use (M 40 - M 43, N 31). See also ref. (A 2) for a complete discussion of this process.

8.1.13 Precipitation

Precipitation covers a wide range of operations, which are classified thus:

a) Chemical precipitation; producing an insoluble compound by chemical reaction.

b) Physical precipitation; may be termed crystallisation (see also sect. 8.1), and is achieved by adding a miscible organic solvent or the acid of the anion in a concentrated form. This is also known as "salting out".

c) Biological precipitation.

d) Oxidative precipitation; see sect. 8.1.12.2

e) Reductive precipitation; see sect. 8.2

f) Electrodeposition precipitation; see (G 1)

Precipitation has long been a major method of separating compounds, and is probably the one most generally used (N 1), usually for removing trace impurities. This obviously requires insoluble (relatively) iron compounds, and there are few common ones. (see sect. 8.5)

8.1.13.1 Chemical precipitation

Most work on the chemical precipitation of iron has been performed on spent pickle liquor. Before iron and steel manufacturers became cost-conscious, the favourite method of handling this waste acid was by neutralization with a cheap alkali. Excellent reviews are given by Hoak (N 2), Hodge (N 3) and Swindin (N 4) (see also sect. 8.4.2). The problems are twofold: a sufficiently cheap alkali, and a precipitate that is easily filtered and handled. Generally, the usefulness of the precipitate was not considered. Hoak considers high calcium lime, dolomitic lime, limestone, sodium hydroxide, soda ash, ammonia and magnesia. Hodge and Swindin only consider those processes that are actually practised industrially, using lime, limestone, marl and basic slag. The patent literature shows a much wider variety of neutralizing agents: sodium carbonate (N 5), blast furnace flue dust (N 6), ammonia (N 7), coke oven gas (N 8, N 9), alkali waste (N 10), manganese dioxide (N 11), sodium hydroxide (N 12), carbonated ammonia (N 13), waste ammonia liquor (N 14), and lime (N 15-N 17). In every case the end product is iron oxide; either directly or indirectly via the carbonate or hydroxide. Similar work on stainless steel spent pickling liquor also precipitates the iron by neutralisation with alkali: as the hydroxide (N 18) or as a double salt with ammonia (N 19). Matsubara (N 20) patented a process for making red iron oxide from titania waste acid, and Clark (N 21), a process for the pressure precipitation of basic sulphate from spent pickle liquor.

The recovery of the individual constituent metals from the leach liquor of a mixed ore was investigated by Alchudzhan et al. (N 22) who oxidised the iron with hydrogen peroxide, then precipitated it with ammonium carbonate together with aluminium. The cobalt and nickel were then precipitated as sulphides and magnesium as the double carbonate. Afonskii and Zosimovich (N 23) separated chromium and iron by selective precipitation with lime. The possibility of selective precipitation by controlling pH does not appear to have been investigated. Several patents have been taken out with a purified iron oxide as the end product after precipitation with ammonium hydroxide or carbonate (N 24), ammonium carbonate, sodium carbonate, or hydroxide (N 25) and unspecified (N 26). The latter patent precipitates part of the iron (15-50%) with the impurities, then by a two stage air-oxidation and pH adjustment, precipitates ferrous/ferric hydroxides (approx. ratio 1.3). Dobos and Kovacs (N 41) carried out similar work on precipitating mixed hydroxides, using sodium nitrate to partially oxidise and sodium hydroxide to precipitate. Other experiments on the formation of iron ores were performed by Guenzler and Muehl (N 27), and Funaki et al. (P 38) who purified the iron salt solution by solvent extraction prior to precipitation. Srwastava and Kulsreshtha (Q 14) precipitated ferrous oxalate which was then thermally decomposed to the oxide. Very little work has been carried out on iron sulphide precipitation probably due to the difficulty of filtration. Carlson and Simons (N 28) precipitated cobalt and nickel sulphides at 150 psi, when iron appears to stay in solution. McGauley (N 29),however, precipitated iron as the sulphide at high pressure.

8.1.13.2 Physical precipitation

Both "salting out" and precipitation by altering the solubility product equilibrium are included here. Crystallisation is covered in sect. 8.1. As in the previous section most of the work on the physical precipitation of iron has been in the waste acid field, either spent pickle liquor (see sect. 8.4.2), or used sulphuric acid from the titanium dioxide industry.

The former waste acid regeneration was investigated by Belyakova and Bruk-Levinson (N 30) who scaled up a laboratory experiment in which hydrogen chloride gas was passed through spent hydrochloric acid pickle liquor, precipitating hydrated ferrous chloride. The acid was thus regenerated, and the ferrous chloride calcined to recover the hydrogen chloride for recycle. From 41 to 95% iron extraction was claimed by the authors, and only 3.4% acid make-up required. This basic process was patented by Weingaertner (N 31), and Ruthner (N 32) also patented a similar process where hydrogen chloride gas precipitated ferrous chloride from spent sulphuric acid pickle liquor. Spent acid from titanium dioxide manufacture has been treated likewise: Kubo et al. (N 33 - N 35) investigated the precipitation of ferrous chloride and other metal chlorides (aluminium and magnesium), by passing gaseous hydrogen chloride through the used sulphuric acid. Reeve and Blakey (N 36) patented a process for recovering pure iron oxide from iron ore by leaching with hydrochloric acid and reducing any ferric iron to ferrous with scrap. The ferrous chloride is then precipitated by passing gaseous hydrogen chloride, which is recovered by calcining the ferrous chloride. (See also sect. 8.1.10.1).

Similar work with concentrated sulphuric acid was performed by Atwood and Hodge (N 37), who regenerated spent pickle liquor by adding concentrated sulphuric acid, precipitating the ferrous sulphate heptahydrate and thus recycling the acid. This suffers from the disadvantage of not being able to recover the sulphuric acid from ferrous sulphate as easily as with the chlorides. Petlicka et al. (N 38) patented a process for selective salting out of manganese and iron using concentrated sulphuric acid. Another patent taken out by the National Lead Co. (N 39) separates the iron from spent pickle liquor as an "alum".

Some work has been carried out by Watanabe and Kawakami (F 4), on the regeneration of spent pickle liquor by adding acetone, which precipitates ferrous sulphate and thus regenerates the acid. The acetone may be easily recovered by distillation. De Lattre (F 6) patented such a process using a fatty alcohol instead of acetone. There is no evidence of many of these ideas being put into practice.

8.1.13.3 Biological precipitation

In addition to the autotrophic oxidising bacteria discussed in sect. 8.1.2, there are also autotrophic reducing bacteria. These reduce, for example, sulphate to sulphide. Freke and Tate (N 40) investigated this in relation to the removal of iron from aqueous solution as the sulphide, by the action of such bacteria. As in biological leaching this suffers from the disadvantage of long reaction times, and inability to treat large iron concentrations.

8.1.14 Solvent extraction

A considerable amount of work on the solvent extraction of iron and its compounds has been carried out. A large proportion of the references is devoted to fundamental investigations with no commercial potential. Accordingly, these references are presented in tabular form. Table 11 gives references to groups of solvents and Table 12 refers to individual solvents. Some of the solvents are in fact solutes in inert solvents, the chemical named is what may be termed the active component. In every reference iron is extracted from the aqueous phase, and usually only the ferric iron or compound is extracted.

There has been very little work carried out on large scale

TABLE 11

Solvent Group	Reference
Acetates	P 1
Alkyl Phosphates	P 2
Alkyl Phosphoric Acid	P 3
Amines (High molecular weight)	P 4
Aminophosphoric Acid monoesters	P 5
Carboxylic Acids	P 6, P 7, P 8
Diketones	P 9
Ethers	P 10, P 11
Hexanones	P 1
Ketones	P 1
Quaternary Ammonium halides	P 12

TABLE 12

Solvent	Reference
Amyl acetate	P 13
Amyl acetate + Methyl isobutyl ketone	P 13
Benzene	P 14
Benzyldimethyloctadecylammonium chloride	P 15
bis 2 Ethyl hexylphosphoric acid	P 3
Butyl acetate	P 16, P 17
Butyl alcohol	P 18, P 19

TABLE 12 (Contd.)

Solvent	Reference
Butyl methyl ketone	P 19
Carbon tetrachloride + Cyclohexanone	P 20
Chloroform	P 11, P 21, P 22, P 23, P 24
Chloroform + Cyclohexanone	P 20
Cyclohexyldidodecylamine	P 25
Dialkylorthophosphoric acid	P 26
Dibutyl ether	P 27
b b Dichloroethyl ether	P 1, P 28
b 2.4. Dichloro-phenylethylamine	P 29
Diethyl ether	P 1, P 28, P 30, P 31
Di 2 ethylhexylphosphoric acid	P 32, P 33, P 34
Di isopropyl ether	P 35, P 36, P 37, P 38
Di phenylguanidinium chloride	P 39
n.n. Disalycylidineethylenediamine	P 40
Ethyl acetate	P 11
Ethyl acetoacetate	P 18
2 Ethylhexanol	P 41
Hexone	P 18
8 Hydroxyquinoline	P 42, P 43, P 44
8 Hydroxyquinoline n. oxide	P 42
Iso Amyl acetate + Cyclohexanone	P 19
Iso Amyl alcohol	P 18
Iso Butyl alcohol	P 45, P 46

TABLE 12 (Contd.)

Solvent	Reference
Iso Butyl methyl ketone	P 45, P 46
Iso Propyl ether	P 1, P 28
Mesityl oxide	P 18
Methyl amyl ketone	P 1, P 28
Methyl hexyl ketone	P 27
Methyl isobutyl ketone	P 13, P 47
Methyl isobutyl ketone + Amylacetate	P 13
Methyl thiocyanide	P 48
Mono alkylorthophosphoric acid	P 26
Mono ethyl hexylphosphoric acid	P 32
Napthenic acid	P 49
Nitrosophenylhydroxylamine	P 50
Octyl alcohol	P 18
b Phenoxyethylamine	P 29
Phenyl bromide + Cyclohexanone	P 19
Sodium diethyldithiocarbamate	P 51
Tetrabutyl ethylene diphosphonate	P 52
Tetrabutyl methylene phosphonate	P 52
Tetraphenylarsonium chloride	P 39
2 Thenoyltrifluoro acetone	P 53
Thioglycollic acid	P 54
Tri amyl phosphate	P 1
Tri aurylamine	P 25

TABLE 12 (Contd.)

Solvent	Reference
Tri butyl phosphate	P 1, P 18, P 45, P 46, P 55, P 56, P 57, P 58, P 59, P 60 P 61
Tri butyl phosphate + Iso propyl ether	P 30
268 Tri methyl 4 nonyl phosphoric acid	P 3
Tri octylamine	P 4, P 62, P 63
Tri octylphosphine oxide	P 64
Xylene	P 14

or commercial solvent extraction of iron. Roblin (P 60) described and designed a complete process for recovering iron from spent pickling acid by extraction with tri-butyl phosphate reclaiming the acid, and converting the recovered iron to the oxide form. A number of patents (P 8, P 33, P 49, P 54, P 61, P 63, P 65, P 66) have been issued claiming successful extraction of iron, although there is no evidence of these or Roblin's design being practised industrially.

Fletcher (P 67) investigated the costs of solvent extracting metals in some detail. He came to the conclusion that for world metal production of more than 20,000 tons per annum (this includes iron, copper, aluminium, zinc, lead, manganese, magnesium, nickel, tin, arsenic, antimony and chromium: in descending order of world production), solvent extraction is definitely not economic. For metals in the range 20-20,000 tons per annum (from tungsten down to tantalum and beryllium), this method of purification might be economic if a cheap solvent were used, and if the metal is required in a high state of purity. This economic aspect is probably the reason for the lack of commercial interest in solvent extracting iron and similar low value metals. It is important to note, however, that although Fletcher gives no detailed analysis of the costs, his claims are probably justified. More detailed appraisals of the economics of this method are required.

Theory and design is well covered by Perry (P 68) and Treybal (P 69). Treybal (P 70) has recently reviewed solvent extraction generally; and Green (P 71) reviewed the solvent extraction of metals. Pertinent references are included in Tables 11 and 12. The metallurgical application of solvent extraction is fully discussed by Bridges and Rosenbaum (P 72) based mainly on the extraction of uranium.

8.1.15 Thermal decomposition

8.1.15.1 Organic compounds

True organometallic compounds usually vapourise before decomposing, for example iron carbonyls (A 2) and acetylacetonates (Q 1), which are covered elsewhere (see sect. 8.1.11 and A 2). This section reviews those iron organic compounds which break down before vapourising. In fact only carboxylic acid salts fall into this definition as far as the literature is concerned. (see also sect. 8.1.11).

References to the thermal decomposition of iron salts of carboxylic acids are few and scattered. The earliest is by Brochet (Q 2) who claimed to decompose nickel, iron and cobalt formates to give the metal according to the equations:

$$Fe(HCOO)_2 = 2CO_2 + H_2 + Fe$$

and similarly for the oxalates:

$$Fe(COO)_2 = 2CO_2 + Fe$$

In fact, he admits to there being some metal oxide present as well, saying that this cannot be predicted. The whole equilibrium for metal and metal oxides plus decomposition gases may in fact be calculated. Markevich (Q 3) went into this rather more deeply, analysing all the products at different stages of decomposition, coming to the conclusion that the initial stage of reaction was:

$$Fe(HCOO)_2 \;=\; Fe + 2CO_2 + H_2$$

followed by the main reaction (possibly catalysed by the metallic Fe formed - A.V.B.)

$$Fe(HCOO)_2 \;=\; FeO + CO_2 + CO + H_2$$

$$4FeO \;=\; Fe_3O_4 + Fe \text{ (to a lesser extent)}$$

$$2CO \;=\; CO_2 + C \text{ (even lesser)}$$

His work is supported by Kornienko (Q 4) who further investigated this in relation to free energy changes, energy of formation and temperature (Q 5); and the cation involved (Ni, Co, Cu, Fe, Mn) (Q 6). The conclusion reached in the latter reference was that the composition of the product is not associated with the cation activity of the metal, but depends almost completely on its oxide reducibility.

Boulle and David (Q 7) worked along similar lines, reporting on the decomposition of cobalt and nickel oxalates to give metal and metal oxide; and later, Doremieux and Boulle (Q 8) investigated the influence of surrounding atmosphere on the products of decomposition of metallic formates and oxalates. Their conclusions were that atmospheric oxygen acts as a promoter for iron, cobalt and nickel formate decomposition; and the method of preparation and age of iron and zinc formates was important. Dollimore et al. (Q 9, Q 10) investigated the thermal decomposition of ferric oxalate at different temperatures giving iron or iron oxides. There is a substantial amount of literature available on the effect of simple gases on metals, particularly with reference to blast furnace atmospheres (e.g. Q 64).

The texture of metal powders, produced by reducing ferrous formate with hydrogen at varying flow rates, was analysed with X-rays by Amiel et al. (Q 11); with no positive conclusions. Isherwood (Q 12) patented a process for producing iron from ferrous formate; passing it through an iron furnace, in cans, co-current with hydrogen. Iron-nickel alloys were prepared by Ananthanarayanan and Peavler (Q 13) by thermally decomposing and reducing co-precipitated, mixed crystal, iron-nickel formate powders. The manufacture of "ferrites" by a similar method (without the reduction step) was the subject of a patent (Q 14); and the manufacture of magnetic iron oxide from ferrous oxalate was patented by Srwastava and Kulsreshtha (Q 15), and investigated by Wolski et al. (Q 16). Henneberger (Q 17) patented a process for producing fine grained iron powder by thermal decomposition and reduction of iron oxalate; and Eisenkolb and Ehrlich (Q 18) investigated chemically produced microfine iron powder and came to the conclusion that the best starting material was iron oxalate. The Societe d'Electrochimie (Q 63) also patented a process to produce iron powder by reduction of thermally decomposed ferrous formate.

The decomposition of iron formate is an interesting possibility but practical details of an economic process employing the method, are not covered in the literature, although there is probably sufficient theory.

8.1.15.2 Inorganic compounds

There is a much more complete literature on the thermal decomposition of inorganic iron compounds, but this is almost exclusively based on iron sulphates, often from spent pickle liquor. The chemistry of inorganic iron compounds may be found in standard text-books.

8.1.15.2.1 Sulphates

Several authors have investigated the decomposition of iron sulphates as a fundamental study, obtaining dissociation rate constants (Q 19, Q 20), and studying kinetics (Q 21) and effects of temperature (Q 22 - Q 24). The possibility of separating iron from mixtures of metal sulphates has also been investigated (Q 25, Q 26) as iron sulphates decompose at a lower temperature than most other metal sulphates, which may then be leached leaving iron oxides. The reverse of this, namely selective sulphation followed by leaching is an interesting possibility for mixed ores. Both Stephens (Q 65) and Smithson et al.(Q 66) have worked on this. The decomposition step has been fluidised, utilizing ferrous sulphate from spent pickle liquor to produce either red iron oxide (Q 27) or iron oxides for blast furnace feed and sulphur oxides for recycling to make acid (Q 28 - Q 30). All four references (Q 27 - Q 30) also give design and operating information with a view to large scale practice, although there is no evidence of this being done. Iron oxides may also be obtained from the sulphates by hydrolysis, i.e. thermal decomposition in the aqueous phase. This is reported by Bruhn et al. (Q 31), and also discussed under precipitation, (see sect. 8.1.12.2).

A large number of patents pertaining to the products of decomposition of iron sulphate have been taken out. These all use ferrous sulphate as starting material, sometimes as raw spent pickle liquor, sometimes of no specified origin. The majority offer straightforward roasting to oxides and sulphuric acid (by collecting, condensing and reacting the offgases) (Q 32 - Q 39). Lewis (Q 40) employs a two-stage spray-drier to effect the decomposition, while Hansford et al. (Q 41) uses a spray-drier to dehydrate the ferrous sulphate from hepta to monohydrate and a fluidised bed to decompose the monohydrate. Patterson (Q 42) and Blickle and Kaldi (Q 43) also employ fluidised beds.

Fackert (Q 44) and Petrdlik (Q 45) take this one stage further to give iron as the end product, by decomposing the ferrous sulphate with hot reducing gases. Francis (Q 46), White and White (Q 47) and McGauley (Q 48) all employ the thermal decomposition of sulphate to oxide, followed by reduction as the last stages of a complete process from iron ore to iron; none of which has been taken up commercially.

Reviews on the subject of iron sulphate decomposition as a useful by-product in waste disposal are given by Dembeck (Q 49), and with particular reference to waste pickle liquor disposal, by Hodge (Q 50), Swindin (Q 51) and Hoak (Q 52).

8.1.15.2.2 Nitrates

The mechanism of the thermal decomposition of metal nitrates, including ferric nitrate, was investigated by Wendlandt (Q 53). A process for the continuous decomposition of metal nitrates with recovery and recycling of the acid was patented by Nossen (Q 54), and Koslov (Q 55). Mancke (Q 56) patented a process for nitric acid pickling, with regeneration of the acid and production of iron oxides. A similar idea was presented by Poliskin (Q 57) only in a more round-about way: the pickling acid is sulphuric, and the iron removed by ion exchange, thus regenerating the acid. The iron is eluted with nitric acid and decomposed as an aqueous solution of nitrate to the oxide. Cleaves and Thomas (Q 58) found, in their study of routes to very pure iron, that ferric nitrate is one of the best compounds to employ as an intermediate.

8.1.15.2.3 Ores

The oxidising roasting of iron pyrite to iron sulphate and oxide is covered in sect. 8.1.12. The thermal decomposition of pyrite to give elemental sulphur, and increase the Fe : S ratio of the ore was investigated by Ishikawa and Yoshizawa (Q 59), and patented (as part of a larger process) by McGauley (Q 48, Q 60). Interest in processing sulphide ores of iron, however, will not be very great while there are still large deposits of reasonably high grade oxide ores, due to the extra processing step and high risk of undesirable sulphur impurities.

Investigations into the thermal decomposition of carbonate ores have been carried out by Powell (Q 61) and Zvez-din and Pechkovskii (Q 62). This operation has long been known as calcination, and is often based on empirical designs.

8.1.16 Zone melting and refining

Aluminium, antimony and tin were the first metals to be purified by zone refining in 1954. Most work has been performed on the ultra-purification of semi-conductor materials for transistors, but there has been some interest recently in the properties of ultra-pure common metals. The standard text-book by Pfann (R 1) was first published in 1958 containing approximately 100 references while the second edition (R 2) in 1966 contains more than 1000, showing how rapidly interest is growing. Parr (R 3) has written a book describing zone refining techniques, and gives considerable practical information on apparatus and methods used. A symposium, held in 1961, is presented in book form by the American Society for Metals (R 4) which discusses ultra purification processes, including much work on iron. All four books discuss the theory of zone refining and distribution of impurities in some detail.

The earliest recorded zone refining of iron was in 1957 (R 33), subsequently a considerable amount of work has been carried out on procedure, apparatus, analysis and properties. For convenience the references are tabulated on this latter basis:

Procedure for zone refining iron:

R 2, R 3, R 4, R 5, R 18, R 23, R 26, R 27, R 30, R 33, R 35.

Apparatus for zone refining iron:

R 2, R 3, R 4, R 5, R 18, R 23, R 24, R 26, R 27, R 30

Analysis of zone refined iron:

R 3, R 7, R 8, R 11, R 12, R 18, R 23, R 24, R 26, R 27, R 29, R 30, R 32, R 33

Physical (including mechanical) properties of zone refined irons:

R 7, R 8, R 9, R 10, R 11, R 12, R 13, R 14, R 15, R 16, R 17, R 19, R 20, R 21, R 22, R 25, R 27, R 29, R 30, R 31, R 32, R 34

Chemical properties of zone refined iron:

R 6, R 8, R 11, R 12, R 28, R 29

There are no cost data or information on the probable economics of zone refining. It is obviously expensive, and normally applicable only to small scale operation.

8.2 Reduction

This review is classified by the phase of the reducing agent and the initial phase of the compound to be reduced; in all cases to give a metallic product.

	Phase of Reducing agent	Phase of compound to be reduced	
a)	Gas	Gas	see (A 2)
b)	Gas	Liquid	see below
c)	Gas	Solid	see (A 4)
d)	Liquid	Gas	see (A 2)
e)	Liquid	Liquid	see below
f)	Liquid	Solid	no references found
g)	Solid	Gas	see (A 2)
h)	Solid	Liquid	see below
i)	Solid	Solid	see below
j)	Electro - reduction		see (G 1)

Both the reduction of iron compounds in the gaseous phase (A 2); and the reduction of solid iron compounds by a gaseous reducing agent (A 4), are the subject of separate reports. The latter category covers all conventional reduction.

8.2.1 Gas - liquid systems

A considerable amount of work has been carried out on precipitating metal powder by gaseous reduction under pressure. Some of the earlier work employed as the reducing gas, sulphur dioxide (S 1 - S 3), carbon monoxide (S 4), hydrogen (S 5, S 6), and hydrocarbons (S 5). Most of this work involved the preparation of copper powder, apart from Ipatiev et al. (S 6, S 7) who explored this whole subject in great detail for most common metals. Schaufelberger (S 8) provides a very comprehensive review on hydrogen precipitation up to 1956, which is brought up to date by Birkin (S 9), together with other reducing agents employed and details of theory and practice. Commercial application was introduced on a large scale with the Sherritt - Gordon ammonia leaching process to recover copper, cobalt and nickel (K 66 - K 71).

Very little, however, has been performed on the pressure precipitation of iron. This is due mainly to the higher reduction potential than nickel etc., and hence higher temperatures and pressures are required to effect reduction. Ipatiev and Werchowsky (S 6) claimed reduction to metallic iron at 400°C and over 6000 psi, but only in trace amounts. Under these conditions however, the apparatus repeatedly exploded, so they were unable to pursue this subject any further.

Burkin (S 10) postulates the hydrogen reduction of iron salts to metal powder, but admits that thermodynamically it is a borderline case, and would necessitate expensive reagents requiring recycling to be economic. He amplifies this statement in his book (S 9) concluding that the thermodynamic data available for predicting the iron reducing reaction is "totally inadequate". Investigations into the hydrogen precipitation of iron are proceeding at Imperial College, London, (S 11). In spite of this pessimism, several Russian workers have claimed reduction of ferric chloride with hydrogen (S 12) and carbon monoxide (S 13), under mild reaction conditions with a catalyst: platinised asbestos and palladium salts respectively. The reduction product appears to be ferrous chloride.

8.2.2 Liquid - liquid systems

The manufacture of acicular iron powder by reducing aqueous ferrous salt solutions with sodium borohydride solution has been patented (S 14). The product is contaminated with up to 3% boron and up to 15% oxygen (mainly from air oxidation). No details of borohydride recovery are given, which would render the method very costly. Alkyl-aluminium compounds have also been used to reduce organic solutions of ferric chloride (S 15); the resulting alkyl-aluminium chloride may be recycled, but only with difficulty. The iron powder obtained is very pure. Another process has been patented in which ferric chloride is reduced with an emulsion of sodium in napthalene, o-xylene, toluene and linseed oil (S 16). No claims are made as to the purity of the product. Rochow et al. (S 17) mention that the reaction of Grignard reagent with iron halides results principally in pyrophoric iron powder; and again there is the economic problem of recycling the Grignard reagent.

The reduction of iron halides with molten aluminium (S 18, S 35), and calcium (S 36) is reported, and patents have been taken out for the reduction of iron halides with sodium (S 19, S 20), alkali metal (S 21 - S 23), and alkali metal hydrides (S 21). Patent (S23) is interesting as the alkali metal is produced "in situ" by electrolysis. As more valuable metals than iron are consumed and no recycle is postulated, such processes are probably not economic.

8.2.3 Solid - liquid systems

Iron powder has been made by reducing ferric chloride in an organic solvent with a sodium emulsion (see sect. 8.2.2 and S 16), and the sodium addition product of ethylene glycol dimethyl ether (S 24). Both methods are uneconomic due to the high reagent cost and difficulty of recycling. Iron powder may also be precipitated from aqueous solution of its salts by adding a more electronegative metal such as magnesium (S 25, S 26), zinc (S 27 - S 29), copper - zinc alloy (S 27), and manganese (S 30). This is prohibitively expensive as the precipitating metals are not recovered.

8.2.4 Solid - solid systems

There are a number of references dealing with the reduction of iron oxides and chloride with solid carbon. The mechanism of reduction is complex, but is initiated by a solid - solid reduction reaction. This produces carbon monoxide which also effects reduction. Globus (S 31) patented a process for prefabricating metal shapes, by forming finely ground iron oxide and carbon into the required shape, passing this through an oscillating electric field and thus reducing the oxide, and sintering the metal powder at the same time. Iron chlorides may be reduced with carbon by also adding lime (S 32). The ensuing reactions may be summarised:

$$FeCl_2 + CaCO_3 + C = Fe + CaCl_2 + CO_2 + CO$$

$$FeCl_2 + CaCO_3 + 2C = Fe + CaCl_2 + 3CO$$

Carbon is also used in chloridizing roasting to reduce the iron and thus give ferrous chloride, (e.g. S 33, S 34 see also A 2) but the mechanism is probably similar to the blast furnace: the carbon is oxidised to carbon monoxide which effects the reduction. The extent of the solid - solid phase reduction in most reactions involving carbon is probably quite small. No record of any other solid reducing agent has been found, but if there were, it is improbable that the reduction mechanism would involve solid - solid phase reaction to any appreciable extent, due to difficulties of thorough contacting of the reagents.

8.3 Shaping

It is important that metallic iron is produced in a useful shape. The implications and reasons for this are discussed in sects. 3.3 and 3.4. There are five possible product forms which may be obtained from a reduction step without further shaping operations:

a) Powder, is discussed generally in sect. 3.3.1. It may be produced by gaseous reduction (sect. 8.2.1

and A 2, A 4), liquid or solid reduction (sects. 8.2.2 and 8 2 3, A 2), or electrolytically (G 1). This is the most generally useful product that may be obtained.

b) Electroforming, see sect. 3.3.2 and (G 1) for references. This may be made economic, but at present the outlets are limited.

c) Whisker crystals, are to be the subject of a separate study. Their importance is discussed in sect. 3.3.3.

d) Vapour plating is also discussed fully elsewhere (A 2).

e) Molten iron, apart from conventional iron production (sect. 3.4 and A 4), molten iron may be produced electrolytically (G 1) or by reduction (sect. 8.2.4). The final shaping is orthodox (sect. 3.3.4); but both methods mentioned are very expensive, and not likely to be proposed.

8.4 Established processes (non-conventional)

8.4.1 Complete process from ore to metallic iron

A number of processes have been proposed for the non-conventional production of iron,starting with an iron ore and producing more or less pure metal. Only a few of these, however, have actually been put into commercial operation, including the Eustis process (sect. 8.1.6), which has long been abandoned; and the Peace River Project, (sect. 8.1.10.1.1) which is still in the pilot plant stage. In view of the lack of serious interest in alternatives to conventional ironmaking, there remains considerable scope for the O.S.C.A.T. project.

8.4.2 Pickle liquor regeneration

The literature on the disposal or regeneration of spent pickle liquor from steel mills, is very extensive. In 1954 there were 107 recorded methods or processes (T 1), each well covered by many references. These are summarised:

a)	Disposal with no treatment or recovery of by-products	8 methods
b)	Disposal with preliminary treatment (e.g. neutralisation), but no by-product recovery	14 methods
c)	Recovery of copperas ($FeSO_4.7H_2O$)	4 methods
d)	Recovery of copperas and free sulphuric acid	13 methods
e)	Recovery of ferrous sulphate monohydrate and free sulphuric acid	15 methods
f)	Recovery of ferric sulphate and sulphuric acid	3 methods
g)	Recovery of iron oxide and sulphuric acid	6 methods
h)	Electrolytic recovery of iron and sulphuric acid	4 methods

i) Production of iron oxide pigments and/or polishing rouge	6 methods
j) "Ferron" construction material manufacture	2 methods
k) Manufacture of ammonium sulphate and iron oxide, sulphide or carbonate	11 methods
l) Manufacture of other inorganic compounds	11 methods

Excellent reviews have been written by Hodge (T 1, T 2), Hoak (T 3 - T 6) and Swindin (T 7).

Of particular interest are those groups of methods where the iron is recovered, and the acid regenerated for recycling, as in groups (d), (e), (f), (g), (h). These are analogous to acid leaching of ore with iron values recovery and acid recycle. Hoak (T 5) reviews the disposal of spent pickle liquor, with particular emphasis on the recovery of by-products with regeneration of acid. He provides detailed flow sheets, and much useful design data. Electrolytic regeneration is also comprehensively covered in (G 1). The many references are not individually reviewed here as the authors referred to above provide adequate critical coverage. See also sects. 8.1.5, 8.1.9, 8.1.13.1/2, 8.1.14, and 8.1.15.2.1.

The iron salts obtained from spent pickle liquor or the analogous leaching process may be converted to the oxide form for reduction to iron powder (A 4), or reduced by one of the methods discussed in sect. 8.2.

8.5 Iron compounds

An index of a large number of inorganic iron compounds has been compiled together with physical properties, and will be published as a separate paper at a future date.

APPENDICES

APPENDIX I

Computer programme for selection of processing routes

Language: Elliott Autocode

Computer: Elliott 803, with lineprinter.

```
::0/S/12
::OSCAT ROUTES 2,3,4 STAGES NAMES LINEPRINTER 29/6/66 AVB
SETS ABCDEFGHIJKLMNPQRSTUVWX(15)Y(15)Z(8)
SETF ANLINE ANPRINT ANSPACE ANTITLE
SETR 110
15)JUMP IF A=1@16
JUMP IF A=2@17
JUMP IF A=3@17
JUMP IF A=4@18
JUMP IF A=5@19
JUMP IF A=6@20
JUMP IF A=7@17
JUMP IF A=8@17
JUMP IF A=9@21
JUMP IF A=10@22
JUMP IF A=11@53
16)CYCLE E=1,5,6,11
JUMP IF B=E@24
F=0
JUMP @25
24)F=1
JUMP @23
25)REPEAT E
JUMP @23
17)CYCLE E=1,2,3,4,5,6,7,8,9,10,11
JUMP IF B=E@26
F=0
JUMP @27
26)F=1
JUMP @23
27)REPEAT E
JUMP @23
18)CYCLE E=3,4,8,10
JUMP IF B=E@28
```

```
F=0
JUMP @29
28)F=1
JUMP @23
29)REPEAT E
JUMP @23
19)CYCLE E=3,5,8,10
JUMP IF B=E@30
F=0
JUMP @31
30)F=1
JUMP @23
31)REPEAT E
JUMP @23
20)CYCLE E=1,6,11
JUMP IF B=E@32
F=0
JUMP @52
32)F=1
JUMP @23
52)REPEAT E
JUMP @23
21)CYCLE E=3,5,8,9
JUMP IF B=E@33
F=0
JUMP @34
33)F=1
JUMP @23
34)REPEAT E
JUMP @23
22)CYCLE E=1,2,4,6,7,9,10,11
JUMP IF B=E@35
F=0
JUMP @36
35)F=1
JUMP @23
36)REPEAT E
JUMP @23
53)CYCLE E=1,2,4,6,7,9,11
JUMP IF B=E@54
F=0
JUMP @55
54)F=1
JUMP @23
55)REPEAT E
JUMP @23
23)EXIT
37)G=0
JUMP UNLESS H=D@38
```

```
G=1
38)JUMP UNLESS I=D@39
G=2
39)JUMP UNLESS J=D@40
G=3
40)JUMP IF G&2@41
F=1
JUMP @42
41)F=0
42)EXIT
43)@
2619:000
)
44)W=5
Z1=2
Z2=3
Z3=7
Z4=8
X1=1
X2=2
X3=3
X4=4
X5=5
X6=6
X7=7
X8=8
X9=9
X10=10
X11=11
Y1=1
Y2=2
Y3=3
Y4=4
Y5=5
Y6=6
Y7=7
Y8=8
Y9=9
Y10=10
Y11=11
L=0
M=10
N=0
P=5
Q=0
A=W
CYCLE R=1:1:4
B=ZR
SUBR 15
```

```
JUMP IF F=1@45
L=L+1
V=A
U=ANTITLE V
V=B
U=ANTITLE V
U=ANLINE Q
45)REPEAT R
U=ANPRINT L,N,P,Q
U=ANLINE Q
U=ANLINE M
L=0
CYCLE S=1:1:11
A=W
C=W
100)B=XS
SUBR 15
JUMP IF F=1@46
CYCLE R=1:1:4
A=XS
B=ZR
SUBR 15
JUMP IF F=1@47
L=L+1
V=C
U=ANTITLE V
V=A
U=ANTITLE V
V=B
U=ANTITLE V
U=ANLINE Q
47)REPEAT R
46)REPEAT S
U=ANPRINT L,N,P,Q
U=ANLINE Q
U=ANLINE M
N=0
CYCLE S=1:1:11
A=W
D=W
101)B=XS
C=XS
SUBR 15
JUMP IF F=1@48
CYCLE T=1:1:11
A=XS
B=YT
SUBR 15
```

```
JUMP IF F=1@49
CYCLE R=1:1:4
A=YT
B=ZR
SUBR 15
JUMP IF F=1@50
H=XS
I=YT
J=ZR
SUBR 37
JUMP IF F=1@50
L=L+1
V=D
U=ANTITLE V
V=C
U=ANTITLE V
V=A
U=ANTITLE V
V=B
U=ANTITLE V
U=ANLINE Q
50)REPEAT R
49)REPEAT T
48)REPEAT S
U=ANPRINT L,N,P,Q
U=ANLINE Q
STOP
1)TITLE CRYSTALLISATN
2)TITLE ELECTROLYS AQ
3)TITLE ELECTROLYS FU
4)TITLE ION  EXCHANGE
5)TITLE LEACHING
6)TITLE PRECIPITATION
7)TITLE REDUCTION  -L
8)TITLE REDUCTION  -S
9)TITLE SOLVENT EXTRN
10)TITLE THERMAL DECMP
11)TITLE EVAPORATION
START 43
```

APPENDIX II

Electrolysis of iron - energy requirements.

By Faraday's laws of electrolysis, 1 gram - equivalent of ferrous iron requires 1 Faraday, or 96 500 coulombs of electricity for deposition.

i.e. 28 grams ferrous iron are deposited by 96,500 coulombs and

1 ton iron (2240 x 454 grams) is deposited from the ferrous state by 96,500 x 454 x 2240/28 coulombs

$$= 3.505 \times 10^9 \text{ coulombs}$$

Power requirements for deposition $= \frac{V.A.t}{1000}$ kwh

where V = Volts

A = Amps

t = time in hours.

A and t are related by:

A x 3600t= coulombs required for deposition of 1 ton of iron

Power required for deposition of 1 ton of iron from the ferrous state

$$= \frac{V \times \text{coulombs}}{3600 \times 1000} \text{ kwh}$$

$$= \frac{V \times 3.505 \times 10^9}{3.6 \times 10^6} \text{ kwh}$$

$$= 973.6 \text{ V kwh.}$$

(For ferric iron, the power requirements are 1461 V kwh, as the equivalent weight is only 19)

APPENDIX III

Cost of acid leaching losses for 5% iron loss

5% of 1 ton of iron = 112 lb.

Molecular weights:

Fe	56
HBr	81
HCl	36.5
H_2SO_4	98

112 lb. Fe react with: 324 lb. HBr to give $FeBr_2$

486 lb. HBr to give $FeBr_3$

146 lb. HCl to give $FeCl_2$

219 lb. HCl to give $FeCl_3$

196 lb. H_2SO_4 to give $FeSO_4$

294 lb. H_2SO_4 to give $Fe_2(SO_4)_3$

The cost of acid loss is found by multiplying the number of pounds lost by the cost per pound as given in sect. 5.3.2.1. This gives the costs indicated in the same section.

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