It is already known to recover iron from hydro-

oxygen compounds by subjecting a suspension of

such a compound in an alkaline lye of a high

degree of concentration to an electrolysis proc-

ess at a suitable temperature. It is also known

that besides iron also certain other metals, as

for instance, cadmium, may be obtained as a

result of a reduction process, if the suspended

body except compounds of iron contains hy-

droxides of the respective metals. Hitherto, how-

ever, it was considered impracticable directly to

reduce anhydrous oxygen compounds of iron in

the same way, and it was considered necessary,

if the compounds were to be used as a raw ma-

terial for such a process, to first convert them

in one way or the other into the hydrated state.

This, of course, means a severe drawback, since

the most important and purest iron ores consist

of anhydrous compounds and a conversion there-

of into the hydrated state is a difficult and ex-

pensive procedure.

Contrary to the hitherto general opinion I

have found that, under certain conditions, iron

may be directly recovered as a result of an

electrolysis of anhydrous ferro-oxygen com-

pounds. Said conditions are: A high degree

of subdivision of the anhydrite, an intense

agitation of the suspension during the elec-

trolysis process, a high temperature, preferably

90–110°C, and a degree of concentration of the

lye which is suited to the degree of subdivision

or rate of dissolution of the anhydrite. I have

also found that, should the suspended ferrous

raw material contain other metals than iron or

should such other metals be intentionally added

thereto, preferably in the form of oxides, free

from water, then some of such metals as

manganese, nickel, molybdenum and tungsten,

may be recovered alloyed with iron at the cath-

ode, whereas some other metals, such as

vanadium, remain in the lye as alkali salts of the

higher valence oxygen compounds of the

respective metals, such as, for instance, alkali

vanadate, from which the metals may be then

recovered by well-known methods.

I have further found that the recovery of iron

both from hydrous and anhydrous compounds

does not take place, as hitherto taught, in such

a way that the suspended particles are carried

by cataphoresis into contact with the cathode

to be there reduced, since it has been ascertained

that the particles under the conditions stated

do not move towards the cathode but towards

the anode. On the basis of experiments I have

found that, what actually happens is likely to

be that the suspended ferrous compounds are

gradually dissolved in the lye as alkali ferrite

or similar compounds and deposited on the cath-

ode by electrolysis, that is to say, a galvanic

process. The solubility of the ferro-oxygen com-

pounds in the lye, however, is very low, amount-

ing to 0.04% at most, and varies with varying

concentration of the lye. The rate of disso-

lution is also comparatively low. It increases with

increased degree of subdivision, with increased

rate of agitation, with the concentration of the

lye and the temperature. The rate of dissolu-

tion of hydrous ferro-oxygen compounds is, as

a rule, above that of the corresponding anhydrous

compounds. This is due, substantially, to the

fact that the compounds are produced by an hy-

drolisis of ferrites of sodium or by a precipita-

tion of ferrie salts with ammonia, whereby they

have obtained an incomparably higher degree

dispersion than anhydrides disintegrated

merely by grinding. Probably, however, the rate

dissolution even at the same degree of dis-

integration may be higher in respect to the hydric

compounds than it is in respect to the anhydrous

compounds.

The observations above referred to have two

results: on the one hand, they show why prior

attempts with a view to electrical recovery of iron

from anhydrous compounds have given negative

results and, on the other hand, they teach how to

carry out such a recovery process with good re-

sults.

Owing to the low degree of solubility of the

oxygen compounds in an alkaline lye the con-

tents of iron dissolved in the electrolyte are very

small. It is thus seen that with a rate of dis-

solution below that of precipitation the iron con-

tents of the electrolyte will immediately sink

considerably with resulting decrease of the cur-

rent efficiency. The negative result of prior ex-

periments with anhydrous compounds may be

due to the fact that under the conditions pre-

vailing the rate of dissolution was too low with

relation to the rate of precipitation, that is to

say, with relation to the cathodic density of cur-

rent used.

As the rate of dissolution is substantially

higher in respect to the hydrous compounds than

it is in respect to the anhydrous compounds, it

is, of course, more difficult to obtain and main-

tain a high current efficiency with the former

compounds than with the latter. According to

this invention it is possible, however, to directly

recover iron from anhydrous ferro-oxygen com-

pounds, as magnetite and hermatite concentrates,
while securing a current efficiency amounting to 80-85% as related to trivalent iron. The most important condition for obtaining the result above set forth is that the raw material should be sufficiently finely divided, since the rate of dissolution increases with increasing degree of subdivision. Thus, the particles should be of a diameter not greater than 0.05 mm. and preferably less than 0.01 mm.

In order to increase the rate of dissolution and compensate for differences in concentration of the electrolyte, and prevent baking and depositing of particles, an intense and rational agitation is of utmost importance. In addition to a mechanical agitation, with a view to keeping the lye with the suspended particles in circulation, it is preferred to vibrate the suspension, as for instance, by means of a supersonic wave producer.

A high temperature promotes the current efficiency, the rate of dissolution of the suspended particles increasing and the high chemical polarization at the deposition of iron at the cathode decreasing with rising temperature. A high temperature acts also to avoid too high contents of hydrogen in the deposited iron and a scaling off of the deposited iron from the cathode plates. On the other hand, the attack on the material of the cell walls and agitators and the evaporation increase with increased temperature. It is preferred to effect the electrolysis at a temperature of 90-110° C.

As an electrolyte a sodium lyo containing 37-50% NaOH may be used with advantage. As far as the proper electrolysis process is concerned, it is preferred to use a low degree of concentration of NaOH, yet not less than 37%. On the other hand, however, the rate of dissolution of the suspended particles increases with increased concentration of NaOH. The rate of dissolution being a predominant factor as far as the maintenance of a high current efficiency is concerned, the concentration of the lyo should be chosen in the first place while paying regard to this circumstance. Accordingly, as an example, the concentration of the lyo should be chosen the more high, the larger is the size of group of the particles. From what is stated above it is evident, however, that a maximum of current yield may be obtained by securing a high degree of subdivision of the raw material, an intense agitation and a high temperature of analysis, while at the same time keeping the concentration of NaOH as low as possible without hazard to a sufficiently high rate of dissolution under the working conditions prevailing. In case of a size of grain amounting to 0.01-0.02 mm., a temperature of 100° C. and an intense agitation, a concentration of 50-52% has proved most advantageous.

As a cathode material I may preferably use sheet iron or steel which is suitably prepared so that the deposited iron may be readily removed from the plates after completed electrolysis. If the electrolytically produced iron is adapted to be melted, I may also use cathodes of electrolytic iron which in this case is melted together with the precipitated iron. The cathode density of current should preferably be within the limits 2-6 a./dm.². The higher the rate of dissolution is the higher the cathode density of current or rate of precipitation may be used.

The anodes may be of nickel, iron plated with nickel or nickel iron alloys. Such anodes will not be affected, the primary anode reaction merely comprising a formation of oxygen. The larger portion thereof is removed in gaseous form but a minor portion is required for effecting an oxidation of trivalent iron compounds to hexavalent ferrates as well as for effecting an oxidation of bivalent iron compounds to trivalent compounds, if there are such bivalent compounds present. Said secondary processes of oxidation are not desirable because they reduce the current efficiency in the cathode reduction process. The higher the anodic density of current is, the less will be the loss of current efficiency as caused by the oxidation processes. With the use of anodes of this type, thus, the anodic density of current should be higher than the cathodic one, preferably higher than 6 a./dm.².

It is to be noted, however, that also iron or steel anodes or anodes of an iron alloy may be used. The primary anode reaction comprises in this case, in part, a dissolving of iron and certain alloy components of the anodes and, in part, the formation of oxygen. The iron dissolved at the anode will then precipitate on the cathode together with iron originating from the ferro-oxygen compounds. Some of the alloy components which may be included in the anodic iron will also precipitate on the cathode. Of the oxygen formed the major portion will escape as a gas, whereas a minor portion is required for effecting secondary oxidation processes in the same way as with the use of insoluble anodes. Should it be desired that the main reaction as taking place at the anode would consist in a dissolution of the anodes, so that as large a portion as possible of the electrolytic iron produced originates from the anodes, measurements should be taken which have an activating effect, such as the use of a low anodic density of current, a high temperature and adding of chlorides. If, on the contrary, it is desired that the main reaction taking place at the anode, should consist in the formation of oxygen, so that the major portion of electrolytic iron produced will originate from the raw material suspended, then measurements should be taken which have a passivating effect, such as the choice of a high anodic density of current and a comparatively low temperature.

As raw material I may use, for instance, concentrates of magnetite or hematite, roasted iron purifies, magnetic purifies or waste, or ferro-oxygen compounds free from water in this way obtained as a by-product of chemical or metallurgical processes. The raw material should have a content as low as possible of such impurities as Si, S, F, P, Al, Ti and so on, which remain in the lye, for example, alkali, sulphate, phosphates, aluminate, titanate, and so on, and which cannot with advantage be recovered in any form but cause a contamination of the electrolyte or a loss of alkali hydroxide. It is therefore preferred to start with a raw material in a highly enriched state.

It has proved advantageous to subject the raw material to a preliminary treatment of such a nature as to cause a deranging of the grid structure or an increase of the surface activity, as by this means the rate of dissolution may be increased and the disintegration may perhaps be facilitated. Such changes of the raw material may be effected, for instance, by a roasting or partial reduction thereof. The said last-mentioned treatment has proved specially advantageous as far as the yield of current is concerned, probably due, in part, to the fact that this way I may obtain a great increase of the surface
activity or the rate of dissolution and, in part, to the fact that the ferro-oxygen compounds have been reduced to a lower state of oxidation. According to the present invention it is possible to recover in addition to iron also certain other metals, either in metallic form or in the form of alkali salts of the higher valence oxygen compounds of such metals. This is the case, for instance, when in the electrolytic production of iron according to the method above described the suspended raw material except iron also contains other metals, or if the suspension is intentionally mixed with another finely divided raw material containing other metals than iron, especially in the form of oxide. Then certain of said metals, such as manganese, nickel, tungsten and molybdenum, may be recovered simultaneously as the iron is recovered, on the cathode, whereas certain other metals, such as vanadium, remain in the electrolyte as alkali salts, as for instance vanadinite, from which compounds the metals or compounds of metals may be then recovered according to well-known methods. It is thus possible according to the present invention to produce alloys of iron and certain other metals. It is especially remarkable, that in this way metals, which otherwise cannot be extracted by the usual methods, such as the oxides and hydroxides of manganese, nickel, tungsten, and molybdenum, may be precipitated together with iron. In the manufacture of iron alloys the alloying substances are preferably added in the form of iron ores of the oxide form, containing the respective alloying metals. If, for instance, it is desired to produce iron containing manganese, it is thus evident that iron ore containing manganese should be added in finely divided state. It is of great importance too that a slight percentage of valuable metals, such as vanadium, in the raw material may be recovered according to the invention, even though this metal cannot be obtained in metallic form.

As a current efficiency amounting to 80-85% may be obtained at a cell voltage of 1.7-1.8 v., the consumption of energy amounts to not more than 2.3-3.33 kwh./kg. iron.

What I claim is:
1. A method of electrically producing an alloy of iron comprising forming a suspension of an anhydrous ferro-oxygen compound from the class consisting of water-free magnetite, hematite, roasted ilmenite, and roasted siderite of a grain size less than .065 mm., in an electrolyte comprising an alkali metal hydroxide solution, vibrating the suspension to promote the solution of the raw material, and adding a metal of the group consisting of manganese, nickel, molybdenum, and tungsten to the electrolyte in the form of an anhydrous ferro-oxygen compound containing the metal to be added, and subjecting the resulting fluid to electrolysis at a temperature of about 100° C. to electro-deposit an iron alloy at the cathode.
2. A method of electrically producing an alloy of iron comprising subjecting to a preliminary reduction step for increasing the surface activity and reducing the ferro-oxygen compounds to a lower valence state, a compound from the class consisting of anhydrous magnetite, hematite, iron pyrites, and siderite, forming a suspension of the resulting compounds having a grain size less than .065 mm., in an electrolyte comprising an alkali metal hydroxide solution, and adding a metal of the group consisting of manganese, nickel, molybdenum, and tungsten to the electrolyte in the form of an anhydrous ferro-oxygen compound containing the metal to be added, and subjecting the resulting fluid to electrolysis at a temperature of about 100° C. to electro-deposit an iron alloy at the cathode.
3. A method of electrically producing an alloy of iron comprising forming a suspension of an anhydrous ferro-oxygen compound in finely divided state in an electrolyte, comprising an alkali metal hydroxide solution, adding a metal of the group consisting of manganese, nickel, tungsten and molybdenum to the electrolyte in the form of an anhydrous ferro-oxygen compound containing the metal to be added and subjecting the resulting fluid to electrolysis at a temperature of about 100° C. to electro-deposit an alloy of iron at the cathode.
4. A process of electrically producing iron in a state adapted to be easily pulverized comprising forming a suspension of an anhydrous ferro-oxygen compound in finely divided state in an electrolyte of concentrated alkaline lye, intensely agitating said suspension so as to cause said compounds to gradually dissolve in the electrolyte, subjecting the resulting fluid to electrolysis at a temperature of approximately 100° C. to electro-deposit the iron at the cathode while using insoluble anodes and loading the anodes with a higher current density than that of the cathodes.
5. A method of electrically producing iron alloyed with another metal in a stated adapted to be easily pulverized comprising forming a suspension of an anhydrous ferro-oxygen compound together with an oxide compound of one of the metals of the group consisting of manganese, nickel, tungsten and molybdenum to a grain size less than .05 mm., forming a suspension of the ground material in an alkaline electrolyte containing at least 37 per cent of alkali hydroxide, and subjecting the suspension to electrolysis at a temperature of approximately 100° C. to electro-deposit the metals at the cathode while continuously agitating the electrolyte and its content of solid particles to bring the latter in solution at substantially the same rate as the metals are deposited on the cathode.
6. A process of electrically producing iron alloyed with another metal in a state adapted to be easily pulverized, which comprises grinding an anhydrous iron ore containing a compound of a metal of the group consisting of manganese, nickel, tungsten and molybdenum to a grain size less than .05 mm., forming a suspension of the ground material in an alkaline electrolyte containing at least 37 per cent of alkali hydroxide, and subjecting the suspension to electrolysis at a temperature of approximately 100° C. to electro-deposit the iron and said other metal on the cathode while continuously agitating the electrolyte and its content of solid particles to bring the latter in solution at substantially the same rate as the metals are deposited on the cathode.
7. A process of electrically producing iron in a state adapted to be easily pulverized from an anhydrous ferro-oxygen compound which comprises, partially reducing said anhydrous ferro-oxygen compound, grinding said anhydrous ferro-oxygen compound to a grain size less than .05 mm., forming a suspension of the ground material in an alkaline electrolyte containing
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at least 37 per cent of alkali hydroxide and
subjecting the suspension to electrolysis at a
temperature of approximately 100° C. to electro-
deposit iron at the cathode while continuously
agitating the electrolyte and its content of solid
particles to successfully bring the latter in
solution at substantially the same rate as the
iron is deposited on the cathode.

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