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Roorda et al.

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[54] **EXTRACTION OF METALS FROM IRON OXIDE MATERIALS**

[75] Inventors: **Herm Jan Roorda**, Rijswijk, Zuid, Netherlands; **Paul Etienne Queneau**, Fairfield, Conn.; **Stanley Charles Townshend**, Ammanford, Wales

[73] Assignee: **The International Nickel Company, Inc.**, New York, N.Y. ; by said Paul Etienne Queneau and Stanley Charles Townshend

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[21] Appl. No.: **410,611**

Related U.S. Application Data

[63] Continuation of Ser. No. 187,077, Oct. 6, 1971, abandoned.

[52] **U.S. Cl.** **423/35**; 75/112; 75/117; 75/119; 423/21; 423/10; 423/46; 423/40; 423/150; 423/151

[51] **Int. Cl.** **C22b 15/00**; C22b 23/04

[58] **Field of Search** 75/112, 117, 119; 423/40, 423/149, 153, 23, 27, 38, 46, 493, 496, 150, 151; 42/35

[56] **References Cited**

UNITED STATES PATENTS

350,669	10/1886	Endlich et al.	423/40
489,575	1/1893	Thompson	423/153
1,011,899	12/1911	Ashcroft	423/149
1,103,747	7/1914	Fierz	423/149
1,822,995	9/1931	Meyer	75/112
1,833,686	11/1931	Meyer	75/112
1,990,299	2/1935	Meyer	423/40
2,067,874	1/1937	Brown et al.	75/112
2,341,873	2/1944	Kissock	75/114
2,829,966	4/1958	Reynaud et al.	423/40
3,607,236	9/1971	Brooks et al.	75/112

FOREIGN PATENTS OR APPLICATIONS

15,799	8/1935	Australia	75/112
795,410	5/1958	United Kingdom	75/112

Primary Examiner—Edward J. Meros
Assistant Examiner—Gary P. Straub

[57] **ABSTRACT**

Non-ferrous metal values, such as nickel, cobalt or copper, contained in oxide ores, or roasted sulfide ores, that also contain iron, are selectively reduced to the metallic state, and the selectively reduced metal values are reacted with molecular chlorine by passing gaseous chlorine through an aqueous pulp of the reduced ore to produce a pregnant solution containing the chlorinated metal values from which solution the metal values can be recovered.

8 Claims, 4 Drawing Figures

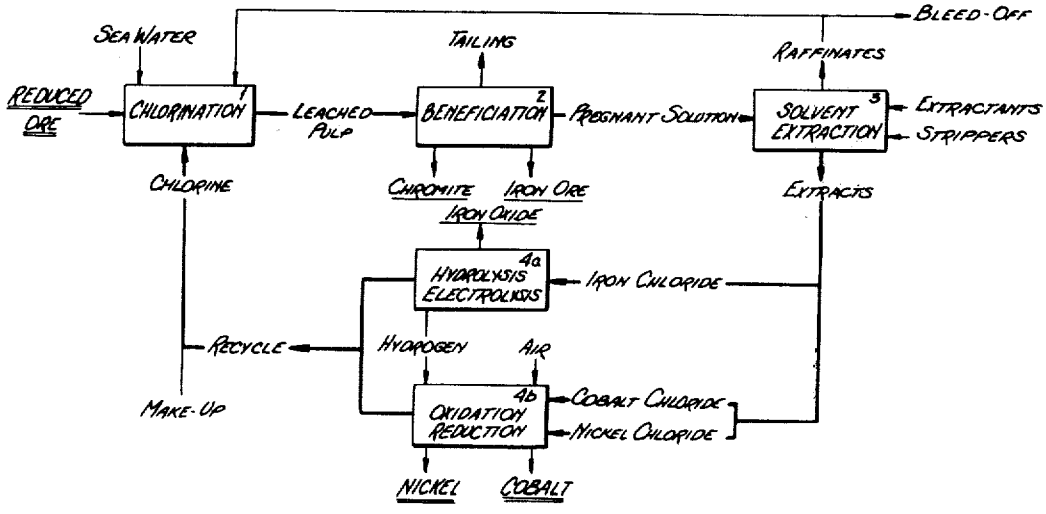


Fig. 1.

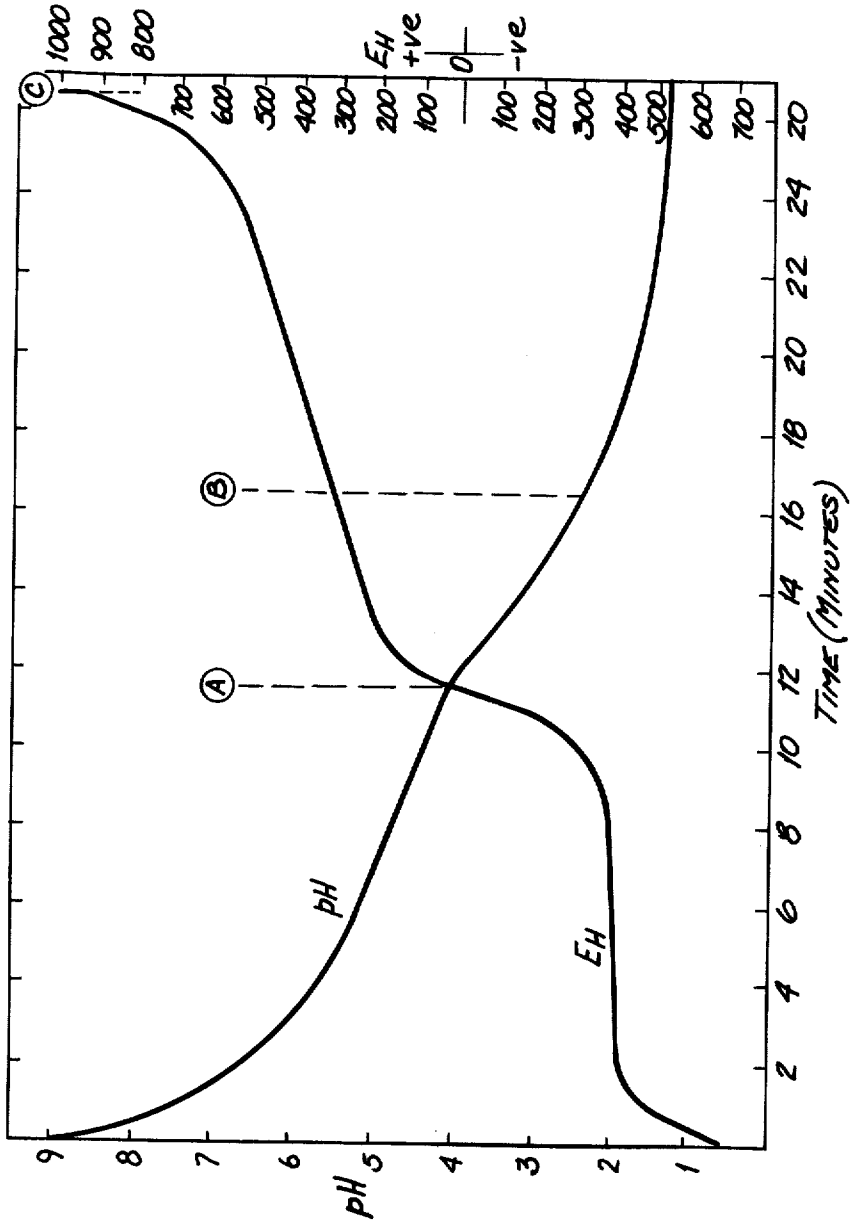
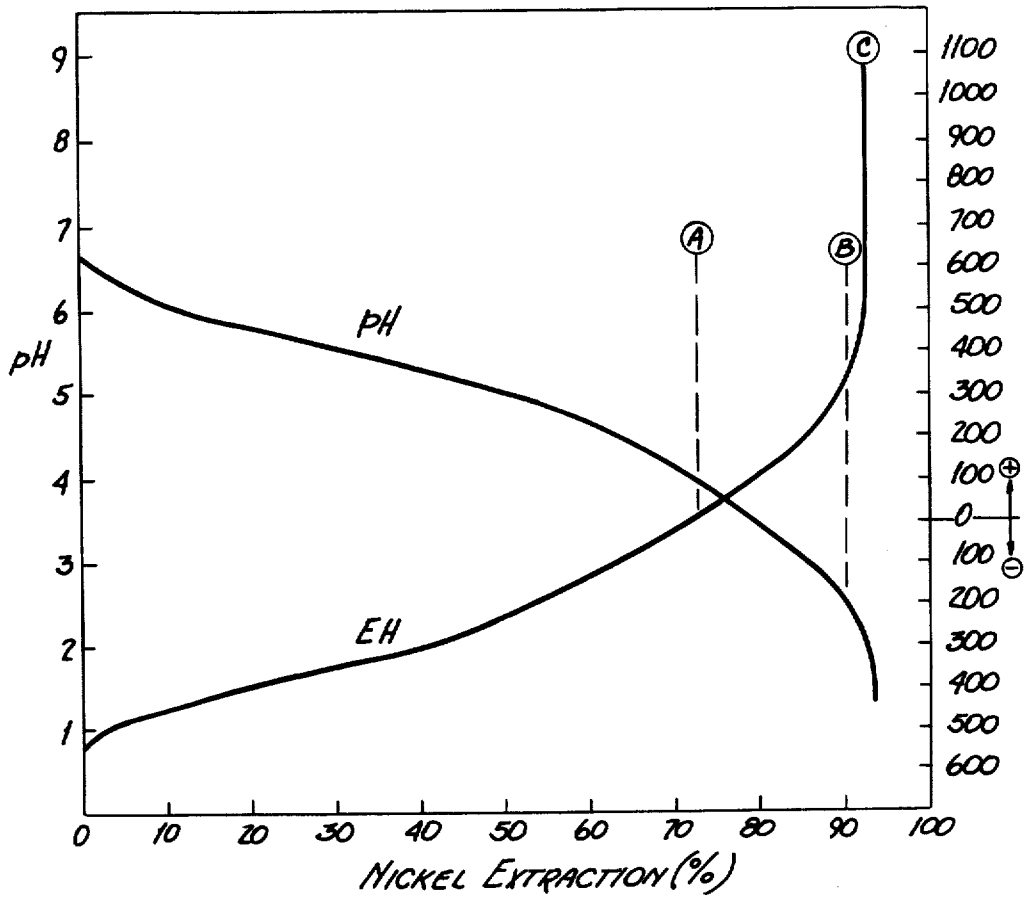

1000
900
800
700
600
500
400
300
200
100
0
100
200
300
400
500
600
700
EH
+ve
-ve
C
B
A
pH
EH
9
8
7
6
5
4
3
2
1
pH
2
4
6
8
10
12
14
16
18
20
22
24
TIME (MINUTES)

Fig. 2A.


pH
EH
A
B
C
pH
9
8
7
6
5
4
3
2
1
1100
1000
900
800
700
600
500
400
300
200
100
0
100
200
300
400
500
600
0
10
20
30
40
50
60
70
80
90
100
NICKEL EXTRACTION (%)

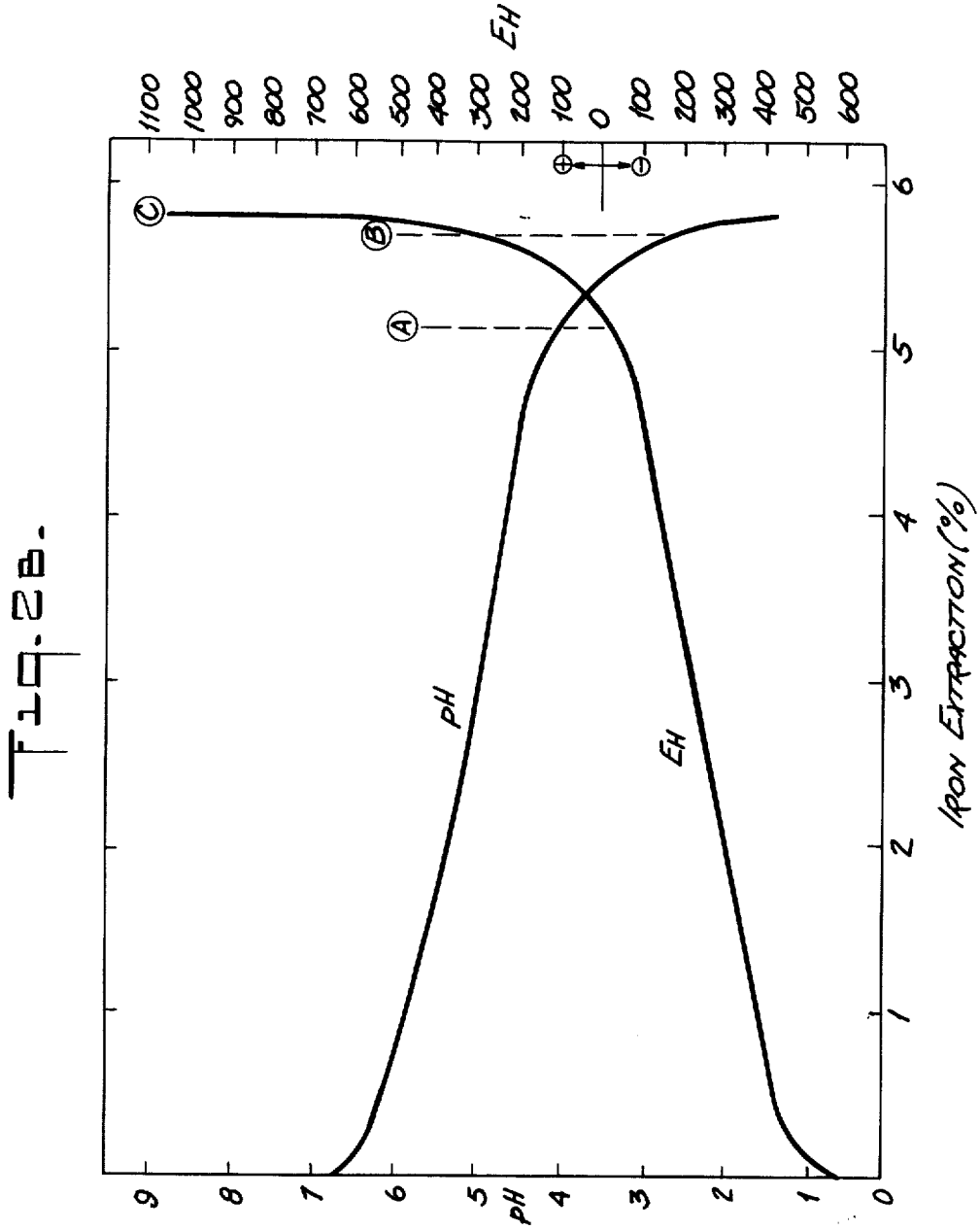
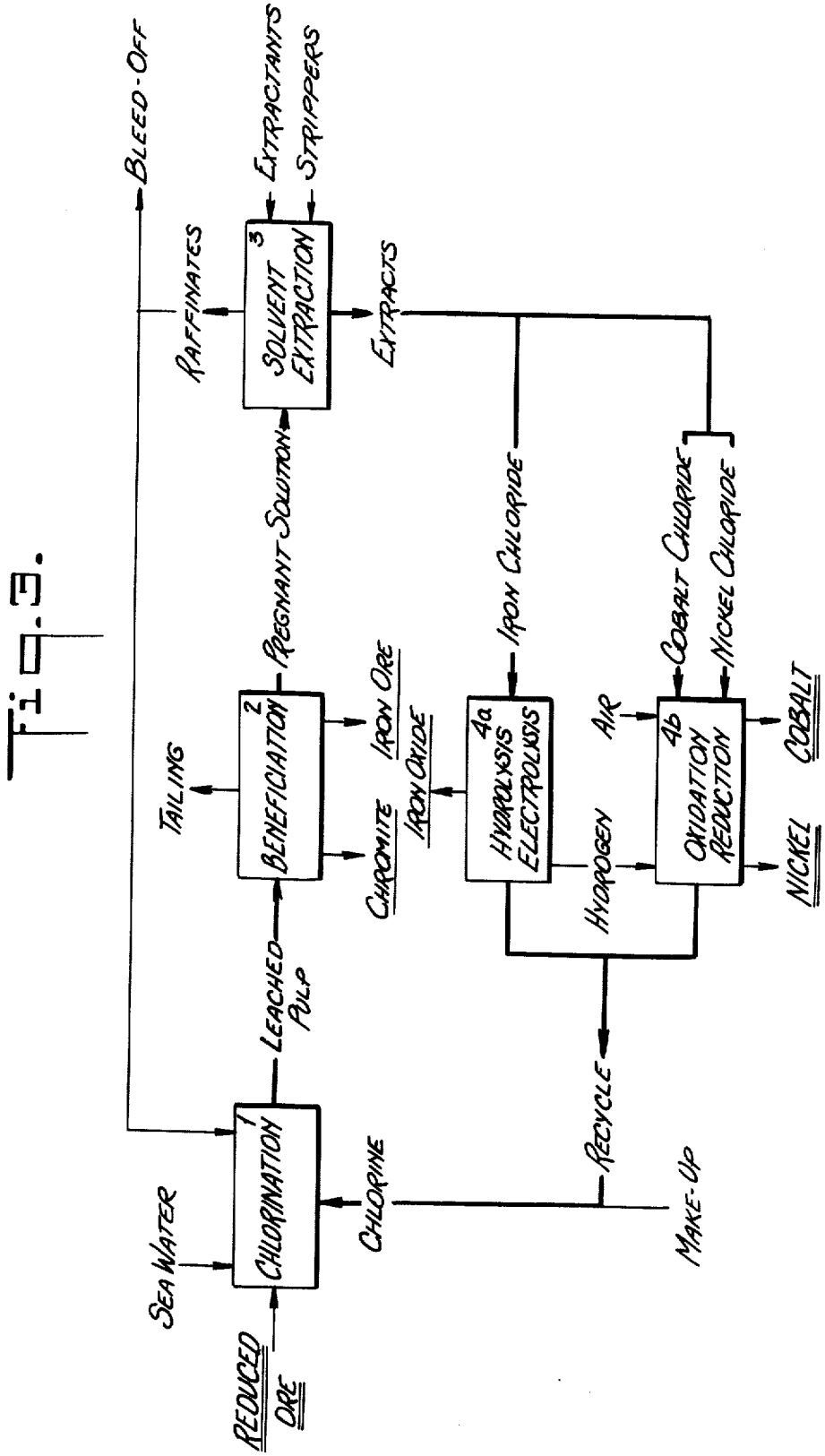

EH
1100
1000
900
800
700
600
500
400
300
200
100
0
100
200
300
400
500
600
C
B
A
pH
EH
9
8
7
6
5
4
3
2
1
0
pH
6
5
4
3
2
1
IRON EXTRACTION (%)

FIG. 2B.

Fig. 3.


BLEED-OFF
EXTRACTANTS
STRIPPERS
RAFFINATES
3
SOLVENT EXTRACTION
EXTRACTS
PREGNANT SOLUTION
IRON CHLORIDE
COBALT CHLORIDE
NICKEL CHLORIDE
TAILING
2
BENEFICIATION
IRON ORE
IRON OXIDE
CHROMITE
4a
HYDROLYSIS ELECTROLYSIS
AIR
4b
OXIDATION REDUCTION
COBALT
NICKEL
HYDROGEN
LEACHED PULP
1
CHLORINATION
RECYCLE
SEA WATER
CHLORINE
MAKE-UP
REDUCED ORE

EXTRACTION OF METALS FROM IRON OXIDE MATERIALS

This is a continuation, of application Ser. No. 187,077, filed Oct. 6, 1971, and now abandoned.

The present invention relates to the recovery of one or more of nickel, cobalt and copper from oxide materials that contain substantial amounts of iron, and more particularly to a combination of pyrometallurgical and hydrometallurgical treatments for recovering nickel, cobalt and/or copper from oxide materials containing the same and substantial amounts of iron.

The metals nickel, cobalt and copper commonly occur in ores, concentrates and metallurgical intermediates in association with much larger proportions of iron. Important examples are the nickeliferous laterites and nickeliferous, cobaltiferous and cupriferous pyrites and pyrrhotite and other sulphide minerals and concentrates, including those containing other elements such as arsenic. It is highly desirable that any process for treating such materials to recover the metal values should extract a large proportion of the non-ferrous metals accompanied by only a small proportion of the iron.

High cobalt recovery from such materials has been a long-sought objective but is particularly difficult to achieve by simple and economic methods applicable to a wide variety of materials.

For instance, Caron's pioneering development of his ammonia-leaching process for the treatment of selectively reduced oxide nickel ores was directed to the recovery of cobalt as well as the nickel. The process developed by Van Nes and Heertjens based on the direct selective chloridisation of the same types of ore by means of hydrochloric acid-steam mixtures also emphasises the importance of high cobalt recovery.

However, these and other processes are not entirely satisfactory for cobalt extraction on a commercial scale either because cobalt recovery is inadequate or because they lack desirable simplicity and flexibility.

Moreover, when the iron content of the material is sufficiently high, it should also leave substantially all of the iron available in a form suitable for further processing to metallic iron or steel.

It has now been discovered that iron-bearing oxide materials containing non-ferrous metal values, e.g., nickel, copper, cobalt, etc., can be pyrometallurgically and then hydrometallurgically treated to recover substantially all the non-ferrous metal value and only minor amounts of iron.

It is an object of the present invention to pyrometallurgically and hydrometallurgically heat ferruginous oxide materials containing non-ferrous values to recover substantially all the non-ferrous values and only limited amounts of iron.

Another object of the present invention is to provide a process for pyrometallurgically and hydrometallurgically treating nickeliferous and cobaltiferous lateritic ores, particularly nickeliferous and cobaltiferous limonitic ores, to recover substantially all the nickel and cobalt and only minor amounts of iron.

Yet another object of the present invention is to provide a process for recovering non-ferrous metal values contained in roasted ferruginous sulfide ores, ore concentrates or other metallurgical intermediates to recover a preponderant part of the non-ferrous metal values and only controlled amounts of iron.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawings in which:

FIG. 1 is a graphical representation of the variation of the hydrogen iron concentration, pH, and the redox potential, E_H, with time when chlorine reacts with a reduced nickeliferous ore in an aqueous suspension;

FIGS. 2*a* and 2*b* depict the changes in pH values and redox potentials that occur as increasing amounts of reduced nickel and iron values, respectively, are dissolved after reacting with chlorine; and

FIG. 3 is a flowsheet illustrating an advantageous embodiment for treating nickeliferous and cobaltiferous lateritic ores to recover substantially all the nickel and cobalt values and only minor amounts of iron.

Generally speaking, the present invention contemplates a process for recovering non-ferrous metal values from oxide materials containing substantial amounts of iron. The process comprises selectively reducing the oxide material to convert to metal substantially all of the non-ferrous metal values and only controlled amounts of iron. The metallic non-ferrous metal values and iron ore contacted with molecular chlorine to form chlorides of the non-ferrous metal and iron, and the chlorides are continually dissolved from the ore to constantly expose fresh surfaces for continuing the reaction between molecular chlorine and the non-ferrous metal and iron.

The present invention is based on the discovery that when ferruginous oxide materials containing non-ferrous metal values are reduced, if necessary after roasting in convert sulphides, arsenides and the like to oxides, and gaseous chlorine is reacted with the reduced material suspended in an aqueous bath under controlled conditions, substantially all the nickel, cobalt, copper and iron that are in the metallic form are rapidly and selectively converted to their respective chlorides and go into solution, while substantially all the iron present as oxides remains undissolved.

According to the invention an oxide material containing iron together with a substantially lesser amount of one or more of nickel, cobalt and copper is selectively reduced so as to convert to metal substantially all of the nickel, cobalt and copper but only a minor proportion of the iron present, and metallic nickel, cobalt, copper and iron are chlorinated and taken into solution by passing gaseous chlorine into an aqueous immersion of the reduced material. The resulting pregnant chloride solution, if desired after separation from the solid residue containing the bulk of the iron and other oxides, can then be treated for recovery of the nickel, cobalt and copper.

It is an important feature of the invention that the free metals in the reduced oxide material are converted to chlorides by the action of chlorine. Such metals can of course also be attacked and dissolved by the action of acids, for example hydrochloric acid, but acids also attack and dissolve iron oxide and other metal oxides, resulting in a much less selective extraction of the nickel, cobalt and copper values. It is therefore important that the immersion medium should not contain a significant amount of free acid. As will be explained in more detail below, the pH of the immersion medium can fall to quite a low value, e.g., to below pH 2, during the reaction of the chlorine with the reduced material. It has been found however that this does not lead to substantial attack on iron oxides in the reduced mate-

rial, and the presence of trace amounts of free acid formed during the chlorination is not significant. In contrast to this, the introduction of even small additional amounts of acid can lead to excessive dissolution of oxidic iron even at pH values higher than those resulting from the action of chlorine alone.

The process is of particular advantage for treating materials containing large proportions of iron, for example those in which the weight ratio of iron to the combined total of nickel, cobalt and copper is more than about 20:1, but it is also useful for materials in which this ratio is lower, e.g., even as low as about 10:1. A wide variety of iron-bearing materials can be treated and included in the term oxide materials are the oxide ores of nickel, including limonitic and silicate types, and also oxide materials produced artificially by roasting nickeliferous, cobaltiferous and cupriferous sulphide ores, concentrates and metallurgical intermediates, e.g., slags, whether or not such materials contain other elements such as arsenic.

The roasting of sulphide materials such as pyrites and pyrrhotite concentrates and mattes to form oxide materials suitable for treatment should be carried out in air or other gas containing free oxygen. Generally speaking, roasting temperatures of at least about 600°C. and up to about 1000°C. may be used, but in any event the temperature should be above that at which the metals form stable sulphates in the atmosphere used. Advantageously the roasting temperature is in the range between about 700°C. and 900°C. In order to obtain a readily reducible calcin when roasting pyrrhotite, however, the temperature should not exceed about 800°C. The roasting should be continued until the sulphide content of the material is as low as practicable, e.g., less than about 1% and most advantageously less than about 0.2%.

Methods of selectively reducing oxide materials containing iron and one or more of nickel, cobalt and copper are well known. In the process of the present invention the selective reduction should be so carried out that substantially all the nickel, cobalt and copper compounds present is reduced to the metallic state while as little as practicable of the iron and other oxides is so reduced. However, in order to reduce substantially all the nickel, cobalt and copper some iron must also be reduced to metal. The ratio of metallic iron to the total amount of metallic nickel, cobalt and copper in the reduced material is usually at least about 1:1 by weight, but preferably this ratio does not exceed about 3:1 or more and advantageously it does not exceed about 2:1. In any case, to avoid the dissolution of excessive amounts of iron and the consequent excessive consumption of chlorine the ratio should be less than about 5:1. The remainder of the iron oxide will be reduced to magnetite (Fe_3O_4) and wustite (FeO) in varying proportions.

It will be appreciated that the rate and extent of the reduction will depend on the temperature, the strength of the reducing atmosphere and the duration of the reduction and the nature of the material being treated, and these must be correlated so as to maximise reduction of the non-ferrous metal compounds to the metallic state while minimising the amount of iron oxide reduced to metal. If the atmosphere is too strongly reducing, the temperature too high or the duration too long, too much iron oxide will be reduced to metal, while the use of an atmosphere having too low a reducing potential results in a decrease in the rate and extent of reduction to metal of the nickel, cobalt and copper compounds. Generally speaking, the temperature in the reduction operation should be below about 950°C. but above about 500°C., advantageously in the range between about 600°C. and 850°C., and the reduction can be carried out in a selectively reducing atmosphere having a reducing potential equivalent to that of a gas containing carbon monoxide and carbon dioxide in a ratio of more than about 1:6 and less than about 2:1, advantageously not more than about 1:1, by volume.

It will be appreciated by those skilled in the art that the desired selective reduction can also be effected with the use of a non-selective reducing gas such as hydrogen by kinetic control of the reaction.

Subject to these considerations, any convenient procedure for selective reduction can be employed. Thus the reducing atmosphere can be a gas mixture generated outside or inside the reduction vessel, or can even be generated in contact with the material to be reduced by the cracking of oil sprayed on to it or from coal admixed with the material.

The reduction conditions for the best results will also depend on the nature of the material being reduced. Thus a nickeliferous limonite ore can advantageously be reduced in the temperature range between about 600°C. and 800°C. For nickeliferous magnesium silicate ores the rate of heating and the extent of reduction within the temperature range at which the hydrated silicates decompose, generally between about 400°C. and 800°C., should be balanced in known manner so as to minimize formation of nickel-containing silicates which can only be reduced with very great difficulty. Moreover a high final temperature, e.g., about 750°C. or above, is generally desirable during the reduction of such ores to ensure that the MgO has been substantially fixed by reaction with silica and other oxides so as to form inactive silicate. Failure to fix MgO in this way can lead to the excessive formation of magnesium chloride during the chlorination, involving increased chlorine consumption and the risk of other disadvantages. The use of high final temperatures improves reduction kinetics, facilitates combustion control of hydrocarbons (particularly liquid hydrocarbons) and enhances solid-liquid separations that follow leaching. In treating silicate ores, small amounts of such agents as pyrites and sodium chloride can, if desired, be added before the reduction to facilitate the operation in known manner.

The limonite and silicate ores of nickel commonly occur together, and it can, therefore, be advantageous to separate them in known manner so that each type of material can be reduced under the most suitable conditions. It may also be advantageous to treat only the limonite fraction of such mixed ores by the present process.

The reduced material should be cooled under conditions such that metallic nickel, cobalt and copper are not re-oxidised, e.g., under a protective atmosphere. If desired, the hot reduced material can be subjected to slow cooling under a protective atmosphere in known manner to cause disproportionation of wustite into metal and magnetite. Nickel and cobalt in the FeO lattice are thus set free as metal and become available for extraction so that less remains in the iron oxide residue.

If excessive amounts of metallic iron are present the reduced material can be selectively reoxidised to con-

vert part of the metallic iron to iron oxides, for example by treatment below the reduction temperature with an atmosphere rich in carbon dioxide or water vapour. Thus, the hot reduced material can be rapidly cooled by direct contact with water, e.g., by spraying, so as to generate steam which serves to reoxidise part of the iron. The attack by the chlorine in the present process is so aggressive that this treatment does not appreciably interfere with the extraction of nickel, cobalt or copper, although it could passivate the reduced material against reaction with such reagents as ammonia and carbon monoxide.

The reduced material, if necessary after comminution, is then immersed in an aqueous medium, and gaseous chlorine, alone or admixed with other gases, is reacted with the reduced material in the immersion to convert the metals to their chlorides. The aqueous medium can be water from any convenient source, and can contain chloride in solution, in a concentration of up to 20% or more by weight. Thus, sea water can be employed in place of fresh water; strong brine can be used to promote the formation of stable anionic complexes of cobalt and iron in solution; or a chloride solution produced by a previous chlorination in accordance with the invention can be used in order to obtain a more concentrated solution of the metals.

If the reduced material is finely divided it can be formed into a suspension in the aqueous medium. In any event care should be taken to ensure good contact between the solid, liquid and gas phases and to avoid localised variations in temperature, pH and concentration, and for this purpose vigorous agitation is desirable. Agitation can be effected by mechanical stirring, pneumatically by cascading in contact towers or by any other convenient means.

The rate at which the metals react with chlorine increases with temperature; and although the chlorination can be carried out at any convenient temperature up to and including the boiling point of the immersion medium, the temperature of the immersion is advantageously at least about 65°C., for example in the range between about 75°C. and 95°C. From the standpoint of heat balances, the optimum immersion temperature for commercial operations is about 80°C., at which temperature provisions for cooling are not required and low viscosity pregnant solutions that are easily filtered after leaching are obtained.

The chlorination is most conveniently carried out at atmospheric pressure, but if desired elevated pressures, e.g., up to about 10 atmospheres, can, in appropriate circumstances, be advantageously used. As will be explained in more detail hereinafter, the rate of reaction of the metals with chlorine decreases as chlorination proceeds, and it can, therefore, be advantageous to employ elevated pressures after a substantial part of the metals has been chlorinated and dissolved. It can also be advantageous to employ elevated pressures in the chlorination of reduced materials containing residual amounts of sulphides, for example those remaining as a residue from the roasting of sulphidic starting materials, or introduced from fossil fuel used to generate the atmosphere used for the selective reduction.

The chlorine passed into the immersion reacts directly and rapidly with the metals present in the reduced material, which are continually leached out of it and go into solution as chlorides. In a batch process, as the chlorination proceeds the pH of the solution progressively falls and the redox potential E_H increases in accordance with the European convention, signifying that the oxidizing potential is increasing. The variation of pH and E_H with time is illustrated by the curves in FIG. 1 of the accompanying drawings, which are typical of the changes taking place when chlorine is passed at a constant rate into a suspension of a reduced nickeliferous limonite ore in water under laboratory batch leaching conditions. The curves in FIGS. 2*a* and 2*b* of the drawings show the relationship of the changes in pH and E_H to the proportions of the nickel and iron going into solution. Unless expressly stated otherwise, the size of the redox potential E_H is in accordance with the International Convention.

The aqueous suspension is initially substantially neutral or slightly alkaline, e.g., a pH value between about 7 and 9. Dissolution of nickel, cobalt and iron begins at about pH 6.5, and proceeds rapidly until at about pH 4 about 70% of the nickel is in solution. This is indicated by point A on the curves. Up to this point the chlorine reacts substantially stoichiometrically with the metals.

With continued passage of chlorine, leaching of the free metals continues, though at a decreasing rate. The pH continues to fall and the E_H to increase until at about pH 2.5 and E_H +300 mv, indicated by point B in FIGS. 1, 2*a* and 2*b*, all but a small fraction of the metals has dissolved. Hence it is advantageous in this case to perform at least a substantial part of the chlorination at pH value below about 4, and to obtain the optimum nickel and cobalt extractions the chlorination should be continued down to a pH value of about 2.5. At this stage substantially all the iron in solution is in the ferrous state.

The addition of further chlorine results in oxidation of the ferrous iron to ferric, with a steep increase in E_H to a value of about +1,000 mv. that indicates the presence of free chlorine and a decrease of pH to a final value that depends on the concentration and temperature of the solution but is generally below 2 but above 1. At this stage (c) chlorination is complete and substantially all the iron in solution has been oxidised to the ferric state, and the solution of metals is virtually complete.

It will be seen that the progress of the chlorination can be monitored for control purposes by means of the pH and oxidation potential of the aqueous medium, by determining the concentration of chloride ion or other ions in solution by means of ion-specific electrodes, as well as by determining the chlorine content of the off-gases and by the consumption of chlorine.

Although the chlorination has been discussed in relation to a batch process in which the pH and oxidation potential vary on an industrial scale it is advantageously done continuously in a system in which the additions of chlorine, reduced material and immersion medium, and the withdrawal of solids and pregnant solution, are correlated so as to maintain a steady state. The chlorination can with advantage be performed in two or more stages controlled at successively lower pH and higher E_H values, the pH in each stage being maintained at a substantially constant value in the range between 1 and 4. Thus the initial rapid reaction to dissolve up to say three-fourths of the nickel, cobalt and copper can be carried out in the first stage, followed by further extraction in one or more subsequent stages in suitable reactors, if desired at elevated pressure.

Means that can be used to control the chlorination in both batch and coninuous operation include variation of the rate of introduction of chlorine, of its partial pressure and of the total gas volume employed. For this purpose inert gas, air or oxygen can be introduced together with the chlorine.

In the last stage of the reaction beyond the point B on the curves chlorine is consumed in oxidising ferrous to ferric iron, with little further extraction of the nickel, cobalt and copper. With some materials, the relatively low pH of the resulting solution can lead to impaired liquid-solid separation. To avoid this additional chlorine consumption and other possible disadvantages, the chlorination can be terminated when dissolved iron begins to be oxidised to the ferric state. For any given system this is indicated by the E_H value. Thus, in continuous chlorination the last stage can advantageously be so controlled that the E_H is maintained at this value, usually in the pH range of about 2 to 3.

Alternatively, if it is important to extract the greatest possible amount of nickel, cobalt and copper, e.g., to meet a specification on residue analysis or for purposes of subsequent treatment of the solution, the chlorination may be continued until oxidation of ferrous to ferric iron is complete. As already indicated, the final pH will then usually be below about 2 but above about 1.

A solution in which all or part of the dissolved iron is in the ferric state can, after separation from the solid residue, be used to leach fresh reduced material so as to dissolve nickel, cobalt or copper therefrom. For example, nickel can be dissolved by the reaction

$$Ni + 2\ FeCl_3 \rightarrow NiCl_2 + 2\ FeCl_2$$

This leaching can conveniently be carried out as part of a multistage process. In the first stage reduced material from which part of the nickel, cobalt and/or copper has been extracted by this means is immersed in water and chlorinated by means of chlorine to yield a fully extracted residue and a pregnant solution containing ferric iron. In a subsequent stage this pregnant solution is used to leach fresh reduced material, yielding a final solution containing a higher concentration of nickel, cobalt and/or copper together with ferrous chloride and a partly extracted residue that is transferred to the first stage for chlorination.

Yet another way of carrying out the process of the invention is to terminate the chlorination before solution of the metals is complete and then to pass gas containing free oxygen through the immersion to dissolve further nickel, cobalt and copper by a reaction such as

$$2\ Ni + 2\ FeCl_2 + 3/2\ O_2 \rightarrow 2\ NiCl_2 + Fe_2O_3$$

Preferably the chlorination is stopped when the solution contains sufficient dissolved ferrous iron to react with all the remaining metallic nickel, cobalt and copper. If the pH of the solution during the treatment with oxygen is too low the oxidation proceeds very slowly, while if it is too high nickel, cobalt or copper will be coprecipitated with the iron. Advantageously, therefore, the pH is maintained in the range of about 3 to 4 during the oxidation. The temperature during the oxidation should preferably be at least about 80°C. Oxidation is most conveniently carried out at atmospheric pressure, but elevated pressures, e.g., up to about 10 atmospheres or more, can be used with kinetic advantages.

The very high rate at which the metals react with chlorine in aqueous immersion enables such techniques as leaching of the solids in contacting towers or fluid-bed extractors or on continuous filters to be used. One attractive method, at least for the first stage of chlorination, is to employ countercurrent leaching in a contacting tower down which the immersion is passed in countercurrent to an upwardly-flowing stream of chlorine-containing gas.

The concentration of nickel, cobalt and copper chlorides in the pregnant solution formed by chlorine leaching will depend in part on the solid-liquid ratio, i.e., the pulp density in the case of a suspension, and advantageously this is as high as practicable.

The residue remaining after the chlorine leaching will contain only small amounts of nickel, cobalt and copper, and the treatment or ores of high iron content, e.g., nickeliferous limonite containing over 45% or more iron, yields a residue rich in iron oxide. Such a residue, if it is sufficiently rich in iron and is sufficiently free from rock and deleterious impurities, e.g., if it contains more than about 50% iron and less than about 10% silica, can be processed for use as a source of iron for iron and steel making. It is an advantage of the process that elements such as zinc and lead that are deleterious in iron and steel manufacture will, if present in the starting material, have been dissolved as chlorides so that they do not appear in the iron oxide residue. Chromium and aluminum, which may be present in the ore as impurities, e.g., as chromite, can be removed by known methods either before or after reduction and chlorination. Such methods include physical beneficiation procedures such as gravity separation, screening, flotation and magnetic separation, and alkaline roasting, e.g., with sodium carbonate, and leaching with water. Combinations of these methods can of course be used.

The pregnant solution containing one or more of nickel, cobalt and copper together with some iron as chlorides can be treated in any desired manner to separate and recover the metal values. If desired the pregnant solution is first separated from the solid residue. Because of the prior selective reduction treatment, this residue generally has a high content of magnetite which facilitates solid-liquid separation and iron oxide-silicate separation by magnetic means.

Iron can be removed from solutions in which it is present in the ferric state by precipitation as oxide, hydroxide or carbonate by the addition of alkali, e.g., lime or limestone. In doing so the pH should generally not be raised above about pH 4, otherwise some nickel, cobalt and/or copper may also be precipitated from the solution.

Again, when the chlorination is performed so as to yield a pregnant solution containing ferrous iron, part of this iron can be oxidised to the ferric state and precipitated by passing gas containing free oxygen through the solution at a suitable pH, advantageously above 3, either before or after separation of the solution from the solid residue. The pH can be adjusted, for example, by the addition of alkali.

A preferred way of separating the metal values is to remove nickel, cobalt, copper or iron from the solution in known manner by means of suitable organic extractants. This can be done either before or after separating the solution from the solid residue, but advantageously the solid residue is first removed and the nickel, cobalt and copper are separated from each other and from iron in the pregnant solution by means of the organic extractants. Stripping of the loaded organic extract-

ants, e.g., by means of aqueous salt solutions, yields aqueous solutions of the metal chlorides. These can be hydrolysed or oxidised to their hydrates or oxides and then reduced to metal or the metal chlorides can be reduced to metal with hydrogen. Extraction with organic agents has the advantage of avoiding the problems arising in precipitation procedures. The chloride solutions of the present invention are particularly amenable to treatment by solvent extraction. Furthermore, as a result of their prior chlorination, the accumulation of organic matter such as bacteria and algae at the solvent-solution interface is inhibited.

As an alternative, the nickel, cobalt and copper and, if desired, any dissolved iron can be simultaneously or selectively precipitated from the pregnant solution, after its separation from the solid residue, as sulphides, carbonates or hydroxides. These can then be treated to isolate the metals by known means, such as those based on carbonylation or fire refining.

For instance, impure nickel sulphide precipitate can be refined by roasting, reduction and carbonylation under elevated pressure as described in British Pat. No. 915,188. Again, a selectively precipitated hydrate of nickel containing some cobalt, copper and iron can be reduced to metal and refined by carbonylation at atmospheric pressure. Yet again impure nickel sulphide precipitate can be melted and cleansed of its cobalt, copper and iron contents in known manner by fused chloride salt solvent extraction and the raffinate surface-blown to nickel metal by means of oxygen-rich gas as described in British Pat. No. 960,698.

Other known means that can be used to recover and separate the metals in the pregnant solution include electrolysis, evaporation-crystallisation, reverse osmosis, electrodialysis and cementation.

Other valuable metals, e.g., manganese, magnesium, aluminum and precious metals dissolved as chlorides from the reduced material can also be recovered from the solution.

Chlorine can be recovered from the chlorides, and advantageously is recycled. Methods of chlorine recovery that can be used include thermal hydrolysis of the chlorides, direct conversion of chlorides to oxides and chlorine with oxygen-containing gas at elevated temperatures, and reduction of the chlorides with hydrogen, preferably after separation, to form metal and hydrochloric acid, which then can be electrolysed or catalytically oxidised to chlorine.

One overall procedure according to the invention including the recovery and recycling of chlorine will now be described with reference to the flow sheet forming FIG. 3 of the accompanying drawings. Although this procedure is particularly suited to the treatment of a nickeliferous limonite containing nickel and cobalt together with chromite, it will be appreciated that with appropriate modification it can be applied to materials containing any one or more of nickel, cobalt and copper, whether or not they contain chromium.

The selectively reduced ore is suspended or otherwise immersed in sea-water and, if desired, recycled raffinate and the reduced values are chlorinated by passing a chlorine-containing gas through the immersion in Step 1, the chlorination being continued until substantially all the metallic nickel, cobalt and iron have been dissolved as chlorides but no significant amount of the iron in solution has been oxidised to the ferric condition. In Step 2 the chlorinated immersion is then beneficiated to separate a concentrate of the chromite present in the ore, and the pregnant solution containing the nickel and cobalt is separated from the iron ore residue and passed to the solvent extraction Step 3.

Nickel, cobalt and iron are then extracted from the pregnant aqueous solution in Step 3 by means of suitable organic extractants, and are stripped from the loaded organic solutions to recover separate aqueous solutions of nickel, cobalt and iron chlorides. These chlorides are hydrolysed or directly oxidised in Step 4 to form nickel and cobalt oxides, which are then hydrogen-reduced to metals, and iron oxide, which is combined with the iron ore residue from Step 2. Alternatively, the nickel and cobalt chloride solutions can, if desired, be reduced directly to the metals by means of hydrogen.

The hydrochloric acid formed by the hydrolysis of iron chloride is electrolysed in known manner in Step 4*a* to form chlorine, which is recycled together with any chlorine formed in Step 4*b*, to Step 1. Hydrogen formed in the electrolysis can be used for reduction of the nickel and cobalt oxides or salts to the metals. All or part of the stripped aqueous solution (the raffinate) resulting from the liquid-liquid extraction of the pregnant aqueous solution in Step 3 can be returned to Step 1 where it is combined with sea water to form the immersion of reduced ore. Bleed-off from the raffinate can be scavenged for copper and other metal values, e.g., magnesium and aluminum, and discharged, e.g., into the sea.

Some examples will now be given.

EXAMPLE 1

Ten grams of a nickeliferous limonite ore containing, by weight, 1.5% nickel, 0.18% cobalt, 46% iron, 0.85% manganese, 1.2% MgO and 0.7% CaO, i.e., a ratio of Fe to Ni + Co of 27:1, was ground finely enough to pass through a 100 mesh B.S. screen. The ground material was selectively reduced by heating it up to 750°C. during one-half hour in a stream of a gas mixture containing, by volume, 30% carbon dioxide, 15% hydrogen and 55% nitrogen, and then heating it at 750°C. in the same gas stream for a further 4 hours. The reduced ore was cooled rapidly in a current of nitrogen and the proportions of nickel, cobalt and iron that had been reduced to metal were determined. It was found that 95% of the nickel, 91% of the cobalt and 6% of the iron were present as metals, i.e., a ratio of Fe to Ni + Co of 1.7:1 by weight.

The reduced material was suspended in 100 ml. of water, the suspension was heated to 80°C. and chlorine gas was passed into it at a constant rate of 1 litre/hour with stirring, the pH being monitored by means of a glass electrode and the E_H by means of a platinum electrode, using a calomel reference electrode in each case. The initial pH of the suspension was 8.0 and the initial E_H was −500 mv. During 14 minutes the pH gradually fell to 2.5 and the E_H rose to +300 mv, and the rate of flow of chlorine was then lowered to maintain the pH and E_H constant at these values for a further 30 minutes. The suspension was then filtered.

Analysis of the filtrate and residue showed that 91% of the nickel, 90% of the cobalt and 6.5% of the iron present had been extracted into solution. The ratio of Fe to Ni + Co in solution was 2.0:1, and substantially all the iron in solution was in the ferrous state.

EXAMPLE 2

The process of Example 1 was repeated using a chlorine gas flow of 2 litres/hour. The pH fell during 14 minutes to a constant value of 1.6, and the E_H rose to +1,110 mv. Chlorination was then discontinued and the suspension was filtered.

The metal extractions were 93% Ni, 88% Co and 5.5% Fe, and the ratio of Fe to Ni + Co in the solution was 1.6:1. Substantially all the iron in solution was in the ferric state.

For the purpose of comparison, tests were performed in which two further 10-gram portions of the same nickeliferous limonite ore used in Examples 1 and 2 were reduced in the same manner, and one of them was chlorinated with dry chlorine gas while the other was leached with hydrochloric acid.

In the dry chlorination test the reduced ore, after cooling in nitrogen, was placed in a tube which was immersed in a water bath maintained at 50°C., and chlorine gas was passed through the tube at the rate of 4.7 litres per hour for 30 minutes. The chlorinated material was then suspended in water and leached at room temperature for 1 hour, after which the suspension was filtered. The metal extractions in the leach solution were 90% Ni, 87% Co and 17% Fe, and ratio of Fe to Ni + Co in the solution being 5:1.

Despite the effort to control the temperature during the chlorination, it will be seen that the amount of iron extracted was about three times as much as in Examples 1 and 2 of the invention. Since only 6% of the iron in the reduced ore had been reduced to metal, it is also apparent that dry chlorination under the conditions of this test results in the solubilisation of about 11% of the iron present as oxide.

In the acid leaching test, the reduced ore was suspended in 100 ml of water at 50°C. and dilute hydrochloric acid (6% HCl) was added dropwise with stirring to maintain the pH between 2.6 and 3.0. After 30 minutes the final pH was 2.6. The suspension was filtered and the metal extractions were 84% Ni, 57% Co, 36% Fe and the Fe to Ni + Co ratio in the solution was about 12:1.

It is apparent that leaching with hydrochloric acid even at a pH of above 2.5, i.e., considerably less acidic than the final pH in Example 2, had dissolved a large proportion of the iron present in the reduced material as oxide, despite the fact that only relatively low extractions of nickel and cobalt had as yet been obtained.

The solubility of iron oxide in hydrochloric acid is confirmed by the results of the following test, which was also performed on a 10-gram portion of the same ore, reduced as described in Example 1.

The reduced ore was suspended in water and treated with chlorine at 80°C. as described in Example 2. After 15 minutes the pH had fallen from an initial value of 7.8 down to 1.4. Passage of chlorine was then stopped, the suspension was filtered and the liquor was analysed. The residue was then re-suspended in water at 80°C., and dilute hydrochloric acid (6% HCl) was added dropwise with stirring so as to maintain the pH at 2.0 for 30 minutes and at 1.5 for a further 30 minutes. The suspension was then again filtered and the amounts of the metals in solution were again determined. The metal extractions were as follows:

	Extraction (%)	
	By Cl_2 treatment	By Cl_2 treatment followed by HCl leaching
Ni	94	95
Co	89	90
Fe	4.5	10
Fe:(Ni+Co) ratio	1.3:1	2.9:1

EXAMPLE 3

This illustrates the use of a chloride solution as the aqueous medium.

A further 10 grams of the same ore were reduced as in Example 1 and the reduced material was suspended in 100 ml of an aqueous solution containing 10% by weight of sodium chloride and chlorinated at 80°C. as in Example 2. The pH fell during 20 minutes from 8.1 to a final value of 1.5 and the final E_H was +1,040 mv.

The metal extractions were 94% Ni, 90% Co and 6.5% Fe, the ratio of Fe to Ni + Co in the solution being 1.9:1.

EXAMPLE 4

This example demonstrates the effect of selective reoxidation of metallic iron in the reduced ore during cooling.

A further portion of the same ore, reduced as in Example 1, was cooled from the reduction temperature of 750°C. down to 500°C. under the reducing gas, and then maintained at 500°C. for 15 minutes while under a stream of carbon dioxide. The reduced material was then rapidly cooled under nitrogen, suspended in water and chlorinated for 10 minutes at 80°C. as in Example 2. During this time the pH fell from an initial value of 8.2 down to a constant value of 1.6.

The percentages of the metals extracted were 94% Ni, 90% Co and 3.5% Fe, and the ratio of Fe to Ni + Co in the solution was 1:1.

It will be seen that the proportion of iron extracted is much less than in Example 2, with a corresponding improvement in the ratio of Fe to Ni + Co.

EXAMPLE 5

This is an example of the removal of ferric iron from solution after chlorination.

Example 2 was repeated, the chlorination being continued for 20 minutes to a steady pH of 1.6 and a final E_H of +1,110 mv. A stream of oxygen was then passed through the suspension at 80°C. at a rate of 5 litres per hour with stirring, while the pH was adjusted to pH 3 by addition of sodium hydroxide and maintained at that value for 15 minutes, and then at 3.5 for a further 8 minutes. The flow of oxygen was then stopped and the suspension was filtered.

The metal extractions were found to be 93% Ni, 88% Co and 0.5% Fe, showing that the major part of the iron dissolved during the chlorination had been precipitated. The ratio of Fe to Ni + Co in the solution was 0.15:1.

EXAMPLE 6

This is an example of the treatment of an ore having a higher cobalt content.

A finely divided limonite ore containing 1.37% Ni, 0.70% Co and 44% Fe, of which 93% was fine enough to pass through a 200-mesh B.S. sieve, was reduced as in Example 1.

A suspension of 10 grams of the reduced ore in 100 ml of water was then treated with chlorine gas as in Example 2 at 80°C. The pH fell during 30 minutes from an initial value of 8.8 to 1.6 and the E_H increased from −700 mv to −1,080 mv.

The metal extractions were 96% Ni, 93% Co and 1.5% Fe, and the ratio of Fe to Ni + Co in the solution was 0.3:1.

EXAMPLE 7

This is an example of the treatment of a material containing copper as well as nickel.

A material obtained by roasting a pyrrhotite concentrate and containing 1.65% Cu, 0.85% Ni and 64% Fe was reduced as described in Example 1 except that the reduction was continued for a total of 6 hours, and the reduced material was treated with chlorine at 80°C. as in Example 2. During 11 minutes the pH fell from an initial value of 7.9 down to 2.5 and the E_H increased from −457 mv to +300 mv. Chlorination was continued for a further 41 minutes to a final steady pH of 1.2 and E_H of +1,070 mv. After filtration, the metal extractions were 99% Cu, 89% Ni and 1.7% Fe, and the ratio of Fe to Cu + Ni in the solution was 0.45:1.

In general the metal extractions obtainable by means of the invention are remarkably high. Thus, in the examples given above about 90% of the nickel and cobalt was extracted from limonitic type ores containing both these metals. A virtually complete extraction of the copper was also obtained from a copper-containing material.

It is noteworthy that these high extractions were obtained without the need to employ elevated temperatures or pressures or highly corrosive condition, and the process is of particular value for the treatment of cobaltiferous materials in an economic manner.

The process of the invention has numerous practical advantages. It is simple and flexible, and because of the very high rate of the reaction with chlorine the chlorination can be carried out in relatively small reactors. The high solubility of the reaction products and the high mobility of their ions ensures that the reaction products do not form a barrier to the diffusion of the chlorine to the metal surface, which remains active. The high solubility of the chlorides formed permits operation with concentrated solutions and also enables high solid-liquid ratios to be used in the leaching stage. Furthermore, the pregnant solution or a slurry of chemical concentrated therefrom, e.g., sulphides, hydroxides or carbonates precipitated therefrom can readily be transported for refining elsewhere. Chlorination in an aqueous medium allows satisfactory control of the chlorinating temperature, and the fact that sea water can be used as the aqueous medium can have major advantages. The high but selective reactivity of the chlorine with the metals to be extracted enables high temperatures to be used in the pyrometallurgical selective reduction, thus avoiding temperature limitations imposed in processes in which extraction is by less reactive agents. Consequently this reduction can be performed simply and rapidly with the use of relatively cheap reductants, and magnesia in silicate materials can be fixed as relatively inactive silicates.

Other advantages of the process include the possibility that since leaching temperature at or near the boiling point can be used, expensive additional cooling arrangements may not be required; the relatively low viscosity of the aqueous medium at the temperatures used; and the relatively low vapour pressure of chlorine over the solution.

Extraction of the metals as chlorides also means that cheap alkalis such as lime can be used for pH control without formation of basic salts which might hinder diffusion of the reaction products from the metal surface, impair the extraction and cause operation difficulties.

The present process may be used in conjunction with other established processes for the treatment of materials containing one or more of nickel, cobalt and copper together with iron. For example the selectively reduced oxide material can be subjected, before chlorination, to carbonylation at either atmospheric or higher pressure, or to ammonia leaching, to extract part of the nickel or cobalt therefrom. The subsequent chlorination then serves to extract nickel, cobalt and copper remaining in the residues from these processes.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for treating an oxide ore containing iron together with a substantially lesser amount of at least one other metal value selected from the group consisting of nickel, cobalt and copper which comprises selectively reducing the oxide ore to convert substantially all said other metal value to the metallic state but reducing to the metallic state no more than 5 parts of iron for each part of said metallized other metal, immersing the selectively reduced ore in water to form a suspension having an aqueous phase, contacting said immersed reduced ore with molecular chlorine through said aqueous phase over a period of time while maintaining the temperature of the suspension in the range of 75°C. up to 95°C. to minimize the concentration of hypochlorous acid in the aqueous phase and while maintaining the total pressure in the range of about 1 to about 10 atmospheres to chloridize said metals, terminating the contact with molecular chlorine when the pH value of the aqueous phase is in the range between about 3 and 2 and the redox potential of the aqueous phase is somewhat in excess of about +300 mv whereby said other metal values have been rapidly extracted into the aqueous phase by the action of molecular chlorine to produce a solution of said other metal chlorides in the aqueous phase and to constantly expose fresh surfaces for continuing the reaction between molecular chlorine and the said other metal and iron and whereby the presence of ferric chloride in the aqueous phase is minimized.

2. A process according to claim 1 in which the reduced material, before chlorination, is slowly cooled under a protective atmosphere so as to cause disproportionation of wustite therein into metal and magnetite.

3. A process according to claim 1 in which the reduced material, before chlorination, is selectively reox-

idised to convert part of the metallic iron to iron oxide.

4. A process according to claim **1** in which the water in which the reduced oxide material is originally immersed contains chloride ions in solution.

5. A process according to claim **4** which is carried out on a continuous basis and replacement water used in said process is sea water or brine.

6. A process according to claim **1** in which the chlorination is carried out at a temperature of about 80°C and is terminated when oxidation of dissolved iron to the ferric state begins as signified by the attainment of a pH of about 2 to 3 and an EH of about +300.

7. A process according to claim **6** in which ferrous iron in the solution produced is oxidised to the ferric state and precipitated by passing oxygen into the solution at a pH above **3.**

8. A process according to claim **7** in which the chlorination is continued until the solution contains an amount of ferrous iron at least equivalent to the remaining metallic nickel, cobalt and copper and further metallic nickel, cobalt or copper is then taken into solution by adjusting if necessary, to pH of the solution to about 3 to 4 and by passing a gas containing free oxygen into the solution having the pH of from 3 to 4 at a temperature of at least 80°C. and a pressure of about 1 to about 10 atmospheres.

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