In Cuba and in various other parts of the world there are very large deposits of Mayari type iron ores. They are oxidic and have a considerable content of iron and therefore should furnish an excellent source of iron for the making of iron and steels. As yet, however, this type of ore has not been practically utilized for iron and steel making except for certain limited purposes. The primary reason for the failure to utilize these deposits of ores on a large scale in the manufacture of irons and steels is due to the presence of small amounts of nickel, cobalt and chromium and the lack of any known and economical methods for removing these elements from the iron.

In describing our invention we shall refer to Mayari iron ore which is probably the best known member of the Mayari type iron ores. Mayari iron ore as it occurs in nature contains considerable free water and also a substantial amount of "combined water." Analyses of the calcined ores vary considerably but in general they run within ranges approximately as follows:

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<th>Constituent</th>
<th>Percent</th>
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<tr>
<td>Fe</td>
<td>64.1</td>
</tr>
<tr>
<td>Ni</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>2.2</td>
</tr>
<tr>
<td>Co</td>
<td>0.15</td>
</tr>
<tr>
<td>Mn</td>
<td>0.6</td>
</tr>
<tr>
<td>Mg</td>
<td>0.4</td>
</tr>
<tr>
<td>CaO</td>
<td>5.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.0</td>
</tr>
</tbody>
</table>

In this table of analyses, the first column indicates the constituents of the ore; the second column indicates an average analysis; and the remainder of the table indicates the ranges.

Our invention is directed to a process for the treatment of Mayari type iron ores particularly for the economical removal of chromium to reduce the chromium content to an amount sufficiently low so that the treated product can be utilized in the manufacture of irons and steels which have low limitations on chromium. In a more specific embodiment of our invention our process is directed to the removal of nickel and cobalt as well as the chromium.

Our process comprises the steps of roasting the ore, or previously treated ore, with an alkali metal carbonate, bicarbonate, or hydroxide, under oxidizing conditions, and leaching such roasted ore with an aqueous medium to remove chromium. It is not new to give an oxidizing roast with alkali metal compounds to form alkali metal chromates and then leach to remove the soluble chromates, but, in the use of such prior processes, it has been practically impossible to remove enough of the excess alkali by leaching to give a sufficiently low alkali metal compounds. This difficulty of such prior art processes would be particularly serious if the processes were to be applied to an iron ore where the product is to be used in the manufacture of irons and steels, as the amount of alkali metal permissible in such raw material is very low indeed. Our invention therefore also comprises steps for the effective removal of any excess alkali during the wash or leach with an aqueous medium.

Our invention comprises the steps of adding calcium oxide, hydroxide, or chloride during the wash or leach of the ore with the aqueous medium. Preferably the addition of calcium carbonate or hydroxide. This addition greatly facilitates the removal of the excess alkali. Preferably the calcium compound is added in installments during the washing. i.e. part of the calcium compound is added at or near the beginning of the wash and other parts are added at later intervals. This addition by installments greatly improves the effectiveness of the alkali removal. Preferably also, the aqueous medium is kept at a temperature at least as high as 125° F. during the treatment with the calcium compound since we find that the presence of such compound tends to limit the removal of chromium from the ore at lower temperatures.

Frequently, we find it desirable during the washing operation of our process to autoclave a mixture of treated ore, wash liquor and calcium compound at a temperature between 230° F. and 320° F., at an intermediate stage of the washing operation.

In a preferred form of our invention we first remove most of the nickel by treatment with nitric acid by the method set forth in Mancke application Serial No. 274,055, filed February 28, 1952, following which the treated ore is roasted with an alkali metal compound and leached with an aqueous medium, using additions of calcium compounds as above outlined. When the ore is thus treated to first remove nickel we find that the subsequent treatment with calcium compounds is particularly effective in the removal of alkali metal compounds.

We shall now give an example of a preferred way of carrying out our invention. In this example, Mayari iron ore is first treated to remove most of the nickel by what we have designated as the N-2 process in the above referred to Mancke application Serial No. 274,055. Following the N-2 treatment the treated ore is mixed with sodium carbonate and sodium hydroxide, and the resulting mixture roasted in the presence of air to change most of the chromium to sodium chromate. The ore thus roasted is then subjected to a countercurrent leaching with water heated to a temperature of 180° F. to remove the sodium chromate, calcium oxide being added at intervals during such washing to facilitate the removal of excess alkali. At an intermediate stage of the leaching, the mixture of ore, leach water and calcium compound is autoclaved at a temperature of 290° F.

Now we shall give the details of the example of our invention just outlined in the preceding paragraph. The coarsest material is removed from the Mayari ore and the balance ground slightly to yield a product of -65 mesh. The ore is then dried at a temperature of not over 300° F. to get rid of excess moisture. Referring to the accompanying drawing, the ore, thus sized and dried, is mixed with water and nitric acid in mixer 1 to make a slurry. In this particular example, the amount of nitric acid used is .525 ton per ton of contained calcined ore treated mixed with 1.225 ton of contained calcined ore being treated. It may be well to explain just what is meant by the expression "per ton of contained calcined ore being treated." The ore actually treated is not a calcined ore which is ore which has been heated to get rid of all or essentially all water, but is ore which still contains a substantial quantity of water since it has been only moderately dried as indicated in the preceding paragraph. While calcined ore is not
used, it is expedient in determining the relative amounts of ore, nitric acid and water, to express the ore in terms of the calcined ore. Before treating a batch of ore, samples of the moderately dried ore are calcined to remove water, both free and combined. In the present specific illustration of our invention 1,158 units of moderately dried ore gives 1.00 unit of calcined ore. From this it will be evident that 1.158 tons of moderately dried ore contains 1.00 ton of ore figured on the basis of the ore when calcined. It is on the basis of the ore figured in terms of the calcined water free or calcined that the relative quantities of ore, nitric acid and water are determined.

When we say in the preceding paragraph that, in the specific example, 0.525 ton of nitric acid is used, we mean that the actual content of nitric acid whether the acid is added as pure acid or in the dilute form. When we say in the preceding paragraph that 1.125 tons of water are used this means that the total water is meant including any added water, water in the acid used, total water content of the moderately dried ore, and water derived from autoclave steam.

The slurry of acid, water and ore is introduced into autoclave 2 and its temperature brought to 400° F. at which temperature it is maintained for about 60 minutes. The solution, containing most of the nickel and cobalt of the ore, is removed from the treated ore containing most of the iron in the solid phase as indicated at 3. The iron bearing product is then washed with water as indicated at 4. The process of this specific example of our invention, as thus far given, is in accordance with the so-called N-2 process set forth in said application Serial No. 274,055, referred to above.

The ore, as thus treated, while still in the moistened state is thoroughly mixed with sodium hydroxide and sodium carbonate in mixer 5 and then the mixture is dried as indicated at 6. The sodium hydroxide is added as a concentrated aqueous solution which is derived from another stage of the process as will later appear. The total amount of sodium hydroxide and sodium carbonate used is such as to be equivalent to 280 lbs. of sodium oxide (Na2O) per ton of ore treated estimated on the basis of calcined ore. The dried mixture is roasted, as indicated at 7, at a temperature of from 1800° F. to 1900° F. for 1 hour.

The roasted ore goes to ball mill 8 where it is ground into a slurry with water and added calcium oxide. The amount of calcium oxide added is equal to 5.25 percent of the weight of ore being treated, estimated on the calcined basis. The water which is fed into the ball mill contains some alkali and some sodium carbonate in solution, this water having previously passed through a series of washing devices as will appear later. The slurry from ball mill 8 passes into leach tank 9. In ball mill 8 and the leach tank 9 a considerable portion of the sodium carbonate and excess alkali of the treated ore is dissolved and the solution produced is relatively concentrated in these substances.

From leach tank 9 the slurry passes to the thickener 10 where settling of the undissolved portion of the slurry occurs. The resulting solution at the top of the thickener is drawn off through launder 11 and passes through a portion of the equipment for removal of the sodium carbonate which will be referred to later.

The thickened slurry from thickener 10 is fed into tank 12 where it is mixed with aqueous wash solution and calcium oxide. The slurry is then fed to thickener 13 where it is settled, the resulting solution at the top of the thickener being drawn off through launder 14 and passing to ball mill 8. The thickened slurry from thickener 13 passes to tank 15 where it is mixed with wash solution and calcium oxide. From tank 15 the slurry passes to thickener 16 and settled, the solution at the top being removed by means of launder 17 and passing to tank 12 where it constitutes the leach solution which has already been mentioned.

The thickened slurry from thickener 16 passes to the autoclave 18 where it is maintained at a temperature of 270° F. for 2 hours, calcium oxide and leach liquor being added to the slurry at this point. The slurry goes to thickener 19 where settling takes place and the solution at the top of the thickener is drawn off at launder 20 and passes to tank 15. The thickened slurry from thickener 19 passes to tank 21 where it is mixed with leach liquor and calcium oxide. The slurry then passes to thickener 22 from the upper portion of the solution drawn off by launder 23 and passes to autoclave 18.

The thickened slurry passes from thickener 22 to tank 24 where it is mixed with leach liquor and calcium oxide. The slurry then passes to thickener 25. The solution at the upper part of thickener 24 passes from launder 26 to tank 21 and the thickened slurry passes to thickener 27 where it is mixed with water. The liquor in the upper part of this thickener is drawn off through launder 28 and passes to tank 24 while the thickened slurry passes to filter 29. The insoluble material from these filters falls in iron and low in nickel, chromium and contained sodium. It contains about 8 percent of calcium oxide. The filtrate which is largely water containing very little dissolved material is mixed with added water and passes to thickener 27.

The amount of calcium oxide added to each of tanks 12, 15, 21, and 24, and to autoclave 18, is equal to 0.6 percent of the weight of the ore being treated, estimated on a calcined ore basis.

Earlier in this description of a specific embodiment of our invention reference has been made to a solution drawn off from the top of thickener 10 through launder 11. This solution is heated to evaporate water vapor and concentrate the solution of sodium carbonate and alkali following which sodium carbonate is crystallized from solution and removed from the liquid by filtration as indicated at 30. There are several stages of such evaporation, crystallization and filtration to remove as much of the sodium carbonate as possible and to secure a highly concentrated alkali solution, the alkali being mainly in the form of sodium hydroxide. The concentrated alkali solution is fed to mixer 5, as already indicated. The water vapor resulting from the evaporation stages is condensed and the resulting water mixed with additional "make-up" water 31 and also with filtrate from filter 29 as indicated at 32 is fed into the thickener 27.

As is evident from the description just given, taken in connection with the drawing, the washing of the roasted ore to remove chromium and alkali involves a countercurrent operation. As viewed in the drawing, the ore moves progressively from left to right and the leach liquor moves progressively from right to left, the treated ore in its movement to the right being subjected to a series of washings, in which the treated ore comes into engagement with water which progressively contains smaller amounts of alkali and sodium carbonate. The solution in its movement from right to left becomes more and more concentrated in chromium and alkali contents.

In the example of our process just given the conditions have been set forth rather specifically. Many of the conditions may be varied considerably, however, and the essential advantages of our process will still be secured. We will now indicate some of the variations of conditions in the process.

In the specific example given above the autoclaving of the slurry of ore and nitric acid solution is at 400° F. The temperature may vary, however, from 310° F. to 650° F., but we usually prefer to use a temperature from approximately 330° F. to 500° F. The amounts of nitric acid to use may vary considerably. The amount should be sufficient to satisfy the stoichiometric requirements of the nickel, cobalt, manganese and alumina of the ore but insufficient to satisfy such requirements and also the stoichiometric requirements of the major part of the iron in the
ore. Preferably we use such an amount of nitric acid as to be somewhat in excess of the stoichiometric requirements of the nickel, cobalt, manganese and alumina of the ore. The concentration of the aqueous nitric acid solution employed may vary considerably. We prefer to employ a sufficient water content of the nitric acid solution so that when mixed with the ore a slurry will be produced capable of being pumped. The length of time of autoclaving may vary substantially. Such lengths of time will vary with different ores.

The amount of alkali metal carbonate, bicarbonate or hydroxide in the roasting operation to form alkali metal chromate may be varied substantially. The amount should be at least sufficient to satisfy the stoichiometric requirements of the chromium contained in the ore and preferably should be sufficient to satisfy the stoichiometric requirements of not only the chromium but the major part of the alumina and silica content of the ore. When the ore has been previously treated by the N-2 process lesser amounts of the alkali metal compound are generally used than when the ore has not been subjected to the N-2 process. Amounts greater than here indicated may be used but ordinarily excessive amounts are not used for reasons of economy.

The temperature for roasting the mixture of ore and alkali metal compound to form an alkali metal carbonate may be varied. Ordinarily we employ a temperature between 1715° F. and 2050° F. Preferably we employ a temperature from 1800° F. to 1900° F. When calcium oxide is used during the washing operation the amount may vary considerably. Preferably we use an amount equal to 5 to 10 percent of the weight of ore material being treated figured in terms of the material in the calcined condition, whether such material is the raw ore or the ore material resulting from a previous treatment by the N-2 process. When using calcium hydroxide or calcium carbonate an amount is preferably used chemically equivalent to the amount of calcium oxide employed as stated just above.

The temperature of the wash solution may vary. It is advisable to employ a temperature of wash solution not less than 125° F. Most frequently we employ temperatures between 225° and 300° F. We frequently desire to raise the temperature above 230° F. at an intermediate stage of the washing operation by heating the mixture of solution, ore, and calcium compound in an autoclave. Preferably, in such autoclave treatment, the temperature is raised to between 250° F. and 325° F.

When we use the term "ore" in the claims it is to be understood that it is to be considered broadly to cover not only the raw ore but also an ore material which has been previously treated as by roasting, drying or other preparatory treatment.

We claim:

1. A process for treating Mayari type iron ore to remove chromium comprising the steps of roasting the ore with an alkali metal compound of the group consisting of hydroxide, carbonate and bicarbonate, washing the ore with water to remove chromium and alkali, and adding a calcium compound of the group consisting of oxide and hydroxide during such washing to facilitate the removal of alkali.

2. A process for treating Mayari type iron ore to remove chromium comprising the steps of roasting the ore with an alkali metal compound of the group consisting of hydroxide, carbonate and bicarbonate, washing the ore with water to remove chromium as an alkali metal chromate, and adding successive installments of calcium compound of the group consisting of hydroxide and oxide during such washing to facilitate the removal of alkali.

3. A process for treating Mayari type iron ore to remove chromium comprising the steps of roasting the ore with an alkali metal compound of the group consisting of hydroxide, carbonate and bicarbonate, washing the ore thus treated with water at a temperature of not less than 125° F. to remove chromium and alkali, and adding a calcium compound of the group consisting of oxide and hydroxide during such washing to facilitate the removal of alkali.

4. A process for treating Mayari type iron ore to remove chromium comprising the steps of roasting the ore with an alkali metal compound of the group consisting of hydroxide, carbonate, and bicarbonate, washing the treated ore with an aqueous medium, adding successive installments of calcium compound of the group consisting of hydroxide and oxide during such washing to facilitate the removal of alkali, and autoclaving the mixture of ore, water, and calcium compound at a temperature between 230° F. and 320° F. at an intermediate stage of such washing.

5. A process for treating Mayari type iron ore to remove chromium comprising the steps of roasting the ore with an alkali metal compound of the group consisting of hydroxide, carbonate, and bicarbonate, washing the ore with water at a temperature of not less than 125° F., adding successive installments of calcium hydroxide during such washing to facilitate the removal of alkali, and heating the mixture of ore, water, and calcium compound at a temperature between 230° F. and 250° F. at an intermediate stage of such washing.

6. A process for treating Mayari type iron ore to remove chromium comprising the steps of roasting the ore with an alkali metal compound of the group consisting of hydroxide, carbonate, and bicarbonate, washing the ore with water at a temperature of not less than 125° F., and adding successive installments of calcium compound of the group consisting of hydroxide and oxide during such washing to facilitate the removal of alkali.

7. A process for treating Mayari type iron ore to remove chromium, which comprises the steps of roasting the ore with an alkali metal compound of the group consisting of hydroxide, carbonate and bicarbonate, washing the ore with water to remove chromium and alkali compound in a series of stages, and adding a compound of calcium of the group consisting of oxide and hydroxide in installments at a plurality of such stages.

8. A process for removing nickel and chromium from oxidic material containing iron as the predominant metal constituent and also containing smaller amounts of chromium and nickel, comprising the steps of autoclaving the material with an aqueous solution of nitric acid at a temperature between 310° F. and 650° F. to produce an aqueous solution of nickel and iron in the oxidic state in solid phase, removing the nickel bearing solution from the iron bearing material, roasting this iron bearing material with an alkali compound of the group consisting of hydroxide, carbonate and bicarbonate, washing the roasted material with water to remove chromium and alkali, and adding successive installments of a calcium compound of the group consisting of oxide and hydroxide during such washing to facilitate the removal of alkali.

9. A process for removing nickel and chromium from Mayari type iron ore which comprises the steps of autoclaving the ore with an aqueous solution of nitric acid at a temperature between 330° F. and 500° F. to produce a solution of nickel nitrate and iron in the oxidic state in solid phase, removing the solution of nickel nitrate from the treated ore, roasting the treated ore with an alkali metal compound of a group consisting of hydroxide, carbonate and bicarbonate, washing such roasted ore with water at a temperature of at least 125° F. to remove alkali metal chromate and alkali, and adding successive installments of a calcium compound of the group consisting of hydroxide and oxide during such washing to facilitate the removal of alkali from the treated ore.

(References on following page)
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<table>
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<tr>
<th>Number</th>
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<tr>
<td>726,802</td>
<td>Nichols</td>
<td>Apr. 28, 1903</td>
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<td>1,678,246</td>
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<td>386,288</td>
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<tr>
<td>441,008</td>
<td>Italy</td>
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