This invention relates to manufacture of chrome ore preparations; and it comprises an ore preparation containing a substantial amount of lime chrome and representing a chrome-iron ore with some, or all, of its combined iron content subtracted and replaced by calcium, the ore preparation being chemically basic, glassy in its solid state and having easy smelting characteristics; and it further comprises a process wherein the ore is fused with an addition of lime in the presence of enough carbon to reduce iron, thereby producing a layer of molten iron of low chromium content and a melt of high chromium content, the iron and the melt being collected and withdrawn separately; all as more fully hereinafter set forth and as claimed.

Chromeite or chrome iron ore is at present substantially the only commercial source of chromium and chromium compounds. In a pure state, chromeite is FeOCrO₃ and contains about 46 per cent Cr and 25 per cent Fe; a chromium:iron ratio of about 64.8:35.2.

In many natural ores, however, the FeO of the ideal chromeite is partially replaced by other oxides such as magnesia, and the Cr₂O₃ is often replaced by aluminas; the chromium:iron ratio being higher or lower, respectively, because of such replacement. A typical replacement of the first-mentioned type, increasing the chromium:iron ratio, is found in New Caledonia chrome ores, which are at present imported into the United States for making chromium alloys. A typical analysis of a New Caledonia chrome ore shows 45.71 per cent Cr₂O₃ and 11.67 per cent FeO; a chromium:iron ratio of 77.5:22.5. This ratio appears to be a maximum for commercial ores. Such an ore, upon reduction in the electric furnace by customary methods gives a ferrochrome of about 70 per cent chromium content as a maximum. Ferro-chromes of higher than 70 per cent chromium content are desirable commercially, but these higher chromium contents it has been necessary to use chromium oxide made from bicromates produced from chrome ore.

One of the principal uses of chrome ore is in the production of ferrochromium and for this it is desirable to have the chromium-iron ratio in the ore as high as possible so as to permit a high chromium content in the product. At present in all cases the richness in chromium of a ferrochrome is limited by the Cr:Fe ratio of the ore used.

In some natural ores, the Cr to Fe ratio is the same as that exemplified in the New Caledonia ores but the content of chromium much less. In others the iron content is increased to such an extent that the chromium ratio is well below that of ideal chromeite. An abundant supply exists of domestic ores and Canadian ores of this type, a typical analysis showing 40.88 per cent Cr₂O₃ and 21.05 per cent FeO or a Cr:Fe ratio of 63 to 37. Such ores have been considered low grade or off grade and are not used for production of high chromium ferrochrome.

In the present invention I make it possible to use these low grade chrome iron ores in high grade ferro-chromium production by first producing in the electric furnace a basic chromeite ore of subtracted iron content and, when desired, of added chromium content. The artificial basic chromeite ore can then be used as a raw material, so to speak, in processes for the production of iron-chromium alloys. I have found that these natural chrome ores can be beneficiated for ferrochrome production by selectively reducing and removing iron from the ores, leaving altered ores of heightened chromium oxide content with iron in any desired ratio lower than that of the raw ore. If desired, the iron in a natural chrome ore can be substantially completely removed, producing an iron product from which there can be obtained, by reduction with silicon, practically pure chromium metal.

Low carbon ferrochromium of any desired chromium content can be produced by reducing the beneficiated ore with relatively low grade ferrosilicon; complete control of the chromium content being attained by coordinating with the extent of iron subtraction from the ore the grade or silicon content of the ferrosilicon used for reducing the beneficiated ore.

While in other ways of operating, I use carbon as the reducing agent, in one embodiment of my invention, a portion of natural chrome ore is reduced in an electric furnace with a suitable reducing agent to produce total reduction and a ferrochromium of a composition corresponding to the chromium-iron ratio of the ore; this ferrochromium being then utilized as a reducing agent. The natural ore to be treated is smelted with this ferrochromium under conditions providing a basic melt. The chromium of the ferrochromium reduces iron from the second ore portion with oxidation of the chromium; the reduced iron leaving the system as a byproduct. The oxidized chromium joins the ore to form a basic ore melt of heightened chromium content, and lowered iron content; this melt constituting the new basic ore. The reduced iron and the melt are separately tapped off and leave the system. Thus chromium
from the first portion of ore is transferred to the second portion to produce a concentrated basic chrome ore product which may be substantially free of iron and from which ferrochrome of any desired grade or chromium metal can be readily produced by reduction with ferrosilicon or with silicon as reducing agent. The iron left after the operation contains a substantial percentage of chromium and constitutes a valuable byproduct.

A portion of it can be used in making ferrosilicon or ferrochrome silicon for reduction of the concentrated chromium ore to produce high chromium ferrochrome; the chromium contained in the iron byproduct so used being added to the ferrochrome. The low chromium iron metal byproduct, being usually low in carbon, is readily and economically converted into low carbon chromium steel by known methods.

In the preparation of the low iron chrome ore of the present invention the natural ore is fluxed by an addition of lime; in effect replacing FeO in the embodiment of my invention as just described, the chromium of ferrochromium serves as reducing agent in removing iron from natural chrome iron ore. This has the advantage of adding to the chromium content of the ore as well as lowering the iron content from the iron content. However, other reducing agents can be used. Carbon as coke or charcoal, silicon, silicon alloys or silicides and aluminum may be used, the proportions being such as to selectively reduce iron from the ore to leave the chromium oxide for the most part unreacted.

In the preparation of the low iron chrome ore of the present invention the natural ore is fluxed by an addition of lime; in effect replacing FeO in the ferrochrome and forming calcium chrome, CaOCrO₃. This replacement has the effect of concentrating the chromium content of the ore to give a product of higher chromium content than the original natural ore. It also makes the process more fusible and easy to smelt for reduction of chromium to metal. In this reduction the silica, alumina, magnesia, etc., of the ore is slagged off in a basic slag and it is advantageous to put the required basic into the ore as CaO and forming calcium chrome.

The altered chrome ore of low iron content is then ready for reduction. Reduction of the contained chromium may be effected without allowing the reduced iron to oxidate. The reduction may be carried on in a single furnace. Usually in preparing the ore melt, lime, CaO, is added in a proportion of about 1.75 or 2 parts by weight for each part of silica contained in the ore. When added in this proportion, sufficient lime is provided to react with the chromium oxide in the ore with formation of a calcium chromite. In fact, when a natural chromite ore is fluxed with lime there is a replacement of FeO by CaO even in the absence of a reducing agent. When the iron oxide is also reduced as it is displaced the reaction between lime and chromium oxide may proceed to completion.

The practice of my invention, considerable leeway is permissible in the amount of carbon or other reducing agent used in reducing iron from natural chrome ore. The amount used in proportion to the ore depends upon the grade of the chromium contained from the concentrated chrome ore product. It is usually advantageous to use sufficient reducing agent to reduce to metal all of the iron in the ore and a small part, say 3 to 10 per cent, of the chromium. This gives a chrome melt substantially free of iron and containing upwards of 90 per cent of the chromium in the original ore. The reduced iron containing a substantial percentage of chromium is useful in making chrome steels. When silicon is used as reducing agent sufficient chromium may be put into the iron to make stainless steel or stainless iron.

The non-metallic portion of the melt is liquid at the temperature of the furnace. On cooling it sets to a vitreous or glassy solid; the new material of the present invention. It has practically the chromic oxide content of the original ore, without substantial diminishment, but the original FeO has been replaced to a greater or less extent by CaO. The new material is basic in nature, and as stated is readily fusible.

All or most of the FeO can be subtracted, giving an ore adapted for making chromium and its non-ferrous alloys. But generally I make an altered ore still containing some iron and adapted for making high grade ferrochromium. Altered ores containing some iron are easier to make, fuse and use than the straight calcium chromite.

The ore products described are most advantageous materials for making carbon-free ferrochromium of any desired content, or pure chromium metal. The material can be further processed directly, while it is still in its molten state, or it can be taken from the furnace and shipped to the ferrochrome manufacturer, to serve as a raw material in ferrochrome alloy manufacturing. It is of a composition and physical condition very suitable for steel making, being superior to natural chrome ores in this respect.

Thus from a low grade chromium-poor, high iron natural ore there is produced a high chromium artificial ore which is equal to or superior to high grade natural ores.

When the ore is prepared free of iron, it is possible to use ferrosilicon of any grade for reducing the chromium oxide of the ore; the chromium content of the ferrochrome product being a matter solely of the grade of ferrosilicon used in reduction of the original ore. Reduction of the chromium oxide is a function of the silicon in the ferrosilicon aided by the base replacing iron oxide in the original natural ore, it is a simple matter to control the chromium content of the ferrochrome produced by having a proper silicon content in the ferrochrome used for the reduction.

For example, a substantially carbon free ferrochromium with over 70 per cent chromium can be produced by reduction of the prepared iron-free basic ore with 50 per cent ferrosilicon. When it is desired to make a low chromium ferrochrome, say 30 per cent chromium content, a 15 per cent ferrosilicon serves for reducing agent. An 88 per cent ferrochromium is made from 75 per cent ferrosilicon. If 99 per cent chromium metal is wanted, it can be made by silicon of 98 per cent grade. Using ferrochrome silicon containing 20 per cent Si and 20 per cent Cr a metal containing 69 per cent chromium is formed. These reductions are advantageously effected in an electric furnace of the Hercul type. The low melting point of the lime-fluxed ore of high CrO₃ content makes for smooth, efficient furnace operation. However, the reductions can readily be effected by known easy means using excess of silicon to furnish heat for melting with sodium nitrate or potassium chloride as accelerator. In this operation the high lime content of the ore and its ready fusibility keeps slag losses of chromium from ferrochrome containing upwards of 70 per cent chromium can be produced directly by this exothermic process.
The ore and coke and lime are ground to pass through a 1\% inch screen and are mixed and charged into an electric furnace of three phase submerged arc type. In a submerged arc configuration, sometimes called "arc resistance heating", the arc is formed by an electrode ending near the surface of the melt and passing through a body of unannealed materials charged for smelting; the electrode is surrounded by the incoming material. The operation of this type of furnace is continuous. The furnace operation requires a temperature of about 1600°C. It is suitable and the charge is melted in a continuous operation. From time to time a metal containing 3.5 per cent chromium, 0.54 per cent carbon and 95.06 per cent iron and a glassy ore melt containing 43 per cent Cr₂O₃, 17.2 per cent CaO, and 10.4 per cent silica is tapped from the furnace and run into separate receptacles. From the charge given the yield of low chromium iron metal is 146 pounds and that of the altered ore is 93 pounds. Iron oxid present in the original ore as ferrous chromate is replaced by lime forming calcium chromate.

The concentrated ore, reduced in a Heroult furnace with 50 per cent ferrosilicon in a ratio of 953 pounds of ore to 220 pounds of ferrosilicon (50 per cent Si) yields 390 pounds of ferrochromium containing 71 per cent chromium and having a carbon content of 0.04 per cent. In producing the new chrome ore material of the present invention from natural chrome iron ores, I have found that the reduced iron instead of being removed as such can be removed as a phosphid or sulfid by adding a phosphate or a sulfur compound to the furnace charge. For example, when phosphate rock is added to the furnace ore burden together with sufficient carbon to reduce the phosphorus of the rock, the iron metal reduced from the ore contains iron phosphid; ferrophosphorus of a desired grade being thus a byproduct of the beneficiated chrome ore, the lime of the phosphate rock replacing iron in the ore. When a high sulfur iron is desired, it can be produced simply by adding iron pyrites to the furnace ore burden.

While the invention as above described has particular utility in making available for chromium alloy production certain chrome iron ores hitherto considered of no value and not used, the new and altered chrome ore can be made with advantage from the high grade chrome ores, thereby making it possible to produce from these ores chromium metal and chromium alloys of higher chromium content than has hitherto been possible.

In the accompanying drawing I have shown diagrammatically flow sheets illustrating processes within my invention. In this showing, Fig. 1 shows the steps of a process in which ore reducable to a low chromium content is reduced to ferrochromium which may be made high in carbon, and this ferrochromium serves as reducing agent for a second portion of chrome iron ore which is beneficiated by removal of iron reduced by the chromium of the ferrochromium and by additions of chromium oxide formed in the reduction. The beneficiated chrome iron ore (ore melt high in Cr), the new product of the present invention, can be cooled and processed separately. In the process outline, in the flow sheet however, the concentrated chrome ore melt is directly reduced by ferrosilicon, advantageously containing some chromium, with production of a ferrochromium containing more than 70 per cent chromium.
The ferro-chrome silicon reducing agent is advantageously made from the chromium-containing iron metal formed as a byproduct of the chrome ore concentration.

Fig. 2 shows a flow sheet of a process of making high grade ferrochromium from a chrome ore of low Ti:Fe ratio which comprises the two steps: (1) raising the ratio of chromium to iron by replacement of iron oxide (FeO) in the ore with lime (CaO) accompanied by selective reduction and removal of the replaced iron and (2) thereafter reducing the iron oxide with ferrosilicon or iron containing iron metal formed as a byproduct in step (1) being advantageously utilized in making the reducing agent for step (2).

Claims to a portion of the subject matter described and originally claimed in this application are being asserted in my copending application Serial No. 164,988, filed September 21, 1937, as a continuation-in-part of this application.

What I claim is:

1. A manufactured chrome ore which consists of an altered natural ferrous chromite ore containing the greater part of its original chromic oxide content and having the greater part of its ferrous oxide content displaced by an added base and removed, said manufactured ore having the physical characteristics of a glassy material set from a molten state and being chemically basic in its nature.

2. As a new article of manufacture, an artificial chrome ore made from natural ferrous chromite ore and containing a substantial amount of lime replacing the original ferrous chromite, said artificial ore being of fused glassy character and basic in its nature and having a low ratio of iron to chromium, said ratio being less than 23:77.

3. A manufactured chrome ore preparation adapted for reduction by ferrosilicon in smelting to produce low carbon ferrochromium of high chromium content which consists of an altered natural ferrous chromite ore containing the greater part of the original chromic oxide content and having the greater part of its ferrous oxide removed therefrom and replaced by lime, being of a fused glassy character and chemically basic.

4. A manufactured chrome ore preparation adapted for reduction by ferrosilicon in smelting to produce low carbon ferrochromium of high chromium content which consists of an altered natural chrome ore of the ferrous chromite type containing the greater part of its original chromium oxide content and having substantially all its iron oxide removed therefrom and containing calcium chromite replacing the original ferrous chromite, being of a fused glassy character and chemically basic.

5. The process of treating natural ferrous chromite ore for production of an artificial ore with a heightened ratio of chromium to iron and with production of metallic iron as a byproduct which comprises continuously fusing such an ore in the presence of sufficient added base to displace a substantial amount of the ferrous oxide in combination with chromic oxide, reducing the displaced ferrous oxide to metal and separating the metal from the fused melt, whereby a melt is obtained rich in chrome of the added base, low in iron and of basic nature.

6. The process of claim 5 wherein the reduction of iron oxide to metal is effected by carbon.

7. In the utilization of natural ferrous chromite ores for making chromium metal and chromium alloys, the continuous process of producing an artificial ore with a heightened ratio of chromium to iron with a byproduct of metallic iron low in chromium which comprises fusing the natural ore mixed with a sufficient quantity of an added base to displace the iron oxide in the ore from combination with chromic oxide, selectively reducing the displaced iron oxide so as to form separable masses of molten iron metal and overlying fluxed ore, sufficient iron being displaced from the ore and reduced to raise the ratio of chromium to iron in the treated ore above 77 to 23 and to increase the percentage of chromium in the ore.

8. A process of utilizing natural chrome iron ore in producing chromium metal and alloys of high chromium content which comprises continuously melting said ore with a fluxing base in contact with a reducing agent, the quantity of reducing agent and base, the temperature and the time of contact being about sufficient to reduce the iron of the ore selectively and in a molten condition and to leave unreduced the greater part of the Cr₂O₃ in the ore, removing the reduced molten iron and thereafter removing the ore melt to obtain metal high in chromium.

9. In the process of claim 8, selectively reducing and removing substantially all the contained iron from the ore melt and thereafter reducing chromium from the ore melt with ferrosilicon to obtain carbon-free ferrochromium.

10. In the process of claim 8, selectively reducing and removing substantially all the iron from the ore melt and thereafter reducing chromium from the ore melt with 50 per cent ferrosilicon in such proportion as to obtain low carbon ferrochromium containing over 70 per cent chromium.

11. In the process of claim 8, selectively reducing and removing substantially all the iron from the ore melt and thereafter reducing chromium from the ore melt with silicon in such proportion as to obtain metallic chromium.

12. In the manufacture of chromium alloys from chrome iron ores, a process which comprises continuously melting the ore in an electric furnace in the presence of a reducing agent and an added base in such quantities as to form an underlying layer of molten metal high in iron and low in chromium and an ore melt containing a chromeite of the added base and a lowered ratio of iron oxide, separating the molten metal from the ore melt and thereafter reducing the ore melt to obtain metal high in chromium and low in iron.

13. In the alteration of natural chrome ore to produce an artificial ore of heightened chromium content adapted for use in making chromium metal and alloys of high chromium content, the process which comprises continuously fusing the natural ore in an electric furnace mixed with an added base, thereby displacing FeO from the chromeite, fusion being at a chromium reducing temperature and with an amount of carbon about that required for the reduction of iron alone, and removing the molten iron thereby produced.

14. The process of treating ferrous chromite ore with production of an artificial ore having a higher ferrous oxide in combination with chromic oxide, reducing the displaced ferrous oxide to iron and with production of metallic iron low in chromium as a byproduct which comprises continuously fusing such an ore in a submerged arc furnace and in the presence of sufficient base to flux the chromite and to displace a substantial portion of the ferrous oxide of the chromite and form a glassy melt, simultaneously reducing the displaced ferrous oxide to iron and separating the metal from the
fused melt so as to obtain a melt rich in chromite of the added base, low in iron and of basic nature.

15. The process of making calcium chromite which comprises fusing a mixture of chromite ore with an amount of CaO sufficient to replace the FeO present, reducing the FeO to metallic iron and separating the metal and the fused calcium chromite.

16. A process which comprises heating a charge mixture comprising lime and chrome ore containing ferrous chromite to produce a molten product comprising calcium chromite formed by substitution of calcium oxide for ferrous oxide of chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable product high in calcium chromite, and separating the metallic iron product and the calcium chromite product.

17. A process which comprises heating a charge mixture comprising lime and chrome ore containing ferrous chromite to produce a molten product comprising calcium chromite formed by substitution of calcium oxide for ferrous oxide of chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable product having a lower ratio of iron to chromium than the original ore, and separating the metallic iron product and the calcium chromite product.

18. A process which comprises forming a charge mixture comprising chrome ore containing ferrous chromite and a basic compound capable of substituting for the ferrous oxide of the ferrous chromite to displace the ferrous oxide from chemical combination with the chromic oxide of the ferrous chromite and form altered or substituted chromite, heating the charge mixture to produce a molten product comprising altered or substituted chromite formed by substitution of the basic compound for ferrous oxide of the chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable product high in altered or substituted chromite, and separately reducing the altered or substituted chromite product to produce metal predominating in chromium.

19. A process which comprises heating a charge mixture comprising lime and chrome ore containing ferrous chromite to produce a molten product comprising calcium chromite formed by substitution of calcium oxide for ferrous oxide of chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable product high in calcium chromite, separating the metallic iron product and the calcium chromite product, and separately reducing the calcium chromite product to produce metal predominating in chromium.

20. A process which comprises heating a charge mixture comprising lime and chrome ore containing ferrous chromite to produce a molten product comprising calcium chromite formed by substitution of calcium oxide for ferrous oxide of chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable calcium chromite product, having a higher Cr:Fe ratio than the original ore, separating the metallic iron product and the calcium chromite product, and separately reducing the latter to ferrochromium.

21. The process of making a synthetic ore adapted for the production of commercial ferrochromium from a natural ferrous chromite ore containing a chromium:iron ratio lower than 70:30, which comprises heating a charge of such ferrous chromite ore to produce a molten product containing calcium chromite formed from ferrous chromite of the ore in the presence of sufficient lime and a sufficient amount of reducing agent to convert enough of said ferrous chromite to calcium chromite to give said molten product a chromium:iron ratio of at least 70:30, and to reduce to metallic form iron liberated from the converted ferrous chromite, while reducing a relatively small amount of CrO₃ and separating a metallic iron product, low in chromium, and a molten ore product, rich in calcium chromite, thereby obtained.

22. In a process for producing chromium-bearing metal involving a reduction treatment of a charge containing a chromium compound, the improvement which comprises employing for the reduction treatment a charge comprising chromite ore altered artificially by the substitution of calcium oxide for ferrous oxide chemically combined in the original ore and having a lower ratio of iron to chromium than the original ore.