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# UNITED STATES PATENT OFFICE

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## PROCESS OF PREPARING ORE

No Drawing. Application filed October 7, 1931. Serial No. 567,473.

This invention relates to the preparation of oxidized ore for subsequent treatment to separate metal values, and particularly to a method of reducing reagent metal compound in such ore to a lower-valent condition in which it exhibits high chemical activity toward acidic reagent gases.

Previously I have invented a process of treating oxidized ore in which the utilization of acidic reagent gas, such as chlorine, for solubilizing metal values is facilitated by introducing lower-valent oxide of what I have termed "reagent metals". Such a process, involving ferrous oxide, is disclosed and claimed in Patent No. 1,822,995. In that process acidic gases are absorbed into ore that is moistened to a special limited degree termed "quasi-wetness".

On reducing oxidized ore by conventional methods with carbonaceous gas or coal to provide lower-valent oxide of reagent metal, the resultant oxide tends to vary considerably in its efficacy for absorbing acidic reagent gas, such as chlorine. Reference is made to lower-valent iron oxide by way of example. I have found heretofore on reducing ore with carbonaceous material that when moisture is eliminated and free oxygen excluded during cooling after reduction, the resulting oxide of iron possesses greater and more constant chemical activity for absorbing acidic reagent gas in quasi-wet ore than when these precautions are not taken. An application of this process to the beneficiation of iron ores, by providing this more active form of iron oxide to facilitate chloridizing of impurities in such ore, is disclosed and claimed in my copending application Serial No. 527,367 filed April 2, 1931, now Patent No. 1,833,686, issued November 24, 1931. In such treatment use may be made also of the fact that this active oxide is magnetic similarly to less active forms of lower-valent iron oxide.

Excellent results may be had by applying this process of obtaining and applying active reagent metal oxide in various ore treatments, such as that of my aforesaid application. More recently I have found that with some ores, or with ores in some conditions, despite the precautions referred to the active magnetic -ous oxide may not be obtained consistently, and that when obtained in active condition it may in some instances revert to a less active form on exposure to air or moisture.

Now I have discovered that in reduction to obtain reagent metal in such active lower valent condition, the results are much more consistent and the active oxide more stable when the reduction is effected with a combustible reducing agent containing an amount of sulfur dioxide. The preferred embodiment of my present invention, predicated on this discovery, contemplates a preparatory treatment of oxidized ore containing reagent metal by reducing it at suitably elevated temperatures with carbonaceous material in the presence of sulfur dioxide, and during cooling protecting the heated ore from free oxygen, and in some cases from moisture also. This provides reagent metal in a lower valent condition that possesses a high degree of chemical activity toward acidic reagent gases and yet is stable against air or moisture at normal temperatures.

Regarding iron for example, the procedure of this invention produces an iron oxide which is magnetic and chemically stable under atmospheric conditions, as will be shown. It is probable, and I now believe, that the activity of the reduced ore toward acidic gases is due to such reduced, or lower valent, reagent metal oxide, which in this case may be an active ferroso-ferric oxide. However, the results of this invention are not limited to the formation of lower valent oxides, as the activity may be due to other reduced forms of reagent metal. In the description and claims of this application the product is designated simply as reagent metal in a condition that is highly active toward acidic reagent gases and yet normally is stable, i. e., retains such activity.

In the practice of this invention, reduction with combustible material may be carried on at temperatures of 300° to 750° C. in simple manner. For example, oxidized

ore is heated as heretofore in conventional furnaces to produce lower-valent material by contact with carbonaceous gas, such as producer gas, which is desirable because of its CO content, or even with natural gas, but in all cases with same amount of sulphur dioxide present. To provide the reducing agent, finely divided coal may be mixed with the ore and in this case it is sufficient to mix the coal with ore at about 600° C., for example as it comes from a roaster, and to store the mixture in bulk so that it retains its heat to accomplish the reduction. Or, hydrogen may be used as the reducing agent.

A muffle furnace or a rotary furnace provided with means to exclude free oxygen from the ore until it is cooled is suitable for the treatment. If air or water is subsequently to have access to the ore this protected cooling will extend to normal temperature, or below approximately 150° C. This protection may be accomplished by an atmosphere of non-oxidizing gas, preferably introduced as a current during cooling for the further purpose of eliminating moisture formed by reaction during the reduction.

Sulfur dioxide in contact with the ore may be provided in various ways. Most simply some amount of sulfur dioxide gas may be introduced into the reducing atmosphere. Mere traces of sulfur dioxide suffice, and in the preferred embodiment less than one per cent of this gas in the reducing atmosphere is used. However, higher concentrations, and even major proportions of sulfur dioxide, for instance up to 50 or 75 per cent may be used. The efficacy, and preferred use of, very low concentrations shows that the production of the active, stable lower valent form of reagent metal is not dependent upon chemical combination of the sulfur dioxide with the reagent metal compound, though one theory of this invention comprehends the possibility of some conversion of an active but unstable FeO to more stable but yet active ferroso-ferric oxide.

In many cases sufficient sulfur dioxide is provided by using a coal having a suitable sulfur content, which with the oxidized ore yields sulfur dioxide. In numerous cases in commercial practice the ore being treated, though of oxidized character, contains some sulphates and small amount of residual or refractory sulfide, and this with the oxides of the ore will provide sufficient sulfur dioxide to assure production of magnetic iron oxide in the chemically active and stable form which characterizes this invention. During reduction, combustible gas and sulfur dioxide in combination effect changes in reagent metal compounds, even in refractory compounds of nickel and the like, to produce these normally stable but potentially active compounds of lower-valent character, though neither sulfur dioxide alone nor combustible gas alone effects such a profound change. That this is not due to permanent combination of sulfur dioxide with metal values appears from the fact that less than one per cent of $SO_2$ is as efficacious as larger amounts.

A great number of ores to be treated contain sufficient iron to supply all the potentially active ferrous material required for subsequent treatment with acidic gases, but such active ferrous material may be prepared separately by this invention and added to the ore. On the other hand, many ores though relatively low in iron, may be concentrated conveniently after this preparatory treatment, since the oxide obtained is highly magnetic and carries other metals that are associated with it. In some cases though magnetic concentration is even the principal objective, as in beneficiating low grade iron ores, the preparatory treatment of this invention nevertheless is of considerable importance, for it assures obtaining a high percentage of magnetic oxide without the losses due to carrying the reduction to such an extreme that relatively non-magnetic FeO results. Thus the care previously necessary not to continue the reduction for too long a time is avoided by this invention, and control of time and temperature are substantially eliminated. Further, by this reduction with combustible gas and sulfur dioxide together, a greater segregation of the metallic compounds is accomplished than heretofore.

In some ores, other metals than iron may play an important part as reagent metals in subsequent treatment. As used herein the term "reagent metal" has reference to a metal capable of existing in its compounds in higher and lower valences, or in "ic" or "ous" conditions; for example, nickel, cobalt, copper, iron, manganese.

The preparation afforded by this invention to provide reagent metal in normally stable but potentially active lower valent condition is important for subsequent treatment of ore with acidic reagent gas with the ore either in dry condition at elevated temperatures upward of about 200° C. or in quasi-wet condition at lower temperature. The active ferrous material, for example, absorbs chlorine with remarkable avidity at elevated temperatures when dry, or at normal temperature when quasi-wet, while inactive ferrous oxide, or ferric oxide, act with such relative slowness as not to afford commercially practicable results.

Ore in quasi-wet condition, under which this active lower-valent material is particularly effective in introducing acidic reagent gas, has been described in my Patent No. 1,822,995 as containing no free liquid, being of maximum volume, and of loose, open

structure. Ferrous material produced by this reduction in a reducing atmosphere of combustible gas containing sulfur dioxide continues stable and active in quasi-wet ore, but ferrous oxide produced by reduction without sulfur dioxide either is inactive or loses its activity when moisture is added to the ore after cooling. This is illustrated by the following treatments.

A Cuban oxidized iron ore practically free from sulfur and containing about four per cent of chromium, 1.25 per cent of nickel, and some silica and manganese, was reduced at about 450° C. with natural gas alone, and then cooled in natural gas to atmospheric temperature. When this reduced material was exposed to air it immediately became very hot, and its color changed from dark brown to red. Moistening a sample of the reduced material with water caused a similar change. When this reduced ore was made quasi-wet with water it was inactive toward chlorine, and very little iron chloride was formed.

Another portion of the same ore was reduced for two hours in natural gas alone at 600° C., and cooled in natural gas to normal temperature. The cooled ore was black and magnetic. When this reduced product was mixed with 10 per cent of water it became warm and dusty, and upon adding another 10 per cent of water the temperature reached 70°–80° C. It required a total of 30 per cent of water to bring this ore to quasi-wet condition. And when this quasi-wet product was contacted with chlorine, it was quite inactive, for less than one per cent of iron chloride was obtained and only 0.11 per cent of nickel was soluble in water.

In comparison, another portion of this iron-nickel-chromium ore was reduced for two hours with natural gas containing a slight amount, less than one per cent, of $SO_2$ at about 600° C., and cooled in natural gas. This product was black and highly magnetic, but when moisture was added it exhibited no change of temperature, nor did its color change and 12 per cent of water sufficed to bring the reduced ore to quasi-wet condition. When this quasi-wet sample was contacted at normal temperature with chlorine it evidenced high chemical activity, as indicated by a marked rise in temperature, and its content of water-soluble iron chloride became 7.5 per cent, while the water-soluble nickel reached 0.81 per cent. On roasting at low temperature 1.15 per cent or 92 per cent of the total nickel became water soluble.

When a portion of this ore reduced with natural gas alone for two hours at 600° C. was contacted with chlorine at 300° C., and then cooled in gas to normal temperature, only 0.12 per cent nickel was water soluble. But when a sample of the ore reduced with gas and sulfur dioxide, as described, was contacted dry with chlorine at 300° C., the water-soluble iron was 6.7 per cent while the water-soluble nickel was as high as 0.76 per cent.

Further, the first sample which had been reduced with gas alone with undesirable results was retreated by reducing it two hours at 600° C. with natural gas containing $SO_2$, and cooled in natural gas. The iron was obtained in very highly magnetic condition and the ore remained stable when exposed to air. When moisture was added, less than 15 per cent of water was required to make the product quasi-wet, and it showed the high activity toward chlorine described for the other test in which $SO_2$ was used.

Similarly, an oxidized iron ore containing as impurities 0.55 per cent of phosphorus and 6 per cent of manganese, when heated at 600° C. with natural gas only, and cooled in natural gas contained a black oxide which was of somewhat magnetic nature, but which was inert toward chlorine when the ore was made quasi-wet. However, both this material and a new portion, when treated again under the same conditions but with a small amount of $SO_2$ present during reduction, on being made quasi-wet with about 12 per cent of water, were highly magnetic, and showed high activity when contacted with chlorine.

When each of these two ores containing iron was treated similarly but using finely divided coal instead of natural gas, the results were the same. In all cases the presence or absence of sulfur dioxide during reduction determines whether or not the product will contain a magnetic oxide that is both stable under atmospheric conditions and highly active toward chlorine.

Though with sulfur dioxide present in the reducing atmosphere, the small amount of water vapor formed by reaction is not deleterious with many ores, it is preferable in some cases that water vapor be removed, as by a current of nonoxidizing gas or by continuing the reduction until water vapor ceases to be evolved. With copper such care to remove water vapor is not essential, but with ore containing nickel or cobalt to be recovered, water vapor should be eliminated as much as possible for it tends to form refractory nickel and cobalt compounds even though $SO_2$ be present.

On reduction of iron-nickel-chromium ores with carbonaceous gas and sulfur dioxide, an effective process of recovery thus is provided to obtain the chromium substantially free from nickel. Thus this treated Cuban ore in quasi-wet condition is contacted with chlorine at normal temperature, or dry at elevated temperatures upward of about 200° C., roasted at relatively low temperatures for chloridization, for instance in the manner disclosed in my aforesaid

application and patent, and then leached. With such treatment, better than 90 per cent of the chromium can be concentrated from the tailings practically free of nickel. The tailings comprise a high percentage of purified iron oxide, and the nickel may be recovered as metal by electrolysis of the leach solution.

By way of illustrating further the scope of this invention reference is made to the following treatments of a copper sulfide concentrate containing 37 per cent of copper and 17 per cent of iron. This material first was self-roasted for four or five hours, the maximum temperature being 560° C.

One portion of this oxidized concentrate was reduced with only natural gas until no moisture was evolved, then cooled to normal temperature with exclusion of oxygen, then made quasi-wet and in such condition contacted with chlorine. As a result there was no water-soluble iron, and only 25 per cent of the copper was water soluble.

A second portion of this oxidized concentrate was reduced with about 10 per cent of coal and no $SO_2$, and otherwise treated as the first portion. As a result there was no soluble iron, and only about 75 per cent of the copper was water soluble.

A third portion was reduced with 10 per cent of coal and $SO_2$, and treated otherwise as the other two portions. It required about 15 per cent of water to bring this product to quasi-wet condition, and the absorption of chlorine was so rapid and penetrating that another 15 per cent of water was required during the chlorine treatment to maintain the ore in quasi-wet condition. On leaching with water 99.7 per cent of the copper dissolved. The water soluble iron was 1.1 per cent. This demonstrates the effect of $SO_2$ during reduction and also the part that copper can play as a reagent metal. The iron content of this material was never sufficient to chloridize all of the copper even at best, but when the efficacy of the iron present was increased and when it was supplemented by an accompanying active form of copper, substantially all of the copper of this high-grade material was made water-soluble by this simple, low temperature treatment.

The efficacy of the invention is shown further by results obtained in treatment of a sulfide ore (25 per cent of sulfur) containing 1.03 per cent of copper, and 1.89 per cent of nickel. This ore was self-roasted to a maximum temperature of about 550° C. during four hours. Duplicate portions of the roasted ore were reduced with 5 per cent of finely ground coal, by heating two hours in a muffle furnace at 600° C. The reduced ore was cooled in an atmosphere of carbon dioxide. Sulfur dioxide was liberated by each portion during the first half of the reduction period, after which the evolution of this gas ceased. One of the portions (Sample B) was treated thereafter, in accordance with the invention, by continuously adding a small amount of $SO_2$ during the latter half of the reduction. Reduction of the other portion (Sample A) was completed without introducing $SO_2$.

Both reduced materials were made quasi-wet with 10 per cent of water, contacted with chlorine, and assayed for soluble copper and nickel. The results were as follows:

| | Sample A | | Sample B | |
|---|---|---|---|---|
| | Per cent | Recovery | Per cent | Recovery |
| Water soluble copper | 0.91 | 88.4% | 1.01 | 98 % |
| Water soluble nickel | 1.55 | 82 % | 1.80 | 95.2% |

These tests show clearly the marked increase in recoveries engendered by the use of sulfur dioxide in accordance with the invention.

With this preparatory treatment, oxidized ores are provided with amounts of normally stable but potentially active forms of reagent metal in lower-valent condition that facilitate subsequent treatment of the ore with acidic reagent gas at relatively low temperature. Such ore even when dry is capable of absorbing large amounts of chlorine, ferric chloride, or hydrogen chloride at 200° C. and upwards, and when made quasi-wet and contacted with chlorine at temperatures up to about 150° C. absorption of the gas is substantially complete, to the equivalence of metals to be chloridized. The chloridized ore may require additional low temperature heating up to about 500° C. in some cases where refractory compounds are present, but chloridization at low temperature in the presence of such effective agents as the potentially active lower-valent material prepared according to this invention, is so complete and retains the product in such open condition that either leaching or volatilization to extract compounds of recoverable metals from the gangue is extremely simple and efficient.

In this description reference has been made to chlorine as illustrative of an acidic reagent gas, but it will be apparent that this invention is not restricted to treatment with chlorine, and that sulfur dioxide and other acidic gases are absorbed readily by ore prepared according to this invention.

According to the provisions of the patent statutes, I have explained the principle of my invention, and have described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. A process of treating oxidized ore containing reagent metal comprising heating the ore with a combustible reducing agent in an atmosphere containing sulfur dioxide in an amount from traces to major proportions, and cooling the thus treated ore with exclusion of free oxygen, and thereby producing reagent metal compound in a lower valent form which is highly active to acidic gases and stable toward moisture, and subsequently treating the material with acidic gases to convert metal values to extractable compounds.

2. A process of treating oxidized ore containing a reagent metal compound comprising heating the ore at 300 to 750° C. with a combustible reducing agent in an atmosphere containing sulfur dioxide in an amount from traces to major proportions, and cooling the thus treated ore with exclusion of free oxygen, to thereby obtain ore containing reagent metal in a lower valent oxide form which is highly active to acidic gases and stable toward moisture, and subsequently treating the material with acidic gases to convert metal values to extractable compounds.

3. A process of treating oxidized ore containing reagent metal for subsequent treatment to separate metal values, comprising heating such ore at about 600° C. in a reducing atmosphere formed of combustible reducing agent and in the presence of sulfur dioxide in amounts from traces to major proportions, cooling the reduced ore with exclusion of free oxygen, to obtain reagent metal compound in a condition highly active toward acidic reagent gases, and then contacting the material with acidic reagent gas to convert metal values to extractable condition.

4. A process of treating oxidized ore containing iron to prepare it for subsequent extraction of metal values, comprising heating the ore at 300 to 750° C. with a combustible reducing agent in an atmosphere containing sulfur dioxide from a substantial and effective amount up to about 1 per cent, cooling the thus treated ore to normal temperature with exclusion of free oxygen, to thereby convert the iron to a lower valent oxide form that is stable toward moisture and highly active toward acidic gases, and subsequently treating the ore with acidic gases to react upon metal values contained in the ore.

5. A process of treating oxidized ore containing reagent metal for subsequent treatment to separate metal values, comprising heating such ore at about 600° C. in a carbonaceous reducing atmosphere, said atmosphere containing sulfur dioxide in amounts from traces to major proportions, to convert the reagent metal to a lower valent oxide condition highly active toward acidic reagent gases, cooling to normal temperature with exclusion of free oxygen, rendering the cooled material quasi-wet and treating with chlorine to convert metal values to extractable condition.

6. A process of treating oxidized ore containing iron, comprising heating the ore at 300 to 750° C. in a carbonaceous reducing atmosphere containing sulfur dioxide in amounts from traces to major proportions, eliminating any moisture and cooling to normal temperature with exclusion of free oxygen, to thereby convert the iron to a lower valent oxide form which is stable toward moisture and highly active toward acidic gases, and subsequently treating the material with acidic gases to render metal values extractable.

7. A process of preparing oxidized ore containing iron for subsequent treatment to separate metal values, comprising heating such ore in a reducing atmosphere of combustible agent containing sulfur dioxide, cooling with exclusion of free oxygen to convert the iron to a condition highly active toward acidic reagent gases and in magnetic condition, magnetically separating the active material and associated metal values from the gangue, and then treating with chlorine to chloridize metal values associated with the active material.

8. A process of preparing oxidized ore containing iron for subsequent treatment to separate metal values, comprising heating such ore at 300° to 750° C. in a carbonaceous reducing atmosphere containing sulfur dioxide in amounts from traces to major proportions, eliminating any moisture and cooling to normal temperatures with exclusion of free oxygen, rendering the thus-treated material quasi-wet, and treating the quasi-wet mixture with chlorine.

9. A process of beneficiating oxidized iron ore containing metallic impurities but substantially free from sulfur, comprising heating such ore with a combustible agent productive of a reducing atmosphere, said atmosphere containing sulfur dioxide in amounts from traces to major proportions, cooling with exclusion of free oxygen to obtain lower valent iron material in highly active condition toward acidic reagent gases, and then treating with chlorine to chloridize said metallic values for removal from the iron.

10. A process of beneficiating oxidized iron ore containing metallic impurities but substantially free from sulfur, comprising heating such ore in a carbonaceous reducing atmosphere together with sulfur dioxide in amounts from traces to major proportions, cooling with exclusion of moisture and of free oxygen to normal temperature to obtain lower valent iron material in normally

stable but highly active condition toward acidic reagent gases, rendering the cooled material quasi-wet and treating with chlorine to chloridize metal values associated with the active material for removal from the iron.

11. A process of treating oxidized iron-nickel-chromium ore comprising heating the ore at approximately 600° C. with combustible agent productive of a reducing atmosphere, said atmosphere containing from traces to major proportions of sulfur dioxide, eliminating moisture and cooling the ore to normal temperatures with exclusion of free oxygen and of any moisture to provide a reagent material in a condition highly active toward acidic reagent gases, bringing the active material and associated metal values to quasi-wet condition, contacting the quasi-wet mixture with chlorine and roasting at about 350° C. to chloridize the nickel, and leaching to separate soluble nickel and to leave the chromium in the residue.

In testimony whereof, I sign my name.

RALPH FREDERICK MEYER.

## CERTIFICATE OF CORRECTION.

**Patent No. 1,898,018.** **February 21, 1933.**

**RALPH FREDERICK MEYER.**

**It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 6, for "same" read "some"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.**

**Signed and sealed this 8th day of August, A. D. 1933.**

**(Seal)**

**M. J. Moore.**
**Acting Commissioner of Patents.**

stable but highly active condition toward acidic reagent gases, rendering the cooled material quasi-wet and treating with chlorine to chloridize metal values associated with the active material for removal from the iron.

11. A process of treating oxidized iron-nickel-chromium ore comprising heating the ore at approximately 600° C. with combustible agent productive of a reducing atmosphere, said atmosphere containing from traces to major proportions of sulfur dioxide, eliminating moisture and cooling the ore to normal temperatures with exclusion of free oxygen and of any moisture to provide a reagent material in a condition highly active toward acidic reagent gases, bringing the active material and associated metal values to quasi-wet condition, contacting the quasi-wet mixture with chlorine and roasting at about 350° C. to chloridize the nickel, and leaching to separate soluble nickel and to leave the chromium in the residue.

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