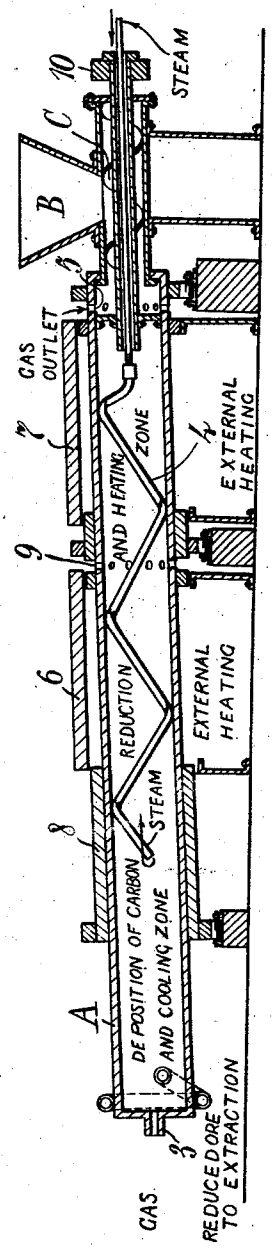
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PROCESS FOR EXTRACTING ORES AND THE LIKE

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PROCESS FOR EXTRACTING ORES AND THE LIKE

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The process relates to extracting ores and the like and more particularly to recovering copper and cobalt from oxide ores, including silicates and roasted sulphides.

The application is a continuation in part of the application Serial Number 118,685, filed Dec. 31, 1936, for "Process for extracting ores and the like". My prior application describes and claims a method of extracting metals (specifically nickel) having a lower heat of combustion than iron from their oxide, silicate and roasted sulfide ores, wherein such an ore is heated in the presence of a reducing gas containing steam under conditions producing the reduction of said metals, while iron and metals having a higher heat of combustion than iron are retained in the oxidized state, and thereafter recovering the so-reduced metals. My present application is directed to the use of the same general process in recovering metals selected from a group consisting of copper and cobalt from ores of the general character described.

In order to obtain the desired metals the raw material must be made extractable. According to the present process this is effected by the application of short-circuited element-couples in the mass which has to be extracted, from which local cells are formed by subsequently adding extraction electrolytes. Hereby care has to be taken that the metal to be obtained forms the most electronegative electrode of the couple and that a more electronegative undesired element is not present in the metallic form.

It is necessary that the local cells are accessible for the extraction electrolyte. This may be attained in an appropriate manner by bringing the ore after being made extractable into an extraction electrolyte in a more or less finely ground condition. The penetration of the electrolyte into the interior of each individual local cell may be increased by changing the pressure, the temperature and the surface tension.

In order to be able to form in the mass to be extracted the metal-couple in which the desired metal is the most electronegative one, it is necessary that a more electropositive element is present in the mass.

If such element should not be present it may be formed from constituents of the mass or it may be introduced from outside.

From the techniques of the generation of current by primary cells it is known that the amount of the current delivered is considerably increased by the presence of a depolarizer in such a cell, for instance, manganese dioxide in the known Leclanché cell.

In order to obtain a higher yield of metal a depolarizer may be advantageously used in the extraction operation. If for instance it is desired to extract nickel, ferric oxide may be used as such.

If the raw material is an ore one of the constituents of this ore may be used as a depolarizer or converted into it. In another case it will be necessary to introduce the constituents, from which a suitable depolarizer may be formed from outside into the ore. The place of the depolarizer is in the vicinity of the most electronegative element. The depolarizer will retain a favourable action on the extraction only if the access of the electrolyte to this most electronegative element is not hindered by too large an extent of the depolarizer. Also a depolarizer may be used in the dissolved state, e. g. cupric salts or cobalti salts.

With regard to a certain electrolyte the metals are ranged in a distinct electromotive tension series.

Premising that in the mass to be extracted these metals are converted into the metallic form the logical consequence will be that for one and the same electrolyte they would be obtained following that series and that also undesired metals would be obtained.

By application of another electrolyte by which another sequence in the E. M. F. series is caused, the undesired metal being the more electropositive does not dissolve.

Applicant has found the following ways of preventing the dissolving of an undesired metal:

(*a*) From the undesired metal a compound being insoluble in the electrolyte is formed before adding the electrolyte. This may be carried out by reducing the oxide ores and the like with a suitable mixture of reducing gas and steam at a temperature of at least 400° C.

(*b*) By choice of a certain electrolyte, causing the undesired metal even if it be present in the metallic state to form compounds insoluble in that electrolyte, whereas the desired metal does form soluble compounds.

The following examples illustrate the process:

Example 1.—A sulphide copper ore from Tasikmalaya, Java, having approximately the following composition: S 27, Cu 5, 5, Te 26, SiO_2 36, was subjected to an oxidizing roasting.

a. Part of the so oxidized ore was reduced during about 2 hours at 700° C. with a reducing gas consisting of 60 parts by volume of illuminating

gas and 70 parts of steam. Then the supply of steam was shut off and the so reduced ore cooled down in an atmosphere of illuminating gas.

b. Another part of the roasted ore was reduced at 700° C. with illuminating gas and subsequently cooled in an atmosphere of illuminating gas.

The copper content of *a* was 6.4%.

The copper content of *b* was 6.6%.

50 grams of *a* were extracted with 1280 c. c. of 0.20 N. sulphuric acid. After 12 hours of stirring and of aerating the solution contained 2.76 gr. of copper equal to 86.2%.

50 grams of *b* were extracted in exactly the same way. After 12 hours of stirring and of aerating no copper at all could be found in the solution.

In case *a* the local cells copper-carbon are formed, whereas the iron is brought into an insoluble oxide form.

In case *b* the local cells "copper-carbon" as well as "iron-carbon" are formed, the local cell "iron-carbon" having an electrical tension of 1.4 volt at pH=1 and of 1.8 volt at pH=14, the local cell "copper-carbon" having an electrical tension of 0.65 volt at pH=1 and of 1.35 volt at pH=14.

Therefore in case *b* iron goes into solution before copper, consuming the available sulfuric acid, leaving no extraction electrolyte for copper extraction.

Example 2.—A Rhodesian oxide copper ore, containing 2.8% of copper, 12% of iron, 60% of silica was ground to a grain size of 1 millimeter.

I. Part of this was reduced at a reduction temperature of 700° C. with a mixture of illuminating gas and steam to the proportion of 80 volume parts of illuminating gas and 225 volume parts of steam, cooled to 200° C., the steam supply shut off and cooled to room temperature in an atmosphere of illuminating gas.

II. Another part was reduced without the addition of steam at the same temperature.

III. A third part was reduced without the addition of steam, however at a lower temperature (about 350° C.). Extraction was carried out by percolating 40 grams of the reduced ore with a solution containing:

	Cubic centimeters
Saturated ammonium carbonate solution	20
Ammonia 25%	20
Water	20

The height of the ore layer amounted to 20 centimeters.

In the first case (part I) 97.3% of the copper could be extracted in 6 hours of percolation.

In the second case (part II) no copper at all could be extracted in 6 hours of percolation.

In the third case (part III) only 4.3% of the copper could be extracted in 6 hours of percolation.

In the second and third case, iron went into solution in the ferrous form and was afterwards precipitated in the ferric form.

The solutions became highly contaminated with iron which precipitated in the ore layer and caused the layer to become clogged preventing percolation in the second case and hindering percolation in the third case (layers of 20 c. m. of height).

Increasing the height of the percolation layer increases the troubles from clogging the layers with ferric hydroxide in the second and third case. With a height of 4 meters in the first case no troubles were encountered. In the second case with a height of 20 centimeters only the percolation became impossible within two hours because the layer was absolutely clogged.

In the third case with a height of 1 meter percolation became impossible after three hours.

If percolating with cupric ammonium carbonate solution the same difficulties arise in the second and third case. In the first case no troubles by clogging were encountered because no iron could go into the solution and precipitate therefrom.

Example 3.—A Rhodesian oxide and silicate copper ore, containing copper 4.01, iron 3.41, alumina 2.64, silica 63.27, calcium oxide 6.1, magnesium oxide 5.75 and loss by calcination 13.6, was ground to a grain size of 1 mm. calcium and magnesium were present as carbonates. In order not to decompose these carbonates a reduction temperature of 450° C. was chosen and a mixture of gas and steam to the proportion of 75 volume parts of illuminating gas and 220 volume parts of steam.

The reduction time was 45 minutes, after which the reduced ore was cooled to 200° C., the steam supply shut off and cooled to room temperature in an atmosphere of illuminating gas.

Extraction was carried out by percolating the reduced and cooled ore with a solution, containing ammonia, ammonium-carbonate and water. In 6 hours of extraction time 98% of the copper could be dissolved. If reducing another part of the ground ore at the reduction temperature of 450° C. without the addition of steam to the reduction gas, troubles from clogging with ferric-hydroxide were encountered. After 3 hours of percolation through a layer of 2 meters of height the rate of flow was very low and after 4 hours it stopped entirely. Only 14% of the copper was found in the solution.

If reducing a third part of the ground copper at a temperature of 650° C. in a mixture of gas and steam to the proportions of 73 parts of illuminating gas and 245 parts of steam the troubles encountered were not due to iron, but to a hydraulic binding of the decomposed calcium magnesium carbonate with the aid of the carbon-dioxide content of the extraction-solution, which meant an uneconomic consumption of the ammonium carbonate as well as hindering of proper entrance of the leaching solution into the local cells "copper-carbon".

Therefore the reduction temperature of 450° C. and the gas steam mixture 75:220 were chosen.

The composition of the illuminating gas of Examples 1, 2 and 3 was: CO_2 3, hydrocarbons 3, O_2 1, CO 18.4, H_2 46.5, CH_4 16.5, N_2 10.

Example 4.—The Rhodesian copper ore as described in Example 2 was ground to a grain size of 1 mm.

The ore was reduced at a reduction temperature of 680° C. with a mixture of generator-gas and steam to the proportion of 1 volume part of gas and 1 volume part of steam, cooled to 180° C., the steam supply shut off and cooled to room temperature in an atmosphere of generator-gas.

On leaching by percolating with a solution of ammonia, ammonium-carbonate and water 96% of the copper was dissolved in 7 hours. The composition of the gas was: CO_2 4, CO 26, H_2 13, hydrocarbons 1, CH_4 2.3, N_2 56.

Example 5.—The Rhodesian copper ore of Example 3 was ground to a grain size of 1 mm.

The ore was reduced at a reduction temperature of 450° C. with a mixture of coke furnace gas and steam to the proportion of 82 volume parts

of the gas and 230 volume parts of steam cooled to 210° C., the steam supply shut off and cooled to room temperature in an atmosphere of coke furnace gas.

Extraction was carried out by percolating with a solution of ammonia, ammonium carbonate and water. In 6 hours 97.6% of the copper was dissolved. The composition of the gas was: CO_2 1.2, hydrocarbons 1.6, O_2 0.4, CO 5.9, H_2 63.5, CH_4 23.9, N_2 3.5.

Example 6.—A sulphide cobalt ore was ground to pass 30 mesh sieve, then roasted and after roasting reground to pass 30 mesh sieve. The composition after roasting was: iron and alumina 42.4, silica 30.5, sulphur 0.60, copper 0.94, cobalt 1.5.

I. Part of the roasted and ground ore was reduced at a temperature of 700° C. with a mixture of illuminating gas and steam to the proportion of 70 parts by volume of illuminating gas and 84 parts by volume of steam during one hour and a half. The steam supply was shut off and the reduced ore cooled in an atmosphere of illuminating gas.

The so reduced and cooled ore was extracted with a 0.02 N. sulphuric acid solution which was aerated during the extraction.

After 5 hours 78% of the cobalt was found in the solution together with 83% of the copper. The amount of sulphuric acid was equivalent to twice copper+cobalt.

II. Part of the roasted and ground ore was reduced at a temperature of 700° with illuminating gas and cooled in an atmosphere of illuminating gas.

After stirring with an aerated solution of 0.02 N. sulphuric acid, containing twice the quantity of sulphuric acid equivalent to copper+cobalt in the reduced ore, during 5 hours no copper was found in the solution and only 0.4% of the cobalt.

III. Part of the roasted and ground ore was reduced at 680° C. with a mixture of illuminating gas and steam to the proportion 50 parts by volume of illuminating gas and 115 parts by volume of steam and cooled to 450° C. in the atmosphere of this gas-steam mixture. The steam supply was shut off and the reduced ore cooled to room temperature in an atmosphere of illuminating gas.

The reduced ore was extracted with a solution containing ammonia, ammonium-carbonate and water by stirring the ore with said solution and aerating the solution.

After 9 hours of extraction 91% of the copper and 72% of the cobalt were found in the solution.

The composition of the illuminating gas in the three cases of Example 4 was: CO_2 2.8, hydrocarbons 3.1, oxygen 0.2, CO 18.2, H_2 47.1, CH_4 15.9, N_2 9.8.

The reduction as described may be carried out in a long revolving drum furnace,. The ore is reduced at the chimney end of this furnace. At the ore discharging end gas is introduced which moves countercurrent to the ore. At some distance from the gas inlet, so nearer to the chimney end steam is blown into the furnace. Still nearer to the chimney end air may be introduced into the furnace by which the combustion of the residual gas and at the same time heating of the ore to 700° C. is obtained.

A furnace of this kind is represented in the drawing showing a pilot plant furnace.

In this drawing, which only is to be taken by way of illustration, and not as a limitation,

A designates a rotary kiln, mounted and rotated in conventional manner. This kiln is functionally divided into reduction zones **6** and **7**, heated from outside, and cooling zone **8**. The upper portion of the cooling zone is lagged with non-conducting material to conserve the heat, while the lower end is free from lagging to facilitate rapid cooling.

B designates a feeding device which comprises a feeding screw C, whose axis is tubular and is rotated by pulley **10**.

Within this tubular axis, a pipe for conveying steam into the kiln is located, which pipe assumes a spiral form **4** inside the kiln and ends at or near the upper end of the cooling zone.

The lower end of the kiln is closed, and the upper end is furnished with means for excluding air as shown.

Between the two heating zones, means designated by the numeral **9**, for the introduction of air, are located. These means are shown simply as apertures in the wall of the kiln but would be constructed with conventional regulating means in actual practice.

The lower end of the kiln has a discharge device which is shown as a conduit passing around a major portion of its exterior and which opens into the kiln at one end and into the atmosphere at the other end. By this device the ore always fills a portion of the conduit and excludes air from the kiln.

In operation the kiln is set in rotation, the heating zones are heated to the proper temperature, and the ore fed therein.

Steam is passed into the kiln through pipe **4**, and reducing gas at its lower end, and if desired, air may be introduced between the two heating zones.

The reducing gas meets the descending ore and passes out of the kiln through apertures **5** at its upper end.

Means for controlling the amount of steam, air and reducing gas are of conventional form and are not shown.

I claim:

1. The process of extracting metals selected from a group consisting of copper and cobalt from their oxide, silicate and roasted sulfide ores which comprises heating such an ore with a reducing gas containing steam at such temperatures and for such time that only the said metals are reduced to the metallic state while iron and metals having a higher heat of combustion than iron are retained in the oxidized state and recovering the so-reduced metals from the product.

2. The process of claim 1 wherein the ore is heated for at least 20 minutes at temperatures above 400° C.

3. The process of claim 1 wherein the reduced ore is cooled in a reducing atmosphere prior to recovery of the metals.

4. The process of claim 1 wherein the reduced ore is cooled in an atmosphere of a reducing gas selected from a class constisting of carbon monoxide and hydrocarbons for at least 15 minutes prior to recovery of the metals.

5. The process of claim 1 wherein the reduced metals are recovered by extraction with an electrolyte.

6. The process of claim 1 wherein the reduced metals are recovered by extraction with an electrolyte and atmospheric oxygen.

7. The process of claim 1 wherein the ore treated is a copper ore and copper is recovered therefrom.

8. The process of claim 1 wherein the ore treat-

ed is a cobalt ore and cobalt is recovered therefrom.

9. The process of extracting metal selected from a group consisting of copper and cobalt from their oxide, silicate and roasted sulfide ores which comprises subjecting such an ore for at least 20 minutes at a temperature of at least 400° C. to the action of a reducing gas containing steam in such an amount that said metals are reduced to the metallic state while iron and metal having a higher heat of combustion than iron are retained in an oxidized state, then cooling the so-reduced ore for at least 15 minutes in the presence of a reducing gas comprising carbon monoxide and hydrocarbons and then treating the reduced and cooled ore with an extraction electrolyte and atmospheric oxygen.

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