UNITED STATES PATENT OFFICE.

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RECOVERY OF NICKEL FROM ITS ORES.

1,091,545. Specification of Letters Patent. Patented Mar. 31, 1914.

No Drawing. Application filed April 3, 1913. Serial No. 758,677.

To all whom it may concern:

Be it known that we, HENRY LIVINGSTONE SULMAN and HUGH FITZALIS KIRKPATRICK PICARD, subjects of the King of England, and residing in London, England, have invented certain new and useful Improvements in the Recovery of Nickel from Its Ores, of which the following is a specification.

This invention relates to improvements in the recovery of nickel from its silicate ores and particularly from garnierite ores in which this metal occurs as a double silicate of nickel and magnesia. Garnierite usually occurs in a matrix of serpentine, with magnesia-micas and with other hydrated silicious magnesium minerals, which it closely approaches in specific gravity and in certain other physical characters; this similarity renders ordinary methods for the concentration of the garnierite from these ores ineffective.

According to this invention a process for the extraction of nickel from garnierite and like silicate ores comprises the treatment of the ore with a mineral acid in such a quantity as to act as a selective solvent of the nickel.

As is well known both garnierite and its matrix are decomposed by mineral acids, especially sulfuric and hydrochloric acids, with the liberation of silica and the production of soluble sulfates and chlorids of nickel and of magnesium. It is impossible to dissolve all the nickel (together with its associated magnesia) from garnierite by acid treatment without dissolving a large quantity of magnesia from the gangue minerals also, and this occurs, indeed, to a degree which would render the consumption of acid excessive and commercially impracticable. We have found, however, that by using a much smaller quantity of acid a substantial proportion of the nickel can be dissolved by acids from garnierite ores even of low grade, the magnesia minerals being simultaneously attacked, but to a degree much less than in the former case. In any event considerably more magnesia is dissolved than nickel, but nevertheless the solution of nickel by acid is profitable if the extraction operation be not pushed too far. In other words the solution of the last portions of the nickel by acid is accompanied by an excessive break up of other magnesia minerals with a correspondingly heavy loss of acid.

This extraction process is designed mainly to recover substantial proportions of nickel from garnierite ores which are too poor to stand the cost of carriage for treatment at a place other than that at which the ore is mined: and involves a supply of sulfuric acid which may be suitably manufactured at or near the mines or may be imported from a manufacturing center not too distant therefrom. For example we have obtained an extraction of over 70% of the valuable metal from a garnierite ore containing two per cent. of nickel, and a recovery of nearly 60% from garnierite ore from another source which contained 5½% of nickel, with the same amount of acid in each case; viz:—a quantity of sulfuric acid amounting to 25% of the weight of the ore. Having regard to the local conditions each of these extractions showed a substantial economical result, that in the case of the richer ore being the more profitable notwithstanding the lesser recovery. Neither operation would have been commercially successful had the extraction of the nickel been carried to a high figure, say 95%, as under such conditions the acid consumption involved would amount to about 80% of the ore weight. It is obvious however that richer garnierite ores will be able to stand a greater acid consumption cost than poorer ores, and we therefore do not confine ourselves to any definite consumption of acid as this will be regulated by the economic conditions pertaining to each ore.

Our method is thus based upon a selective dissolution action which certain mineral acids exert upon a mixture of nickel-magnesia and magnesium silicates within certain economical limits, which will be determined in each case by the peculiar nature of the mixed minerals, their specific behavior to acids, and by the economic factors available at the mines. We have also found that the hydrated silicates of magnesia, etc. which are contained in large proportion in low grade garnierite ores undergo rapid "weathering" or change when exposed to air, especially in a crushed condition. This weathering action results in a growing solubility of the magnesium compounds in acid, that

is to say in an increased consumption of acid relatively to the nickel dissolved.

A feature of this invention therefore consists in applying acids to the ore in a freshly mined and non-weathered condition directly it has been suitably crushed. The degree of crushing will vary with different ores, but a screen mesh of from 30 to 50 per linear inch will generally be found suitable. We find no increased selective action of the acid solvent, in favor of nickel, with very finely pulverized ore material.

The solvents we employ are sulfuric or hydrochloric acids, or mixtures of these. For example, we may add a certain proportion of salt to the sulfuric acid, or spent liquors containing magnesium chlorid. Thus we may use 25% of sulfuric acid and 10% or more of salt in a first extraction, thereafter employing 25% sulfuric acid together with the spent-liquors containing the equivalent of magnesium or calcium chlorid, on the next and successive quantities of ore.

We find the best results are obtainable by keeping the proportion of water fairly low—say sufficient (in admixture with acids etc.) to give a more or less thick paste with the ore, or the ore may be mixed directly with concentrated sulfuric acid; we allow the well-mixed mass to stand in a suitable tank or vat for a period of an hour or two, and then heat by steam, or on a suitably heated furnace-hearth, until the temperature of the whole is raised to from about 120 to 130° C. Thus it is a feature of this invention that the crushed ore together with a proportion of acid substantially as above specified and a small proportion of water sufficient to form a paste is heated to a temperature between 100° and 150° C. until the conversion of the nickel into the soluble salts has been effected to the desired extent. The dried mass in which the separated silica has mainly been rendered insoluble is then extracted with water, preferably hot and slightly acidified; and the solution (containing the nickel and the magnesia as sulfate and/or chlorid) is separated from the insoluble ore residues by any suitable mechanical filtration device; the residues being washed free *in situ* from soluble nickel salts, in the usual well known manner.

We find garnierite ores so treated yield solutions which contain nickel and magnesium sulfate and/or chlorid, and but little iron. If the mixture has been kept from contact with metallic iron during the extraction process, as is of course desirable, little or no ferrous iron is found dissolved in the filtrate. Moreover but little ferric iron is dissolved, the somewhat readily decomposable basic substances present in the ore decomposing any ferric salts that may be locally dissolved, and leaving ferric oxid or hydrate in the residues.

If the solutions obtained by the treatment of the ores with sulfuric acid contain iron as ferrous sulfate, it may be oxidized to ferric sulfate by a suitable chromate or bi-chromate. Then powdered carbonate of lime is stirred into the solution whereby any free sulfuric acid existing is neutralized and all iron, alumina and chromium salts are precipitated together with sulfate of lime, and the pure nickel and magnesium solution is filtered therefrom. The resulting product is a purified solution of sulfates of nickel and magnesium. The nickel is precipitated from this solution by stirring in powdered magnesia (MgO) and the precipitation may be aided by warming the solution and by adding the magnesia a little at a time with constant stirring in order to avoid carrying down magnesia with the nickel hydrate precipitate. The reaction is represented by the following equation:

$$NiSO_4+H_2O+MgO=MgSO_4+Ni(OH)_2$$

The nickel hydrate is not quite pure and in nearly all the cases will contain some magnesia but on heating to dull redness to dehydrate it, a powdered nickel oxid is produced carrying from 70 to 74% of nickel (Ni). The magnesia is recovered for re-use by crystallizing a sufficient quantity of magnesium sulfate from the solution and calcining it on a furnace-hearth and rabbling in a sufficiency of carbon. The changes taking place are represented by the following equation:

$$MgSO+C=MgO+SO_2+CO.$$

It is only necessary to crystallize and calcine enough magnesium sulfate to give the amount of magnesium oxid required for precipitation. This process affords a method of producing magnesia as an additional product (for the garnierite ore), if it be required.

What we claim as our invention and desire to secure by Letters Patent is:—

1. The herein described process for the extraction of nickel from silicate ores containing other metals, which consists in treating the ore with a mineral acid in such quantity as to act as a selective solvent of the nickel over the magnesium compounds forming the gangue materials and precipitating the nickel from the solution of the salts of nickel and other metals.

2. The herein described process for the extraction of nickel from silicate ores containing other metals which consists in treating the ore with sulfuric acid in such quantity as to act as a selective solvent of the nickel over the magnesium compounds forming the gangue materials, extracting with water so as to obtain an aqueous solution of nickel sulfate and other metal sulfates, purifying the solution by eliminating

metals other than magnesium and nickel and precipitating the nickel from the remaining solution.

3. The herein described process for the extraction of nickel from silicate ores containing other metals, which consists in treating the ore with a mineral acid in such quantity as to act as a selective solvent of the nickel over the magnesium compounds forming the gangue materials and precipitating the nickel from the solution of the salts of nickel and other metals by means of magnesia.

4. The herein described process for the extraction of nickel from silicate ores containing other metals which consists in treating the ore with sulfuric acid in such quantity as to act as a selective solvent of the nickel over the magnesium compounds forming the gangue materials, extracting with water so as to obtain an aqueous solution of nickel sulfate and other metal sulfates, purifying the solution by eliminating metals other than magnesium and nickel, stirring into the purified solution powdered magnesia to precipitate the nickel as a hydrate and separating the precipitated hydrate.

5. The herein described process for the extraction of nickel from silicate ores containing other metals which consists in treating the ore with sulfuric acid in such quantity as to act as a selective solvent of the nickel over the magnesium compounds forming the gangue materials, extracting with wafer so as to obtain an aqueous solution of nickel sulfate and other metal sulfates, purifying the solution by precipitating with calcium carbonate the metals other than magnesium and nickel and precipitating the nickel from the remaining solution by means of magnesia.

6. The herein described process of extracting nickel from silicate ores containing other metals which consists in treating the ore in a freshly crushed and non-weathered condition with a mineral acid in such quantity as to act as a selective solvent of the nickel and precipitating the nickel from the solution of the salts of nickel and other metals.

7. The herein described process of extracting nickel from silicate ores containing other metals which consists in treating the ore in a freshly crushed and non-weathered condition with sulfuric acid in such quantity as to act as a selective solvent of the nickel, extracting with water so as to obtain an aqueous solution of nickel sulfate and other metal sulfates, purifying the solution by precipitating with calcium carbonate the metals other than magnesium and nickel and precipitating the nickel from the remaining solution by means of magnesia.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

HENRY LIVINGSTONE SULMAN.
HUGH FITZALIS KIRKPATRICK PICARD.

Witnesses:
O. J. WORTH,
H. D. JAMESON.